CARBIDE CHEMISTRY AND OPARIN'S THEORY ON THE ORIGIN OF LIFE

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The first and foremost question concerning the origin of life on our planet (abiogenesis) is the synthesis of complex organic compounds (sugars, amino acids, proteins, nucleic acids, etc.) without the help of a living cell. The problem was apparently solved in the 19th century by the first organic synthesis, Wöhler's preparation of urea in 1828 (1), but this is not that simple. To regard Wöhler's synthesis as "a chemical legend" (2) is an exaggeration, as it is also an exaggeration if we take it as a revolutionary discrediting of vitalism (3) and judge it as "in the true sense of the word an epoch-making discovery" (4). The truth is that there are no really crucial experiments, for science actually progresses "in an organic and evolutionary manner" through many small incremental changes and frequently simultaneous discoveries (5).

Products of biogenic and abiogenic synthesis are frequently the same, but their chemistry is different. "It must be noted, however, that the chemist employs in his syntheses altogether different means than the living cell," (6) wrote A. I. Oparin (1894-1980), the founder of the first modern theory of the origin of life. This raises a primary question about the origin of life: does inanimate nature employ the same means as a chemist? This was and still is a great enigma because there were no "halogens [i.e., derivatives of chlorine, bromine, etc.], mineral acids, strong alkalies, high temperatures and pressures, and various other powerful agents" (7) in prebiotic nature.

Oparin goes on to assert that prebiotic organic chemistry proceeded without these powerful agents, and of course without enzymes, but incredibly slowly. Therefore it is a bit misleading to propose that abiogenic synthesis occurs on the modern Earth, but remains unnoticed for it is immediately consumed by living organisms, as Darwin speculated in his famous letter to Hooker written in 1871 (8):

> But if (and oh what a big if) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present, that protein compound was chemically formed ready to undergo still more complex changes, at the present day, such matter would be instantly devoured or absorbed, which would not have been the case before living creatures were formed.

Conditions on Earth were quite different in those remote times when life had come into being than they are at present. More recent theories, starting from that of Urey and Miller (9) assume that the primary organic synthesis occurred in the primordial, undoubtedly reducing atmosphere consisting of carbon monoxide and dioxide, methane, ammonia, water, hydrogen, and the like, mostly by free-radical photochemical reactions. Oparin's theory took a different course, though. Oparin also assumed the primitive Earth's atmosphere was reducing, but the first organic compounds were produced by hydration of hydrocarbons (to summarize it in the simplest possible terms), which in turn were originated by volcanic and other tectonic activities from carbides.

Carbide Technology

The idea that hydrocarbons were originated from carbides and subsequently transformed into more complex compounds by reaction with water, as Oparin put it, has close resemblance to a chemical technology used in his time, namely in utilization of calcium carbide (10) for the production of organics. Curiously, that substance was prepared by the chemist associated with the first organic synthesis, Friedrich Wöhler in 1862, by heating an alloy of zinc and calcium with charcoal to a high temperature (11). However, the real father of calcium carbide as well as acetylene technology was Thomas L. Willson, who accidentally invented a method for its production in 1892, trying to reduce calcium oxide with charcoal (12). By the end of the century it was "produced commercially in many places—notably at Niagara Falls, New York, where the requisite electric current to produce the high temperature needed (4500 Fahrenheit) can be readily and cheaply obtained" (13). It became the raw material for almost all the products of organic chemical industry, especially Buna synthetic rubber, via reactions of acetylene (14).

Acetylene gas was a miracle of the age for "The illuminating power of acetylene, in a proper burner, is greater than of any other known gas; the flame is absolutely white and of great brilliancy; its spectrum closely approximates that of sunlight, and consequently it shows the same colors as daylight" (13). Not less important was its reaction with water at 300°C on an iron oxide catalyst, producing acetaldehyde, described in 1915 by Russian-French chemist Aleksei Yevgen'yevich Tchitchibabin (Chichibabin) (15, 16). This and similar reactions were, according to Oparin, crucial for the formation of complex organic compounds on the early Earth (16):

> Considerable quantities of various oxidation products of hydrocarbons, such as alcohols, aldehydes, ketones, and organic acids must have originated as result of such transformations on the Earth's surface. In the above described reaction, as Tchitchibabin points out, if the heated moist acetylene gas contains ammonia, it is possible to observe with the naked eye the formation of a crystalline precipitate of an aldehyde-ammonia; i.e., under these conditions ammonia very rapidly combines with the acetaldehyde formed by hydration. Similarly, other oxidized derivatives of hydrocarbons (the above mentioned alcohols, aldehydes and acids) can enter into variety of reaction with ammonia, giving rise to ammonium salts, amides, amines, etc.

It is clear that Oparin used the hydration of acetylene as a key reaction for the abiogenic formation of organic compounds. This is not at all surprising because the same reaction led to a number of products in acetylene-related chemical industry, but at lower temperatures and with a different catalyst (Hg_2SO_4). But acetylene has not been produced only by reaction of calcium carbide with water. In 1859 French chemist Marcel Morren synthesized it in an electric arc between carbon electrodes in an atmosphere of hydrogen (17), and in 1931 it was demonstrated that methane, heated to 1000°C was converted to acetylene without any catalyst (18), a process which is now widely employed for its production. The reaction was, according to Oparin, also instrumental in abiogenic synthesis, but methane as well as other hydrocarbons were originated by reaction of carbides with hot water vapor.

Abiogenic Origin of Hydrocarbons

Oparin founded his carbide theory of abiogenic synthesis mostly on the Mendeleev's theory of the inorganic formation of petroleum. After his visit to American oil fields, at the session of Russian Chemical Society of October 15, 1876, Mendeleev launched a hypothesis that hydrocarbons were originated from iron carbides by the action of water vapor according to a somewhat cumbersome equation (19):

$$3\ Fe_mC_n + 4m\ H_2O \rightarrow m\ Fe_3O_4 + C_{3n}H_{8m}$$

"As the igneous rocks were folded, cracks must have been formed which at the crests opened outwards while at the depression they opened inwards," says Mendeleev. "Both these types of cracks became in time filled in, but the more recent the origin of the mountain the more open must these cracks be, and water must have entered through them into the Earth's interior to such depths as would be impossible normally from a plane surface" (20). Oparin expressed his disbelief in Mendeleev's explanation because "it would be difficult to imagine how drops of liquid water could possibly reach the glowing mass of carbides, from which they were separated by more than a thousand kilometers' (about 600 miles) thickness of igneous rocks," (20) both of them ignorant of the existence of the Earth's mantle (moho), discovered by Croatian seismologist Andrija Mohorovičić in 1910 (21). They namely supposed that the interior of Earth (barysphere) was composed of melted iron containing dissolved carbon, above which a rock layer (lithosphere) was formed (19). However, Oparin accepted Mendeleev's theory in general terms assuming that "Hydrocarbons must have originated on the Earth by a similar process during the remote past of its existence, when carbides were erupted onto its surface and were acted upon by the superheated aqueous vapor of the atmosphere of that epoch," leading to the final conclusion (his italics): "*Carbon made its first appearance on the Earth's surface not in the oxidized form of carbon dioxide but, on the contrary, in the reduced state, in the form of hydrocarbons*" (22). This hypothesis contradicts modern theories of the origin of life, which propose the primordial Earth's atmosphere was composed mostly of carbon monoxide and dioxide (23), which were the primary source of organic carbon (24), as was speculated even in Oparin's time (25). However, there are also theories which find its primary source in tectonic processes and extraterrestrial material (26).

Oparin's theory was supported by many experiments with carbides in these times. The first such experiment seems to be that of Schretter who in 1841 obtained a liquid resembling naphtha by action of diluted acid on cast iron, and this reaction was further studied by Hahn and Cloëz (27). These experiments were known to Mendeleev who repeated them. He was also informed of the more elaborate experiments of his former student K. B. Haritchkov (1865-1921), an eminent Russian oil chemist (28), who, at the end of the 19th century, produced hydrocarbons by action of water vapor and hot water solutions of magnesium chloride, magnesium sulfate and sodium chloride on cast iron containing 3% carbon (29).

The problem of prebiotic synthesis of nitrogen compounds Oparin solved in a similar way. He namely hypothesized that they were produced from ammonia, that was in turn produced by action of water and water vapor on nitrides. Nitrogen needed for their synthesis was provided by thermal decomposition (at about 1000°C) of nitrogen(II) oxide which further combined with free metals, especially iron in the Earth core (30). This hypothesis was confirmed by the finding of free nitrogen and ammonia in volcanic gases, as well as nitride mineral osbornite (TiN) in chondrites which "may reflect the dominant form of nitrogen in early Earth" (31). These new findings are in line with Oparin's hypothesis that the dominant reaction was that of iron(III) nitride with water converting it to ammonia. Oparin wrote, "Thus, it can be assumed with a high degree of probability that *nitrogen, like carbon, first appeared on the Earth's surface in its reduced state, in the form of ammonia* (31, his italics)."

Oparin did not go further to elaborate prebiotic chemistry in detail; he simply assumed that by reaction of aldehydes and ammonia in the primordial ocean many compounds resembling those found in living beings were formed, including sugars (by the formose reaction, discovered by Butlerov in 1861 (32)), pyruvic acid (by reaction of acetaldehyde with carbonic acid), etc. (6):

> We cannot follow the extremely varied and numerous processes of evolution of organic matter in detail, and for our purpose this would be superfluous. We can certainly establish the general trend of these transformations and changes on the basis of our knowledge of the properties of these compounds.

Conclusion

In the carbide theory of prebiotic synthesis lies more or less conscious belief that for its purposes nature uses human technology. The notion is both naive and reasonable. It is naive because the laws of nature are immutable in contrast to technological procedures which are constantly developing and adapting to the needs of humanity (33). It is however reasonable because it leads to the use of new ideas, methods and approaches to solve old problems.

As virtually all organic chemical industry rested on calcium carbide and its water product (acetylene), it was quite natural to "believe" that abiogenic synthesis started with the same or similar substances. This is the first root of Oparin's theory. The second is undoubtedly the growing interest in petroleum, with the first oil well in the world drilled in Canada 1858, immediately followed by the 1859 well in Pennsylvania (34). In this respect we also have to understand Mendeleev's interest in the origin of petroleum because he was engaged in the research of coal and oil deposits of Russia, which had begun to transform itself from a rural into an industrial nation (35).

Mendeleev's theory of abiogenic formation of oil was forgotten after the advent of biogenic theories (36) until Thomas Gold resurrected it in 1992, as a part of his theory of the origin and propagation of life. Gold proposed that the first organisms were originated and developed in the pores of rocks deep in the Earth's interior thriving on "hydrogen, methane and other fluids percolating upward" (37). But from another perspective, the problem of prebiotic synthesis ceased to be in the focus of modern scientists. The last bastion of vitalism, that abiotic ("inorganic") nature is poor in organic compounds, i.e., carbon compounds, has fallen by the finding of millions of organic compounds in carbonaceous chondrites, of which 683 were positively identified (38). In addition, nearly two hundred different organic molecules were detected in interstellar gas (39). The apparent chemical complexity of biotic in contrast to abiotic nature turned to be the consequence of poor analytical methods. However, the organizational complexity of living beings cannot be denied, so new theories of the origin of life are concerned primarily with the development of self-reproducing systems (40).

From another perspective, the carbide theory of abiogenic synthesis points to the fact that every hypothesis, either right or wrong, can have a positive influence on the development of science, or as Joan Oró (1923-2004) put it (41):

> … the irony of Oparin being inspired by Mendeleev's incorrect assumption together with my own independent involvement with the idea to study the origin of life inspired by a biochemically incorrect assumption demonstrates the creative importance of a hypothesis, whether completely correct or not, to develop breakthroughs in the obtention of new scientific knowledge.

This theory "also reveals the role of intuition, serendipity and the tortuous and winding roads of scientific discoveries" (42).

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Ladies in Waiting for Nobel Prizes: Overlooked Accomplishments of Women Chemists

A full-day symposium sponsored by HIST and the Women Chemists Committee (WCC) will be presented at the 254th American Chemical Society (ACS) meeting in Washington, DC, Tuesday, Aug. 22, 2017. Magdolna Hargittai, author of *Women Scientists: Reflections, Challenges, and Breaking Boundaries* (Oxford University Press, 2015) will be keynote speaker. After the symposium the Portal Theatre Group from the Pacific Northwest will present "No Belles," which tells the tale of eight female scientists, six of whom won Nobel Prizes.

"Ladies in Waiting" builds upon the well-received symposium "The Posthumous Nobel Prize in Chemistry," held in March 2016 at the San Diego ACS meeting. That symposium was covered in a popular article in *Chemical & Engineering News* and is now in the process of publication as an ACS Symposium Series book. E. Thomas Strom, organizer of the earlier symposium, joins Vera Mainz as organizers for "Ladies in Waiting."