JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Perspective

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Chemical Formation of Methanol and Hydrocarbon ("Organic") Derivatives from CO_2 and H_2—Carbon Sources for Subsequent Biological Cell Evolution and Life's Origin

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ABSTRACT: Formation of methanol and hydrocarbon derivatives from CO_2 and H_2, their simplest molecular building blocks, under biocompatible conditions is proposed. Alternate panspermia of similar extraterrestrially formed and observed hydrocarbons to earth is also discussed. The simple molecular building blocks derived from CO_2 and H_2 are carbon sources in the initial stage of biological evolution of cells leading to life's origin.

1. BACKGROUND

Formation of the universe from the energy released by the Big Bang event followed by expansion and cooling, allowing its conversion to matter, as expressed by Einstein's $E = mc^2$ equation, is now generally accepted.[1] The origin of life (so far only recognized on our planet Earth) is one of humankind's existential questions, which has challenged our ancestors since the beginning of the recorded time. It is, however, still not fully understood. We know that the earliest fossils point to the emergence of life ~4.1 Ga ago.[2]

Miller and Urey's classic experiment[3] under conditions similar to those of the primordial soup of warm ponds[4] showed the formation of varied amino acids—the building blocks to polypeptides and eventually proteins (with programmed sequence)—fundamental to the formation of living systems. They were formed in vitro from the simple inanimate precursor molecules, hydrogen, ammonia, methane, and water, under electric discharge or effective radiation. Though evidence from recent studies suggests that the composition of Earth's original atmosphere might have been different from Miller's conditions, his results give a significant insight into the chemical aspects of the evolutionary process toward further terrestrial life. Besides formation of amino acids—the molecular building blocks of proteins—many other building blocks, such as sugars and nucleotides, were also formed in simulation experiments with other combinations. The chemical significance of this pioneering experimental work was, however, subsequently questioned by Wächtershäuser,[5] who pointed out why no real proof was provided by the "hot pond" concept of conversion of inanimate to any living matter or even to the simplest forms of precursors of cells. Crick and Watson's fundamental scientific breakthrough[6] and the explosive development of modern biology essentially advanced our understanding of biological systems, particularly the quest to understand how life could have been originated from inanimate precursor molecules including methane as a carbon source, but that essential question remains unanswered. We now discuss the significance and possible role of methanol, the reactive oxygenate of methane, and its derivatives from terrestrial and extraterrestrial chemical origin in the molecular evolution of life's building blocks.

2. CHEMICAL FORMATION OF METHANOL AND "ORGANIC" (HYDROCARBON) DERIVATIVES FROM CO_2 AND H_2

It is known from our terrestrial chemistry that methanol is much more reactive than methane in forming "organic", i.e., hydrocarbon, derivatives.[7−10] The formation of methanol from CO_2−H_2 of geological origin under biocompatible moderate conditions is also proven. The formation of simple heterosubstituted molecules, such as HCN, NH_3, HCHO, $HCONH_2$, and CH_3OH, and their transformation to higher hydrocarbon derivatives, including more complex prebiotic molecules such as sugars, nucleic acid bases, amino acids, polypeptides, and proteins, have been revealed by continuing extensive studies.[11−15] We now suggest that the reaction of CO_2 with H_2 to methanol has substantial significance in the initial stage of forming simple abiological molecules, which are fundamental "organic" building blocks for the formation of simple prebiotic cells for subsequent biological evolution to cells.

Hydrogenation of CO_2 with molecular hydrogen (H_2) is exothermic, but a significant kinetic barrier must be overcome to initiate the reaction (high temperature, high pressure, suitable catalyst, etc.).[16] The hydrogenation of CO_2 eventually gives the thermodynamically most stable derivative, methane, through the stepwise reaction shown in Scheme 1.

Scheme 1. Hydrogenation of CO_2 to Methane

$$CO_2 + H_2 \longrightarrow HCOOH \xrightarrow{H_2} HCHO + H_2O \xrightarrow{H_2} CH_3OH \xrightarrow{H_2} CH_4 + H_2O$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \quad \Delta H_{298\,K} = -11.8 \text{ kcal/mol} \quad (1)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad \Delta H_{298\,K} = -39.4 \text{ kcal/mol} \quad (2)$$

Once initiated and not controlled, the CO_2 hydrogenation goes to the most stable but least reactive product, methane (methanation reaction, $\Delta H_{298K} = -39.4$ kcal/mol).[16] Methane,

Received: September 29, 2016
Published: December 16, 2016

however, cannot be converted to hydrocarbon products under biologically compatible conditions. Therefore, the intermediate reactive hydrogenated products, such as formates, formaldehyde, and best of all, reactive methanol, are needed for forming the essential building blocks for evolution of cells while avoiding further hydrogenation to methane. As discussed by Lane and others,[17] selective formation of the intermediate molecules in substantial concentration by suppressing continued hydrogenation to methane is a difficult challenge.

The Sabatier reaction,[18] discovered in the 1910s, was the first industrially developed CO_2-H_2 reaction for producing mainly methane, the least reactive C1 hydrocarbon. The reaction was conducted at elevated temperatures (300−400 °C) and pressures in the presence of a nickel catalyst. Since the discovery of the Fischer−Tropsch process[19] using syngas ($CO-H_2$) to produce long-chain hydrocarbons, the application of the Sabatier reaction has diminished. Methanol, the most significant oxygenated product, has long been produced industrially from syngas (with CO and H_2 in the ratio 1:2, now called metgas[20]).

Conversion of methanol to thermodynamically more preferred products such as formaldehyde and formic acid and their conversion to formamide, formation of sugars from formaldehyde, and formation of nucleic acid bases and amino acids as well as peptides from formamide are all terrestrially observed and studied processes. Transformation of methanol to higher hydrocarbons and derivatives by methanol-to-olefin (MTO)[7−10] and methanol-to-gasoline (MTG)[7b,21] processes is well known. Therefore, it is obvious that our terrestrially observed CO_2-H_2 chemistry serves as the basic molecular core toward the evolution of complex molecular building blocks for cells and life's origin, irrespective of the venue and time of its origin. It is noteworthy that the CO_2-H_2 to methanol process is now widely practiced industrially in many countries, and the first industrial plant using geothermal CO_2 and hydrogen derived from water by electrolysis using geothermal electrical energy is the George Olah Renewable Methanol Plant at Carbon Recycling International (CRI) in Iceland.

3. EXTRATERRESTRIAL METHANOL AND DERIVATIVES: TRANSPORTATION TO EARTH

Observation and study of extraterrestrial methanol in vast interstellar clouds or on protoplanetary space dust and its transportation via comets and meteorites to Earth became possible through the pioneering astrophysical and developed space technology.[22] Similar to water, which was formed extraterrestrially and transported to Earth, methanol and its hydrocarbon derivatives could have been transported by these comets and meteorites to the young Earth with its favorable "Goldilocks" conditions.[23] Subsequent transformation to more complex prebiotic molecules and protocells via chemical evolution over a long period of time is suggested to be the key to transformation of inanimate matter to increasingly more complex cells, leading eventually to life.[24] Since Townes's discovery of interstellar water vapor and ammonia,[25] astrophysical studies showed the presence of not only the simplest molecular matter but also a variety of more than 200 "organic" molecular species, some of which were directly observed by onboard instruments of spacecrafts such as the Cassini−Huygens spacecraft from surface of Titan (the moon of Saturn) and the Philae lander that landed on comet 67P/Churyumov-Gerasimenko.[26,27] These studies showed the presence of "organics"—hydrocarbons, their derivatives, and their ions similar to those previously studied by our group. Using these data, it was possible to make a comparison with our terrestrial chemistry, showing remarkable similarity. In our recent papers,[28] we have also discussed the relevant probable astrochemical pathways for the formation of these molecules extraterrestrially. In this Perspective, we now suggest to extend the relevance and significance of methanol (and not methane) under biocompatible conditions to the still unsolved questions of the probable biological formation of cells and the subsequent evolution of increasingly complex living cells and systems on the way to origin of life as we presently know only here on our planet Earth. Even though the presence of similar systems with "Goldilocks" conditions is not yet confirmed, the data obtained from other planets or moons, such as Enceladus (moon of Saturn) by the Cassini spacecraft[29a] and Europa (moon of Jupiter) by the Hubble space telescope,[29b] showing the presence of water plumes and interior reservoirs of water, suggest the possibility of the evolution of living cells and some form of life in other extraterrestrial bodies if they have suitable conditions.[29]

4. SIMILARITY WITH EVOLUTION IN HYDROTHERMAL SEA-BOTTOM VENTS

Pioneering studies by Lane, Martin, and Russell[17] on alkaline hydrothermal vents emphasized the essential role of CO_2-H_2 hydrogenation as the initial stage of the molecular evolution to complex prebiotic molecules and subsequent biological evolution of cells. We discussed recently the role of methanol—the reactive monooxygenate of the simplest C1 hydrocarbon CH_4—toward the formation of various "organics" (including building blocks of life like proteins, nucleosides, sugars, etc.) for biological evolution of cells.[28] Under deep-sea vent conditions also, methanol—the hydrogenated derivative of CO_2 and preferred reactive intermediate—can act as a key synthon toward the evolution of cells. We now suggest that, under conditions similar to those of sea-bottom hydrothermal vents, methanol, the partially hydrogenated reactive derivative of CO_2, is the preferred reactive intermediate acting as the key synthon toward the evolution of cells, though it cannot be isolated in significant concentration due to its high reactivity.

Wächtershäuser[5a,30] reported that CO_2 reduction by "pyrites pulling" (catalyzed by pyrites, i.e., iron or nickel sulfide) at "black smokers" was shown to be unsuccessful in his own experiments, and he thus considered hydrogenation of CO_2 by molecular hydrogen not feasible. However, Lane and others found that alkaline deep-sea vent structures formed from serpentinite by the hydration of olivine minerals[31] (derived from Earth's mantle rocks, not from volcanic magma), in a process known as serpentinization, are capable to effect the reduction.[17c−e] Since olivine is rich in ferrous iron (Fe^{2+}) and magnesium, its reaction with water results in the exothermic oxidation of Fe^{2+} to Fe^{3+}, producing hydrogen and heat. Water on the seafloor sweeps them close to tectonic spreading centers (even several kilometers) and reacts. They cool down and react with dissolved salts in the ocean, producing vents with a labyrinth of interconnected micropores. The H_2 formed in the vent labyrinth reacts with CO_2, driven by the prevailing proton gradient at the semiconductor walls of the protocells, and allows the formation of hydrogenated carbon dioxide molecules, leading to "organic" (hydrocarbon) building blocks for the evolution of bacteria, which then allow biological evolution of complex cells and eventually life.[17b−e,32] Once bacteria are formed, they take over from original primitive cells

DOI: 10.1021/jacs.6b10230
J. Am. Chem. Soc. 2017, 139, 566−570

(formed by slow evolution) to reproduce and multiply with the continuous supply of carbon and hydrogen as well as proton gradient energy.[17a]

5. METHANOL, THE KEY MOLECULAR SYNTHON OF CELLS

After scientists realized that neither the "hot pond"[33] nor oceanic "black smoker"[30] could be considered as the source for cell evolution, the focus turned to viable transformation in alkaline hydrothermal sea-bottom vents.[17b−d] Alkaline hydrothermal vents act as a sub-marine flow reactor operating under substantial pressure. It has been shown that formaldehyde can undergo redox disproportionation (usually called the Cannizzaro reaction) in hot water (heated up to 250 °C) at a pressure of 4 MPa (~40 atm), even without a catalyst, to form methanol (and formic acid, which can undergo a hydride transfer reaction with formaldehyde, increasing the yield of methanol).[34] Alkaline hydrothermal vent conditions under pressure can promote the Cannizzaro reaction to form methanol from formaldehyde.

Unlike "black smokers", alkaline hydrothermal vents (as in Lost City) provide the required gradients and chemical energetics,[17b] acting as a hatchery for reactive simple molecular synthons, including methanol. As hydrothermal vents are formed from reactions in Earth's crust, various metals, including transition metals, are present in significant amounts, which can catalyze further molecular evolution to more complex prebiotic molecules, and eventually to cells, resulting in life's origin. Methanol produced by the "sub-marine Cannizzaro reaction" may be unstable under deep-sea hydrothermal vent conditions and can also undergo a "sub-marine MTO process", leading to the formation of olefins, higher hydrocarbons, and their derivatives. Conversion of olefins to most "organic" functionalities is proven by the wide scope of organic synthetic reactions. Metals and their minerals, such as Fe(Ni)S, olivine, serpentinite, and zeolite sediments, together with the walls of deep-sea floor vents, can act as efficient catalytic pockets and surfaces for further transformations. Studies revealed that oxidized iron-containing zeolites are capable of rapid hydroxylation of methane to methanol at room temperature.[35] Aldehydes, acids, amides and esters, aminonitriles (by Strecker reaction), amino acids, polypeptides, and proteins—the building blocks of cells—can be obtained through the MTO process and subsequent transformations. These studies have shown the versatility of the terrestrial MTO process, which is already industrially established.[7−10]

Laboratory experiments showed that the surfaces of mineral particles in hydrothermal vents have catalytic properties similar to those of enzymes and can catalyze the hydrogenation of CO_2 with H_2 in seawater to methanol (CH_3OH) and formic acid (HCO_2H).[36] Low-molecular-weight (up to C_4) hydrocarbons, formate, hydrogen cyanide, and many "organics" which are precursors for prebiotic molecules are generated by Fischer−Tropsch-type reactions under serpentinization conditions with dissolved CO_2 as the carbon source under aqueous hydrothermal vent conditions.[32a,37] Voglesonger et al.[38] showed that metastable methanol can be directly synthesized from a gas-rich CO_2−H_2−H_2O mixture in the presence of magnetite under conditions resembling sea-floor hydrothermal vent conditions (at 200−300 °C and pressures up to 15−18 atm). Williams et al.[39] showed that interaction of dilute methanol with smectites (expandable clay minerals) under simulated sea-floor hydrothermal conditions (at 300 °C, 100 atm) can form "organic" molecules (up to C_{20} were observed). However, it should be kept in mind that exact laboratory simulation of all conditions at the sea-bottom hydrothermal vents and surroundings or extraterrestrial media (interstellar medium, surfaces of planets, moons, comets, meteorites, or asteroids) is not easy. Recent discoveries using the Cassini space probe in the outer solar system show strong evidence for the presence of active hydrothermal vents similar to those in Lost City also under the sea of Enceladus, the moon of Saturn.[29a,b,40]

The key role of methanol as the fundamental molecular synthon for the formation of complex biological cells is shown in Figure 1.

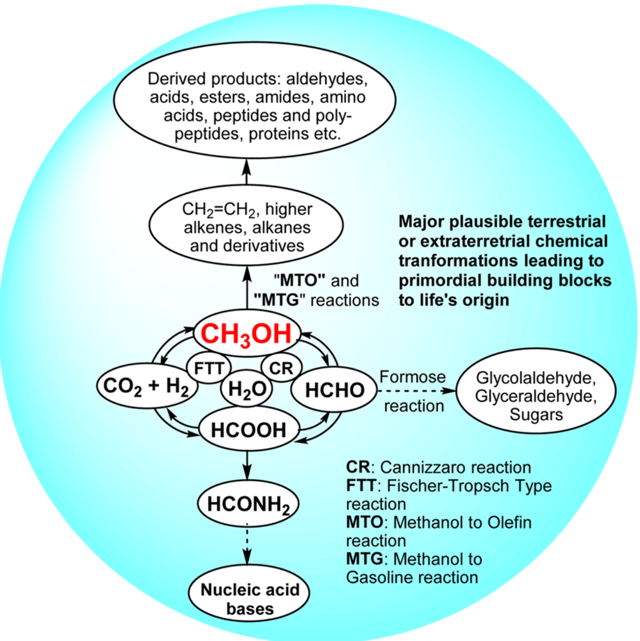

Figure 1. Methanol, the key molecular synthon of life's building blocks.

6. CONCLUSION AND SIGNIFICANCE

Credit for understanding the scientific aspects of the biological evolution of cells, eventually leading to life's origin, goes to modern pioneering studies in biology. Chemical aspects, particularly concerning the initial stage of the biological evolution of cells, leading eventually to life's origin through conversion of primordial terrestrial geological CO_2 and H_2 to reactive intermediate molecular synthons, primarily methanol, for subsequent transformation to "organics", i.e., hydrocarbon derivatives, are of substantial significance. Observed and studied interstellar methanol, its astrochemical transformation to higher hydrocarbon derivatives and systems, and their transportation to Earth represent an alternate carbon source for biological evolution of cells of increasing complexity, leading eventually to life's origin. Available extensive studies and observations, including experiments simulating hydrothermal sea-bottom vents, of the transformation of CO_2−H_2 into many simple and complex organic molecular units also suggest that methanol, a partially hydrogenated reactive carbon dioxide derivative (or, alternatively, monooxygenated methane), is the key molecular synthon toward life's building blocks and origin.

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DOI: 10.1021/jacs.6b10230
J. Am. Chem. Soc. 2017, 139, 566−570

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support of our work by Loker Hydrocarbon Research Institute is gratefully acknowledged.

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DOI: 10.1021/jacs.6b10230
J. Am. Chem. Soc. 2017, 139, 566−570

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DOI: 10.1021/jacs.6b10230
J. Am. Chem. Soc. 2017, 139, 566–570