

Relevance and Significance of Extraterrestrial Abiological Hydrocarbon Chemistry

George A. Olah,* Thomas Mathew, and G. K. Surya Prakash

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, United States

ABSTRACT: Astrophysical observations show similarity of observed abiological “organics”—i.e., hydrocarbons, their derivatives, and ions (carbocations and carbanions)—with studied terrestrial chemistry. Their formation pathways, their related extraterrestrial hydrocarbon chemistry originating from carbon and other elements after the Big Bang, their parent hydrocarbon and derivative (methane and methanol, respectively), and transportation of derived building blocks of life by meteorites or comets to planet Earth are discussed in this Perspective. Their subsequent evolution on Earth under favorable “Goldilocks” conditions led to more complex molecules and biological systems, and eventually to humans. The relevance and significance of extraterrestrial hydrocarbon chemistry to the limits of science in relation to the physical aspects of evolution on our planet Earth are also discussed.

■ INTRODUCTION

We have previously discussed the chemical aspects of observed extraterrestrial methanol and its hydrocarbon derivatives.^{1a} A brief and concise definition of *chemistry* can be suggested as the *science of the elements and their compounds*. We have also previously expressed our perspective of science and chemistry in some detail.^{1b} One of us, in a monograph with Molnár,^{1c} has also dealt in depth with hydrocarbons, defined as the molecular compounds of carbon and hydrogen, and their derivatives incorporating other elements such as nitrogen, oxygen, sulfur, and halogens.

Major sources of hydrocarbons are fossil fuels (oil, gas, coal) as well as CO₂ and other natural and anthropogenic industrial carbon sources. Hydrogen is present only as its derivatives (water, methane, ammonia, etc.) and must be produced by energy-consuming processes. Hydrocarbons are the basis for energy generation, essential products (fuels, chemicals, etc.), and also complex (biological, life) systems. Since their observation in interstellar space, the extraterrestrial “organics”—i.e., hydrocarbon molecules, ions, and derivatives—have been intensively explored.^{2–5} We now know that, besides hydrogen and water, methane and methanol (the parent hydrocarbon and its derivative) are the most abundant molecular matter observed in space, as shown by astrophysical spectroscopic studies.^{2,6–17} The terrestrial significance of methane and methanol as fuels and source materials has been discussed extensively.¹⁸ Recent direct astrophysical studies have succeeded in sending back to Earth data on the composition of the surfaces and atmospheres of some of the planets and their moons, asteroids, and even a comet of our solar system. This

was achieved by landing space vehicles with mass spectrometers and other onboard instruments on their surfaces. Surprisingly, they showed, as in the case of Titan (a moon of Saturn), the presence of varied “organic” molecules, their derivatives, and carbocations,^{18–23} similar to those studied by our group over the years.^{24–29} We have recently reported^{1a} on the chemical aspects of suggested preferable chemical pathways for the formation and transformation of these extraterrestrial hydrocarbons and derivatives. They were formed under abiological conditions, and thus, we prefer not to call them “organic”. In comparison to terrestrial biology and biological processes, there is so far no observed extraterrestrial biology, and thus no astrobiology exists. Hydrogen and helium were formed immediately after the “Big Bang” event, which provided the energy for subsequent transformation (as expressed in Einstein’s fundamental $E = mc^2$ equation) to subatomic particles and eventually to hydrogen atoms (as well as He under the prevailing extremely hot conditions). Carbon, nitrogen, oxygen, and the other elements were formed not directly, but in subsequent thermonuclear reactions (nucleosynthesis), mainly in the hot interior of young stars. The elements were dispersed into the surrounding space by supernova explosions of stars that have become extinct.³⁰ Using NASA’s Kepler probe, astronomers have detected the bright flash of a shockwave from the supernova explosion of a dying star (KSN 2011d) for the first time in the optical wavelength, recently.³¹ In the observable part of the universe, these events resulted in the subsequent formation of the presently identified “organic”, but abiological, hydrocarbon molecules. The relevance and significance of the derived astrochemistry is now discussed. The transportation of the extraterrestrially formed molecular hydrocarbon derivatives to Earth took place over the ages via meteorites and comets,^{32–34} not unlike that of exclusively extraterrestrially formed water delivered to Earth by comets. The favorable and, until now, unique “Goldilocks” conditions (not too much, not too little, but “just right”) of our Earth allowed further evolution to varied molecules and eventually to living biological systems, including us, *Homo sapiens*.

Our discussions in this Perspective will center on only the physical scientific facts that are relevant and significant.^{1a} Any suggested (believed), unprovable spiritual or philosophical aspects are considered outside the limits of science, human comprehension, and knowledge. This is a frequently accepted position of many scientists, usually referred to as “agnostic”. It means acknowledging our limited knowledge (gnosis), but not

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necessarily accepting or denying a higher supernatural (divine) power.

When considering the recent observations of varied abiological hydrocarbon derivatives and their ions (carbocations and carbanions) in extraterrestrial space,^{19–23} it is important to re-emphasize that, so far, no proof for any extraterrestrial biology has been obtained. Of particular interest to us is the remarkable detection of varied carbocations and their similarity with their terrestrial analogues (see representative examples in Figure 1). The proven similarity with our terrestrial studied

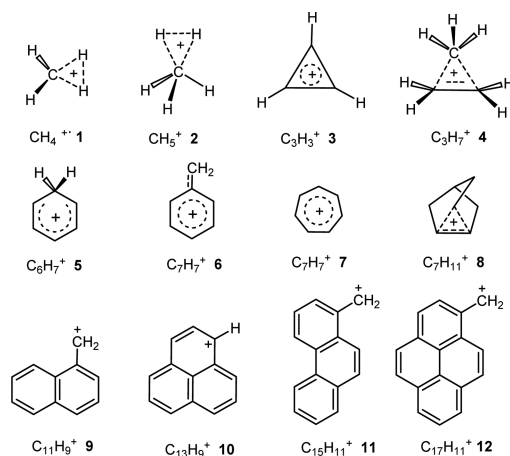


Figure 1. Some astrophysically observed (by mass spectrometry) carbocations and the corresponding carbocations studied.

chemistry provides the first scientific evidence that our Earth is not a unique celestial body for producing the chemical building blocks.

■ EXPANDING UNIVERSE, MULTIVERSES

Until recently and even now, our universe containing the Milky Way galaxy has been frequently called “the cosmos”. Carl Sagan, a well-known astrophysicist, called the cosmos “all that is or was or ever will be”.³⁵ However, this probably is not the case. While studying the “expansion of the universe” and searching for other systems similar to our solar system, astrophysicists have observed many exoplanets and exoplanetary systems in recent years by high-precision radial velocity techniques.^{36,37} Recently, a team of international scientists³⁸ has discovered a monster solar system—the largest solar system ever found—with a gaseous giant planet, which takes almost a million Earth years to orbit its host star. There are indeed suggestions that there may be innumerable universes (multiverses), cycling through their own Big Bang events as well as their extinctions with their “big crunches”. However, with the limited knowledge and capabilities of humankind, one probably will not be able to find any proof for their existence (maybe forever).

The suggestion of an unlimited, large cycle of universes in the cosmos would also mean that there is no beginning or end, with universes continuously being formed and becoming extinct.^{39,40}

■ BIG BANG EVENT AND STELLAR NUCLEOSYNTHESIS

Following the conversion of energy released by the Big Bang into varied subatomic particles, hydrogen was formed through their combination upon cooling. George Gamow first suggested that, in the minutes immediately following the Big Bang, when

the universe was still extremely hot, the initially formed energetic protons and neutrons also underwent nuclear fusion in a process called the “Big Bang nucleosynthesis”, creating helium, some deuterium, and small amounts of light elements such as lithium and beryllium.^{41,42} About a quarter of the mass converted into He in the beginning, while the rest remained as hydrogen. This apparently took place in the first 10–20 min after the Big Bang. As mentioned earlier, nucleosynthetic reactions in the hot interior of the formed young stars produced the other essential elements (like carbon, nitrogen, and oxygen) by nuclear fusion.

The energy for the illumination of stars comes from the nuclear fusion processes occurring in their cores. The first and longest burning phase is the fusion of four protons (4 hydrogen nuclei) into a He nucleus through a series of nuclear reactions at about 5 million °C. The energy equivalent to excess ~0.7% mass according to Einstein’s equation $E = mc^2$ (4 hydrogen nuclei with respect to 1 He nucleus) illuminates the star for a long period of time.^{43,44} Subsequent burning stages, especially in the last 10% of stars’ lives, lead to formation of Be and then C from He through a well-known triple- α process. Continued chemical evolution through further particle capture results in the conversion of carbon nuclei to oxygen, nitrogen, and other heavier elements up to iron in the periodic table. With the formation of iron cores, stellar nucleosynthesis stops, stars lose equilibrium, and supernova explosions occur with the dispersion of newly created elements into the surrounding space (vide infra). As the process repeats, the concentration of heavier elements increases in the surroundings. The formation and cooling of gas clouds with metals embedded in them, leading again to dense mass and their collapse, continue to result in interstellar chemical molecular evolution. Astrophysicists have studied such interstellar events in detail for decades.

It is important to note that all elements (including carbon, nitrogen, and oxygen) could not have been formed on Earth but were also transported by comets, meteorites, and asteroids (vide infra).

■ SUPERNOVA DISPERSION OF STELLAR MATTER FOR COSMIC EVOLUTION

Supernovas are intense massive explosions of stars occurring billions of light years away in the galaxies.³¹ They are basically fatal detonations. Stars are the gigantic core furnaces, the nuclear factories in which formation of heavier elements (heavier than lithium by nuclear fusion) takes place. There are an estimated 100 billion stars in the Milky Way galaxy, and about 100 billion galaxies in the observable universe. When a star’s central core runs out of fuel, it starts to collapse toward the center beginning from the periphery, amassing exorbitant gravitational energy, concentrating everything into a singular point (singularity) of extremely high density. In the case of massive stars, the density becomes infinite and results in the formation of black holes in some cases. This eventually leads to a supernova explosion, releasing all the energy and formed elements to the surroundings. From the elements and energy spewed out into the interstellar medium (ISM), molecular evolution forms varied chemical matter.⁴⁵ Thus, supernovas supply the ingredients, energy, and catalysts leading to astrochemical reactions (molecular evolution) occurring primarily on the surface of star/space dust (which includes water–ice). The products of such reactions are delivered by comets and meteorites to the planets and moons, including Earth.^{32–34}

What makes our planet Earth so far unique are its favorable “Goldilocks” conditions, including moderate surface temperature, suitable atmosphere, and the presence of liquid water, that allowed further evolution of transported extraterrestrial hydrocarbon building blocks to life forms. These or similar conditions indeed may exist on many other celestial bodies in our universe (or even our galaxy), but the probability of all conditions coming together as required for evolution of life is rather low. The time frame of life forms similar to our biological beings is just too short compared to the 13.8 billion years of existence of our universe. Further, the atmospheres of other planets are uninhabitable for our type of terrestrial biological systems due to extreme temperatures and other conditions. The existence of terrestrial-like conditions may be possible in space only at suitable distances from stars or interstellar celestial bodies.⁴⁶

Evolution that began following the Big Bang is a very long time-frame process. It is well known that evolution of living species is a slow process and happens over long periods of geological time. The species formed in Darwin’s evolutionary chain nearly all became extinct, giving way to new ones, and eventually to us, *Homo sapiens*. We humans emerged on Earth over a geologically extremely short period of time compared to the creation of Earth 4.5 billion years ago.^{47–49} Humans may also become extinct on Earth, as happened to many terrestrial life forms in the past.

Science, by definition, is able to answer only the questions regarding the physical aspect of evolution. The “evolution of species” so well proposed by Darwin is proven by our observed biology. As mentioned earlier, the spiritual aspects of evolved human life are outside the scope of this Perspective. We will address our views on the limits of science as we know it now and its significance elsewhere. The observed similarity of astrophysically revealed extraterrestrial hydrocarbons, their derivatives, ions, and related abiological chemistry of the early Earth may offer significant answers to some fundamental questions regarding the origin and evolution of terrestrial life.

■ INTERSTELLAR METHANE

Methane was observed extraterrestrially, inter alia, in brown dwarfs,⁵⁰ the giant planets of our solar system,⁵¹ and beyond (the moons Titan and Triton,^{52,53} the dwarf planet Pluto,⁵⁴ and different comets⁵⁵). Smaller amounts of methane have also been observed in the Martian atmosphere via remote sensing^{56,57} and by in situ measurements from Mars Science Laboratory (MSL) onboard the rover Curiosity, which landed in Gale Crater in 2012.⁹

There are alternate possible routes for the formation of molecules in the ISM,^{58a} and many forbidden reactions can occur by quantum-mechanical tunneling and the formation of hydrogen-bonded association adducts.^{58b,c} They involve ion–molecule interactions in the gas phase, usually by ionization of H₂ by cosmic rays to H⁺ and its interaction with molecules such as H₂, CO, etc., which are abundant in ISM. Other possible routes are circumstellar reactions in which gas molecules freeze and stick onto grains, forming icy mantles and promoting further reactions including hydrogenation of O, C, N, etc. on grain surfaces; reactions catalyzed on dust-grain surfaces; and shock-induced reactions (usually occurring in the dense, hot star-forming regions). The latter reaction occurs when the heating of gases by shock waves overcomes the activation barriers, enabling reactions to proceed between neutral species. Adsorption of hydrogen onto the grain surface, which acts as

catalyst, leads to effective hydrogenation of C, N, and O, forming hydrogenated products such as CH₄, NH₃, and H₂O. Efficient formation and prevalence of methane in the ISM (or atmosphere of planets and their moons, such as Titan of Saturn) point to the sequential hydrogenation of atomic carbon on the cold grain surface (eq 1).⁵⁹



Studies by Bar-Nun et al.⁶⁰ indeed showed the formation of methane by collision of H atoms on graphite at very low temperatures, as low as 7 K. Relative to water–ice abundance, the methane–ice abundance is in the range of 2–13%.^{61a–c} In the solar system, a significant amount of methane remains embedded in the ice crystal lattice in the form of methane hydrate clathrate.^{61d} Developing protostars heat the molecular cloud core, and sublimation of a fraction of methane–ice occurs. Under such highly energetic conditions, reaction with C⁺ occurs, initiating a pool of hydrocarbon chemistry in the gas phase.^{62–66} Other pathways include the protonation of C by H₃⁺, followed by successive hydrogenation of the produced CH⁺ ions by H₂, resulting in CH₃⁺, a relatively stable carbocation in ISM conditions. Instead of abstracting H from H₂, it can undergo radiative recombination to form CH₅⁺. The CH₅⁺ ion can transfer a proton to molecules such as CO, water, or methanol, or undergo dissociative recombination forming methane; successive reduction of CO/CO₂ to methane is yet another probable pathway (Figure 2).

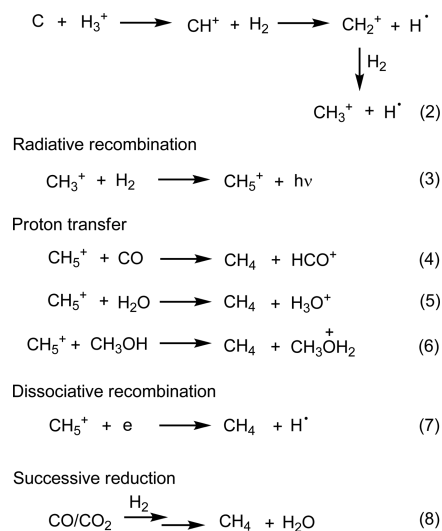


Figure 2. Astrochemical pathways for the formation of methane in the interstellar medium.

■ INTERSTELLAR METHANOL

Released into surrounding space from exploding stars during their extinction, elements started to form varied molecular matter, including the discussed simplest C₁ hydrocarbon molecule, methane (CH₄) (vide supra), and its oxygenated analogue, methanol (CH₃OH). Alternate routes for their formation include the successive hydrogenation of CO or CO₂; selective oxidation or oxygenation of methane; combination of methyl and OH radical, formed respectively from methane and water. Hudson and Moore^{67,68} have shown that proton radiolysis of water–CO mixture at 16 K forms

HCO radical, which leads to the formation of a mixture of formic acid, formaldehyde, and methanol. Wada et al.⁶⁹ have studied the electron irradiation (10–300 eV) of ice-CH₄ mixture (10:1) at 10 K and observed the formation of methanol (Figure 3, route B). Other possible routes involve

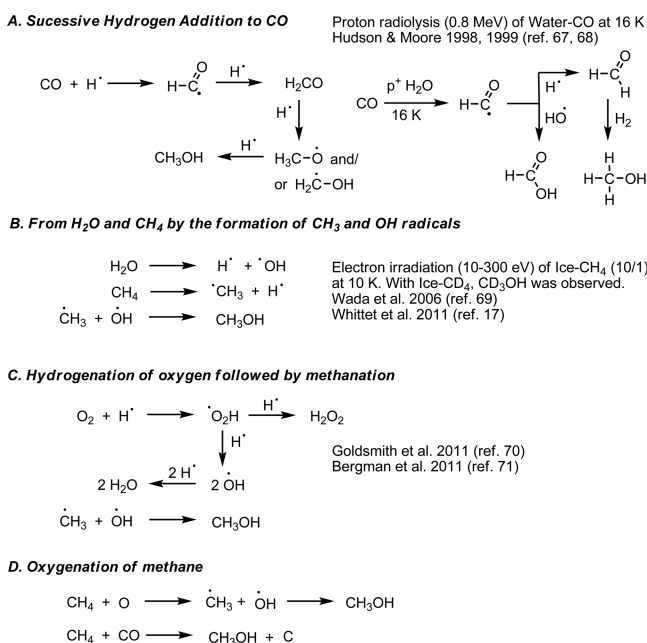


Figure 3. Possible routes for interstellar methanol astrosynthesis based on laboratory experiments under simulated conditions.

hydrogenation of oxygen and oxygenation of methane (Figure 3, routes C and D).^{70,71} Under the high-energy radiation conditions prevalent in the ISM, these routes show probable interstellar hydrogenation pathways, as well as the oxygenation pathways for astrosynthesis of methanol, also proposed in our recent work.^{1a}

In our terrestrial chemistry, it is well understood that methanol is more reactive than methane. It is thus a key intermediate for the building blocks of more complex hydrocarbon molecules and their derivatives. These include the essential building blocks of terrestrial life, such as amino acids and polypeptides, nucleic acids, sugars, etc. The abiological transformation of the discussed molecular matter (evolved from the dispersed elements of exploding stars) to a plethora of hydrocarbon analogues, their derivatives, and ions is now firmly established. These products have been detected and identified most significantly by the onboard instruments of the Cassini-Huygens spacecraft orbiting Saturn's moon, Titan, since 2004.^{22,23} Recently,^{1a} we have also discussed the probable new astrochemical route for their formation from methanol.

As discussed, a series of very large methanol clouds were observed in space, some exceeding the width of our solar system in the Milky Way galaxy and others in different parts of interstellar space. Besides the possible astrochemical routes for the formation of methanol and its derivatives (including various hydrocarbons, their derivatives, and ions), there is also the feasible astrochemical conversion of methanol to olefin (MTO) to be considered. As discussed previously,^{1a} extraterrestrial methanol can also produce ethylene, other olefins, polymers, and their derivatives in an astrochemical methanol-to-olefin (AMTO) conversion process.

RELEVANCE AND SIGNIFICANCE

As mentioned, methane (CH₄) and methanol (CH₃OH) constitute the major molecular matter besides hydrogen and water in the ISM, interstellar clouds, molecular clouds (stellar nursery), and protostars, from which planets, comets, and asteroids are derived.^{65,66,72} They also contain carbon oxides (CO, CO₂), formaldehyde (CH₂O), ammonia (NH₃),⁷³ and varied other compounds, including significant amounts of formamide (NH₂CHO), the simplest amide and key building block for the synthesis of amino acids and peptides.^{66,74,75}

The observation of extraterrestrial prebiotic life precursors manifests their abiotic astrochemistry, but not the formation of living biological matter corresponding to terrestrial life. It should be emphasized that no evidence for extraterrestrial life was ever obtained. It is concluded that, so far, life was formed only on planet Earth. From the observed extraterrestrial building blocks, RNA and DNA chemistry could have evolved if they were transported by meteorites or comets to other celestial bodies of our universe, where water and suitable mild conditions existed, comparable to those of planet Earth. Primitive life forms could, however, also be formed involving water—for example, in hydrated rocks or occasionally melting ice saturated with varied salts (which lowers the freezing point) during a period of relative warming (similar to conditions on Mars).⁷⁶

From the seeding of the simplest inanimate precursor molecules (methane, methanol, and ammonia) under favorable conditions, as in the liquid water lakes or oceans of our Earth, fundamental life building blocks such as amino acids, proteins, and sugars could also be formed, as indicated by Miller's pioneering studies.^{77–79} In a simulated primitive atmosphere (containing a mixture of hydrogen, ammonia, methane, and water), amino acids, the molecular building blocks of proteins were formed upon energetic irradiation. In experiments with other combinations, many other building blocks such as sugars and nucleotides were also synthesized. These observations gave scientists greater insight into the chemical aspects of the evolutionary process involved in terrestrial life forms. It was occasionally also suggested that life forms themselves were transported by comets and meteorites to seed formation of life on Earth, which, however, seems highly improbable. Comparison of astrophysically observed extraterrestrial matter with the terrestrial composition of living matter indicates that only inanimate precursor molecules were formed extraterrestrially and subsequently transported to Earth^{32–34} for further evolution to life forms.

These two steps must have happened not simultaneously but separately, under substantially different conditions. Miller's experiments^{77–79} remain valid, showing that simple molecules, including methane, ammonia, and water, upon radiation (or under electric sparks), form amino acids and even other life precursor molecules. More complex nucleic acid bases, sugars, phosphates, etc.—essential building blocks for RNA, DNA, and other basic molecular species for subsequent evolution of life on Earth—may have resulted from the transport of the inanimate building blocks to Earth. These molecules may have provided starting material for the evolution of life on Earth under its favorable “Goldilocks” conditions. Earth is the only place known so far for harboring life in the universe. If life evolved in this way on Earth, then evolution of different and superior life forms could have been a frequent phenomenon in the universe, although such life forms may have not survived

long enough to continue into thriving biological systems. Humans have long looked for extraterrestrial “little green men” and tried to make contact with beings having advanced knowledge and technology, indicative of a higher level of intelligence, but so far in vain. The age of the Earth is best estimated as about 4.54 billion years (4.54 Ga, where Ga stands for “gigaannum”).⁸⁰ Evidence for life forms present on Earth, obtained from the study of different sources, dates back to the geological time period of the Hadean Eon, during the Eoarchean Era (~3.5 Ga old).⁸¹ Microbial fossils were found in sandstone discovered in Western Australia (~3.48 Ga old),⁸² in biogenic graphite in metasedimentary rocks found in southwestern Greenland (~3.7 Ga old),⁸³ and in the recently discovered graphite preserved in zircon (4.1 Ga old) in old rocks from Jack Hills, Western Australia.⁸⁴ They all suggest that the terrestrial biosphere emerged over 3.5 Ga ago.

Physical matter from our universe dates back to the formation of the universe. The timeline of formation of our universe is estimated to be ~13.82 billion years (13.82 Ga). The observation of the persistent cosmic microwave background radiation by Penzias and Wilson in 1964 is a clear indication of the universe’s dense and hot eventful beginning.⁸⁵

As mentioned earlier, there are increasing suggestions and views (but no evidence) that innumerable universes (multiverses) continuously form and become extinct.^{40,41,86a} Hawking⁴⁹ and others suggested that it is meaningless to consider anything preceding the Big Bang event that formed our universe. Time is therefore only considered after it. Formation from “nothing” was also considered by some,^{86b} pointing out that the quantum vacuum is anything but empty. It is, rather, seething with virtual particles (quantum fluctuations). These particles neutralize each other, but occasionally one can escape and can initiate the process for self-reproducing universes.⁸⁶ The very recently obtained proof of the existence of gravitational waves,^{87–89} originally suggested by Einstein, seems to prove them to be correct.

The discovery of Higgs boson particle,⁹⁰ which produces the Higgs gravitational field, already predicted that gravitational waves would be a proven phenomenon. Based on Einstein’s general relativity theory, it is suggested that gravity is the space–time distortion dependent on the energy and momentum of the particle. Although regular waves resulting from gravity are well known in visible forms, observation of the gravitational waves (the so-called ripples in the space–time fabric, predicted by Einstein in 1915) happened only very recently.^{87–89} It is expected that this break-through—the decades-long search for gravitational waves and their recent detection—will open for humankind studies of the pre-Big Bang condition of our universe.

For us, however, advancing knowledge of the composition and relevance of extraterrestrial matter of our solar system of the universe is of primary interest. The merit of direct observation and study of extraterrestrial matter goes to astrophysicists and their pioneering observations over the years. The evaluation of the chemical aspects, primarily based on similarities with our studied chemistry, is, however, hoped to significantly enhance our understanding of the physical and chemical origin of extraterrestrial matter as well as the subsequent evolution of terrestrial life on planet Earth.

CONCLUSIONS

Astrophysical studies using space telescopes, space vehicles, and landers have sent back to Earth valuable spectroscopic, mass

spectrometric, and analytical data. These show a surprising similarity of the molecular matter of celestial bodies and interstellar space dust or ice with our studied terrestrial chemistry of hydrocarbon derivatives and ions (carbocations and carbanions). Our chemical evaluation of the data and comparison with our studied chemistry now allow us, for the first time, to establish a solid scientific basis for the involved astrochemistry and chemical evolution of the building blocks under abiological conditions. Needed hydrogen was formed directly from the Big Bang, and its further fusion by nucleosynthesis formed the other essential elements, such as carbon, nitrogen, and oxygen, in the hot interior of young stars. Supernova explosions of dying stars dispersed those elements into the surrounding space, forming essential chemical matter, including molecules such as water, methane, methanol, and ammonia. Later, more complex, inanimate molecules and building blocks, such as amino acids, proteins, and nucleic acids, were also formed.

The abiological extraterrestrial formation of increasingly more complex molecular building blocks took place on the surface of space dust (ice) and in celestial bodies. These building blocks were transported to Earth by comets and meteorites. Under Earth’s unique “Goldilocks” conditions, evolution of life, including us *Homo sapiens*, took place. Varied primitive forms of life could have developed on different planets and celestial bodies, but conditions must not have been suitable to maintain them or allow evolution to higher life, as we now understand. Primitive life forms very different than ours could have existed, but have become extinct in our observable surroundings. It also may exist on many celestial bodies of the observed universe. Our universe (or multiverses of the cosmos) probably may contain (or have contained) many forms of “life” not even imaginable to us. But we must confine our consideration to our limited, factual, scientific knowledge and understanding.

AUTHOR INFORMATION

Corresponding Author

*olah@usc.edu

Notes

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