A Hydrothermal Scenario for the Initial Generation of Some of the Key Molecules of Life from Simple Ones

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The universe and Earth are 14 and 4.5 billion years old, and our challenges to monitor their time and space aspects are not always allowed. The Sun came a few generations after the early universe evolved through the explosive expansion of the big bang. On Earth, born from the Sun, the life was born 3.5 billion years ago, and the biological life evolution is now established in the form of tree diagram as evidenced by fossils, at the bottom of which the single-celled bacteria are located. However, the chemical initiation in hot sea water is not completely understood. It needed some raw materials available as interstellar molecules. C0 (zero-carbon containing) molecules like H_2 and H_2O are hydrogen sources, and C1 molecules like CO, CO_2, HCHO (*formaldehyde*), and HCOOH (*formic acid*), are carbon sources. Our study on the supercritical water reactions of simple molecules has made us meet some elementary evolution processes on the primitive hot Earth.[1-8] Molecular chain-length can be increased in water by forming a new C-C bond between C*n* aldehyde and C1 carboxylic acid HCOOH without metal catalysts; metal-catalyzed C-C coupling reactions are popular in nonaqueous solvents. Key life molecules are considered to have been prepared slowly and monotonously by using heat and by spending an extremely long time. The early slow stage has happened long before the biochemical evolution of much large molecules, such as carbohydrates, proteins, DNA, and lipids. The evolution issue was first attacked by C. Darwin (1809-1882) and a rough sketch for the role of enzymes in the self-assembled system (coacervate) in aqueous solution was developed by A. Oparin (1894-1980). More recently, the Miller and Urey experiment showed that amino acids can be formed from methane, hydrogen, steam, nitrogen, ammonia in water by electric sparks.[9] Interesting questions are: Are there any others? Is lightening always required?

Heat effect on the chemical reaction can be kinetically compared with enzyme effect. Heat can make reactants more energized so that the activation barrier crossing may become easier. An enzyme can make some otherwise difficult reaction realized by lowering the reaction barrier itself even at ambient temperature. Generally speaking, the reaction rate is doubled by a temperature increase of 10 K. When a hydrothermal reaction is performed at 200 deg. C the reaction can be accelerated by such a tremendously huge factor of $2^{17} = {\sim}10^5$. Moreover, water-insoluble hydrophobic molecules become soluble and reactive enough due to the properties changed by the hydration effect. Thus otherwise impossible reactions can be realized in hot water. Actually primitive life is said to have originated around the "chimney" or "black smoker" in hot sea water trenches. [10-13]

Hydrothermal coupling reactions we found can be related to an elementary chemical evolution process. In general, aldehyde (RCHO; R = H, alkyl) and formic acid (<u>HCO</u>OH; acid and simultaneously, hydroxyl C1 aldehyde) are coupled to form a C-C bond resulting in α-hydroxyl carboxylic acid under acidic hydrothermal conditions as follows:

$$\mathrm{RCHO + HCOOH \xrightarrow{H^+} RCH(OH)COOH} \qquad (1)$$

Here, for R = H and CH_3, RCHO is formaldehyde and acetaldehyde, and RCH(OH)COOH is glycolic acid and lactic acid (i.e., α-hydroxy propionic acid), respectively. When the OH group is aminated a corresponding amino acid is obtained without light. A higher homologue of HCHO is available as an interstellar molecule, and a variety of amino acids can evolve in hot water. The coupling initiator, formic acid can be hydrothermally generated form CO and

H_2O or CO_2 and H_2.[2,14] These are quite simple and natural reactions in aqueous system. This can be a kind of early starting point for life emergence in sea on the primitive hot Earth. Hydrothermal reactions of carbohydrates will be also discussed in relation to formic acid.

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