

Synthesis of Organic Molecules, R Ribose and S Amino Acids by Adsorption on Carbon at The Birth of Life on The Earth

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Abstract

Reasons for appearance of optically active organic molecules in nature have not been ascertained up to the present, but clarification of conditions on the Earth during the period of their appearance can contribute to this. H₂ and gases, containing H₂, were oxidized by CO₂ with allocation of carbon and H₂O or CH₂O and CHO(OH) in volcanic gas and in the early atmosphere. During adsorption on carbon CH₂O dissolved in water could be the synthesis only of R (rectus, Latin) ribose, and with NH₃ and CHO(OH) synthesis of glycine and only of S (sinister) serine, and on its bases of other S amino acids. Adsorption on the carbon ensured in complex: concentration of initial components, hydrophobic-hydrophilic properties, optical purity, protection from hydration, decay and racemization. It is shown the possibility of the early Archean reactions: dehydration of phosphoric acid, of phosphoester bonds connection formation in nucleotides, with CH₂O fatty acids and nitrogenous bases.

Keywords: Archean, atmosphere, carbon, adsorption, synthesis, optically active, amino acids, ribose

Introduction

This work is the logical continuation of formerly carried out consideration of some questions of gases evolution on inner planets, conditions on the Earth in the Archean and experiments in obtaining optically active organic molecules. The emergences of optically active organic molecules were determined by the conditions on the Earth during the period of their appearance in the early Archean. And here it is necessary to define: conditions on the Earth, source components and their concentrating, synthesis and preservation of organic molecules, reasons of appearance of optical activity and hydrophobic-hydrophilic properties. Conditions on the Earth in the early Archean are considered below in planetary comparison and

according to geological data and synthesis of organic optically active molecules by adsorption on carbon. This factor allows to solving these problems. Natural synthesis of organic molecules by adsorption on carbon depended on many reasons. In large volumes of basins ensured synthesis of organic molecules by scales and duration of the processes but not by high concentrations. That is why the choice of optimal conditions for the experiments is not the aim of this work.

Results

Conditions on the Earth in the Archean

The relative contents (gas mass / planetary mass) of carbon and nitrogen in atmospheres of Venus, Earth (taking into consideration hydrosphere and sedimentary cover), Mars and Jupiter (up to pressure 100 kPa) decrease almost linearly, and water regularly change with distance from the Sun (Zhmakin, 2010). That is why atmosphere of the Earth in the early Archean could not qualitatively differ from atmospheres of Venus and Mars and consisted of CO₂ and N₂, with the small quantity (by diminishing) of SO₂, CO, Cl₂, HCl, H₂S, CH₄, H₂, NH₃ and others as on Venus (Krasnopolskii, 1982). Volcanic gases of the Earth are close to the same composition and contain hydrocarbons (Marchinin, 1985, Bobrowski, 2005). Activated by radiation oxidation reactions of H₂ and gases, containing H₂, by CO₂ with allocation of water and carbon are possible in such atmosphere (reaction 1, 2 here and further the table). The Earth mainly cools by water evaporation at the surface. But on Venus the temperature at the early stages exceeded its boiling point water at the radiation temperature and greenhouse effect which were much higher due to greater volume of CO₂ and smaller of H₂O. After saturation of the atmosphere by vapors the withdrawal of CO₂ by carbon stopped (reaction 1). With liquid phase occurrence it might be irreversible withdrawal CO₂, as carbon (reaction 2) and carbonates as on the Earth.

At the albedo 0.16 as on Mars and luminous emittance of the Sun 71% the radiation temperature of Venus was 222.7 K. Pressure CO₂ (P_{CO2}) at specific greenhouse index – 0.013 (Kelvin m²) / kg, (for H₂O vapor – 0.0704) in the beginning of the early Archean was not less: (373 - 222.7)/0.013 = 11561 kg/m² (113 kPa) (Zhmakin, 2015). From the linear change of CO₂ content of the planets its pressure in the Earth's atmosphere at that period was 4963 (49 kPa) and was in proportion N₂ – 114 (1.1 kPa) and H₂O in the exosphere 41937 kg/m², and mean temperature at the surface was ~ 314 K (Zhmakin, 2015). In ferruginous quartzite from the Mezoarchean magnetite quite often associates with siderite, which are in equilibrium at P_{CO2} in the atmosphere ~ 67 kPa (reaction 3), and muscovite and sphene are present in crust of weathering in absence of kaolinite. The decomposition of

kaolinite occurred at $P_{\text{CO}_2} > 45 - 50$ kPa (reaction 4). Formation of sphene depends on the temperature and P_{CO_2} (reaction 5). To the values of P_{CO_2} 45 and 65 kPa the temperature corresponds to 311 and 318 K (Zhmakin, 2015). Thus, in the early Archean it changed from 305 up to 320 K. This led to intensive evaporation of shallow water pools in the day time during warm season and to rapid cooling in another time lowering of pH and increased dissolution of gases. The greater part of ultraviolet radiation reached the surface in the atmosphere without oxygen.

Abiogenic synthesis of organic substances in the Nature and Archean

Carbon and organic compounds, including carbohydrates and amino acids, were detected in carbonaceous chondrites and products of volcanoes eruption (Marchinin, 1985, Yakubko, Jeschkeit, 1985). Carbon rocks were widely spread in the Archean (Salop, 1982). Volcanic gases, H_2 and H_2 -containing gases atmosphere oxidized CO_2 at activation temperature or sunlight, with stood out carbon and H_2O , and as intermediates, CH_2O and $\text{CHO}(\text{OH})$ (reaction 6 - 12). This process has been expressed well in conditions without oxygen at the formation of carbonaceous chondrites, and in the current conditions is realized at crystallization within lava (Zhmakin, 2010). Carbon stood out in these reactions, like the dark phase of photosynthesis, on the isotopes which often make the conclusion very early appearance of photosynthesis. Interaction of volcanic gases is correlated with pyrolysis obtaining of nanotubes, fullerenes and other carbon structures, with their simultaneous modification by elements-catalysts by minimum of hydrophilic centers in the anoxic atmosphere. Fullerenes were detected in meteorites, carbonaceous and igneous rocks (Rakov, 2006). CH_2O was identified in volcanic gases (Bobrowski, 2005) and could be present in ancient atmosphere (Pinto, Gladstone, Yung, 1980). Because of oxidation and decomposition by radiation content of recovered gases in the atmosphere was low. At high solubility CH_2O , $\text{CHO}(\text{OH})$ and NH_3 preserved in pools (reaction 10 - 12), and formaldehyde (methanale) changed into metyleneglycol $\text{CH}_2(\text{OH})_2$ (metanediol).

Fine fractions of naturally hydrophobic carbon were not moistened by water and remained on the surface of pools for long time, adsorbing dissolved components. According to the rule of P.A. Rebinder during the adsorption of polar molecules, hydrocarbon radical are oriented to non-polar phase, and polar groups - to polar phase. That is why, in C-H bond hydrogen as a part of amphiphilic molecules $\text{CH}_2(\text{OH})_2$, $\text{CHO}(\text{OH})$ was adsorbed from the solution on carbon, and hydroxyl group came into contact with water. High concentration of source components was necessary for the synthesis of organic compounds. Such concentration could not be achieved in water pools, but was ensured by adsorption on carbon. Besides, high

contents of source components could desorb organic molecules into solution with the following decay under natural conditions.

Catalytic properties of carbon (Likholobov, 1997, Glevatskaya, Bakalinsky, Cartel, 2010), influence of radiation, temperature (Yakubko, Jeschkeit, 1985, Gusev, Mineeva, 2003, Sidorov, 1965, Simonov, 2007) contribute to the synthesis of organic compounds. Lowering of the temperature (and pH, proceeding from solubility of pairformaldehyde) increase polymerizing properties of $\text{CH}_2(\text{OH})_2$ in the solution up to $\text{HO}(\text{CH}_2\text{O})_n\text{H}$, but formaldehyde insignificantly volatilizes with water vapors and also polymerizes during solution evaporation (Ogorodnikov, 1984). In connection with that during cold period with NH_3 solubility increase the synthesis of amino acids took place and during warm period – the synthesis of ribose. Glycolaldehyde hydrate (threehydroetanal) as the basis for monosaccharide's synthesis in A.M. Butlerov (formosa) reaction and of amino acids was formed from two molecules of $\text{CH}_2(\text{OH})_2$ in condensation reactions (reactions 13). In the adsorption on carbon can be synthesized its isomer thereof, as in Figure A. At the greater concentration of $\text{CH}_2(\text{OH})_2$ there were synthesized amino acids with a complex radical group and fatty acids (reactions 14). Preferable adsorption of hydrogen by carbon in $\text{CH}_2(\text{OH})_2$ led only to formation of R chiral ribose and, as it is shown below with NH_3 and $\text{CHO}(\text{OH})$, to S amino acids, providing them optical purity and hydrophobic - hydrophilic properties. As a matter of fact, carbon served also primitive membrane protecting organic molecules from hydration, radiation, breakup, racemization. Optical activity could appear during evolution in other molecules (for example, in glucose).

S serine and R ribose obtaining adsorption on carbon

Experiments corresponded methodically to A.M. Butlerov reaction. Trial experiments were conducted to prove the possibility for the synthesis of S (sinister, Latin) serine and R (rectus, Latin) ribose by adsorption on carbon (Zhmakin, 2013). Presence of serine in the solution has been proved by biuret test (proteins, asparagine, histidine and threonine are defined by the same reaction, but their formation is scarcely probable because of the short duration of experiments), and ribose - by Bial reaction. Optical activity in them has been determined according to angle of rotation of plane of polarization, and for serine also according to dispersion of optical rotation. Optical activity is absent in the suspension of distilled water with carbon used in the experiments that was found by the test after heating. During the experiments took place partial desorption of optically active molecules into starting solution, perhaps, because of high concentration of reactants. For determination of optically active molecules involve a lot of other ways with the involvement of optically active reagents or enzymes (Yakubko,

Jeschkeit, 1985, Buxton, Roberts, 2009), that will give rise to doubts in respect of experimental results.

S serine production has carried out at solution pH – 6.1, with 0.267 mol/l of CH_2O , 0.133 mol/l $\text{CHO}(\text{OH})$, 0.22 mol/l NH_3 , 15 g of activated carbon OU-A, and 23 mmole/l dissolved beforehand of CaO. After 4.5 hours of solution heating at the temperature 326 K and 3 hour of periodic radiation exposure over the range 240 – 400 nm 57% and 43% in visible. S serine content was 0,008 g/l in the test. This is 25 times greater than 3.0 mkmmole/l of serine racemate (glycine 7.5 and alanine 1.2) obtained from the solution with 2.5 % of CH_2O , 1,5% of NH_4NO_3 after radiation exposure (254 nm 80%) 250 hour (Sidorov, 1965).

R ribose has been obtained in solution 0.4 mol/l formaldehyde, 10.08 mmole/l dissolved beforehand of CaO, 19.6 g of activated carbon OU – A, with pH 8.84 after 37 hours heating at 328 K and 1.67 hours of periodic radiation (by the same lamp as for serine). R ribose content was 0.021 g/l in the test.

Discussion

Stereochemical reasons of optical activity amino acids and ribose formation

There are some ways of amino acids obtaining (Yakubko, Jeschkeit, 1985). Glycine could be synthesized from the molecule of $\text{CH}_2(\text{OH})_2$ and ammonium formiate in the reaction of condensation by adsorption on carbon. Glycolaldehyde hydrate could be synthesized from two molecules of $\text{CH}_2(\text{OH})_2$ and S serine - from glycolaldehyde hydrate with ammonium formiate (reaction 15, Figure A). During adsorption on carbon synthesis of S serine is conditioned by structural features of glycolaldehyde and ammonium formiate. Valence angle of $\text{H}^4\text{C}^2\text{H}^5$ in the more stable inhibited conformation of glycolaldehyde (as in Figure A, but with carbonyl group $-\text{C}=\text{O}$) according to experimental data was 106.18, and according to four variants of computations and reference it was 106.21–107.24 degrees (Carroll, et al., 2013). Based on the coordinates of atoms (Carroll, et al., 2013) the calculated dihedral angle of $\text{H}^1\text{C}^1\text{C}^2\text{H}^4$ is equal to 40.67 and the opposite of $\text{H}^1\text{C}^1\text{C}^2\text{H}^5$ to 65.5 degrees. That is why in this conformation valence bond C^1H^1 is shifted in respect the bisector of angle of $\text{H}^4\text{C}^2\text{H}^5$ from H^5 to H^4 by 12.4 degrees (and by 6.9 degrees at the angle value of $\text{H}^1\text{C}^1\text{C}^2\text{H}^5$ by 60 degrees according to calculated data (Ratajczyk, Pecul, Sadlej, 2003). During hydration oxygen in carbonyl group stable conformation of glycolaldehyde there takes place additional turn of the bond C^1-C^2 clockwise rotation (from C^1 side) by 10.5 degrees (Aviles-Moreno, Demaison, Huet, 2006), that is why total deviation bond C^1-H^1 from bisector angle of $\text{H}^4\text{C}^2\text{H}^5$ to H^4 may achieve 23 degrees.

Molecule of ammonium formate was fixed in respect to hydrate glycolaldehyde, adsorption on carbon, from the side of C¹ at the due to the dipole-dipole interaction of oxygen atom O⁵ in -C=O (with dipole moment 2.7 D) with H² and H³ (in OH – 1.51 D) and adsorption of hydrogen H⁷ on carbon. Besides, hydrogen of ammonium formate H⁷ could be adsorbed in the space with a minimum electrostatic influence of hydrogen atoms H¹, H⁴ or H⁵. Such position was above O² symmetrical to H¹ because of its angular deviation (Figure A). In molecule CHO(OH) valence angle of H⁷C³O⁵ about 118 degrees almost the same as in H¹C¹O² hydrate glycolaldehyde and during their convergence there appeared stress in O⁵ with O². For its neutralization there took turnabout group C¹ of hydrate glycolaldehyde clockwise up to 39 (a total of 62) degrees, since the group at C² stability was maintained by adsorption on carbon by two atoms of hydrogen. In this connection, hydrogen of ammonium formate H⁷ reacted with hydroxyl group O²-H³, situated closer to him, with education of water and origin of bond C¹-C³. Group ammonium reacted with opposite hydroxyl O¹-H². So there appeared S chirality in serine. Such accession of ammonium formate to the hydrate glycolaldehyde from the side of C² is impossible because of electrostatic repulsion of homogeneous atoms.

However, reactions of ammonium formate, CH₂(OH)₂ or CHO(OH) possible with hydroxyl O³-H⁶ what led to formation of other S amino acids. The same interaction with hydroxyl of carboxylic group serine prevented from neutralization of its dipole moment or charge by amino group (necessity of their activation at artificial peptide synthesis [6] and proximity of dipole moment values indicate on this). Besides, in serine adsorption on carbon there occurred a significant blocking of oxygen at -C=O of reagents incoming from solution to hydroxyl. Direct interaction of reagents with oxygen atoms at -C=O in aqueous medium is difficult because of high energy of activation. Complication of serine radical is linked with reactions of condensation and disproportionate of two molecules metyleneglycol (reaction 16). This is shown on the examples of reactions of the synthesis of alanine (reaction 17, Figure B), asparagines (reaction 18), valine (reaction 19), phenyl alanine (reaction 20) and other amino acids. In other amino acids radicals were formed in the same way but at other molecular relations of reagents. R selectivity in ribose (as in erythrose and allose) was achieved by selective adsorption of hydrogen in CH₂(OH)₂ by carbon.

The most likely reactions of formation of vital important organic compounds

Daily and seasonal changes in temperature and pH led to realization of biologically important reactions. Phosphoester bond in nucleotides could occur in dilute solutions of pools when pH > 7.2 and dissociation of H₂PO₄⁻

is up to HPO_4^{2-} (reaction 21). Dehydration of aqueous calcium phosphates is possible in a slightly alkaline environment and at increased temperature (reaction 22), and hydration of such phosphates could energetically activate separate reactions. When calcium is substituted by ammonium, ammonium dihydrogen diphosphate could selectively produce the approach of two amino acids depending on the pH, and energy for peptide bonds due to reaction 23, was provided by hydration diphosphates. Nitrogen bases appeared in more complex reactions (uracil, reaction 24).

Conclusion

In the early Earth's atmosphere the formation of carbon and CH_2O or $\text{CHO}(\text{OH})$ was happened. At adsorption on carbon last optically active R ribose and S amino acids synthesized. Apparently, it is possible to obtain optically active preparations adsorption on carbon after additional studies with the selection of coals and catalysts, and their subsequent use in medicine and long-term space flights. Undoubtedly, the issues examined require

Table. The most likely reaction of the formation of carbon and organic molecules in the Archean

№	Reaction	$\lg K_T$ at T, K		
		298	323	348
1	$\text{CO}_2 + \text{H}_2 = 2\text{H}_2\text{O}_g + \text{C}_{gr}$	10.9	9.7	8.6
2	$\text{CO}_2g + 2\text{H}_2g = 2\text{H}_2\text{O}_{liq} + \text{C}_{gr}$	14.0	11.6	8.9
3	$\text{FeCO}_{3am} + 2\text{Fe}(\text{OH})_{3am} = \text{Fe}_3\text{O}_{4am} + \text{CO}_{2s} + 3\text{H}_2\text{O}_{liq}$	-2.2	-	-
4	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_{4k} + \text{H}_2\text{CO}_3 = 2\text{Al}(\text{OH})_{3k} + 2\text{SiO}_{2am} + \text{CO}_{2r}\uparrow$	0.59	0.78	0.94
5	$\text{CaCO}_{3c} + \text{TiO}_{2c} + \text{SiO}_{2am} = \text{CaTi}(\text{SiO}_4)\text{O}_c + \text{CO}_{2g}\uparrow$	-0.73	-0.05	0.54
6	$\text{CO}_{2g} + 2\text{H}_2g = 1/2\text{CH}_2\text{O}_g + 3/2\text{H}_2\text{O}_{liq} + 1/2\text{C}_{gr}$	2.8	1.5	0.5
7	$\text{CO}_{2g} + 4/3\text{NH}_3g = 1/3\text{CH}_2\text{O}_g + 5/3\text{H}_2\text{O}_{liq} + 2/3\text{C}_{gr} + \text{N}_2g$	2.7	1.9	1.2
8	$\text{CO}_{2g} + \text{CH}_{4g} = 1/2\text{CH}_2\text{O}_g + 3/2\text{H}_2\text{O}_{liq} + 3/2\text{C}_{gr}$	- 6.0	-	-
9	$\text{CO}_g + \text{H}_2\text{O}_g = \text{CHO}(\text{OH})_{liq}$	- 0.5	-	-
10	$\text{CO}_{2s} + 2\text{H}_2s = 1/2\text{CH}_2\text{O}_s + 3/2\text{H}_2\text{O}_{liq} + 1/2\text{C}_{gr}$	12.2	11.0	10.0
11	$\text{HCOOH}_s + \text{H}_2s = \text{CH}_2\text{O}_s + \text{H}_2\text{O}_{liq}$	2.1	2.0	1.9
12	$\text{CO}_s + \text{H}_2\text{O}_{liq} = \text{CHO}(\text{OH})_s$	2.6	2.4	2.1
13	$2\text{CH}_2(\text{OH})_{2a} = \text{CH}_2(\text{OH})\text{CH}(\text{OH})_{2a} + \text{H}_2\text{O}_{liq}$	-	-	-
14	$4\text{CH}_2(\text{OH})_{2a} = \text{CH}_3\text{CH}_2\text{COO}_a^- + \text{CHOO}^- + 4\text{H}_2\text{O}_{liq} + 2\text{H}^*$	-	-	-
15	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})_{2a} + \text{CHOONH}_4 = ^+\text{NH}_3\text{CHCH}_2\text{OHCOO}_a^- + 2\text{H}_2\text{O}_{liq}$	-	-	-
16	$2\text{CH}_2(\text{OH})_2 = \text{CH}_3(\text{OH}) + \text{CHO}(\text{OH}) + \text{H}_2\text{O}_{liq}$	-	-	-
17	$-\text{CH}_2\text{OH}^* + 2\text{CH}_2(\text{OH})_2 = -\text{CH}_3 + 2\text{CHOO}^- + \text{H}_2\text{O}_{liq} + 4\text{H}^+$	-	-	-
18	$-\text{CH}_2\text{OH} + \text{CHOONH}_4 = -\text{CH}_2\text{CONH}_2 + 2\text{H}_2\text{O}_{liq}$	-	-	-
19	$-\text{CH}_2\text{OH} + 2\text{CH}_2(\text{OH})_2 = -\text{CHCH}_3\text{COO}^- + 3\text{H}_2\text{O}_{liq} + \text{H}^+$; $-\text{CHCH}_3\text{COO}^- + 3\text{CH}_2(\text{OH})_2 = -\text{CHCH}_3\text{CH}_3 + 3\text{CHOO}^- + 2\text{H}_2\text{O}_{liq} + 2\text{H}^+$	-	-	-
20	$-\text{CH}_2\text{OH} + 12\text{CH}_2(\text{OH})_2 = \text{CH}_3 - \text{C}_6\text{H}_5 + 6\text{CHOO}^- + 13\text{H}_2\text{O}_{liq} + 12\text{H}^+$	-	-	-
21	$2\text{C}_5\text{H}_{10}\text{O}_{5a} + \text{H}_2\text{PO}_4^- + \text{H}^+ = \text{C}_5\text{H}_9\text{O}_4\text{HPO}_4\text{C}_5\text{H}_9\text{O}_{4a} + 2\text{H}_2\text{O}_{liq}$	-	-	-
22	$\text{Ca}(\text{H}_2\text{PO}_4)_2s + \text{OH}^- = 2\text{H}_2\text{O}_{liq} + \text{CaHP}_2\text{O}_7^-$	6.0	-	-
23	$\text{COO}^- + ^\delta\text{NH}_4\text{H}_2\text{P}_2\text{O}_7^- + ^+\text{NH}_3^- \rightarrow -\text{CO}-\text{NH}- + \text{NH}_4^+ + 2\text{H}_2\text{PO}_4^-$	-	-	-
24	$\text{CH}_2(\text{OH})_{2a} + \text{CHOONH}_4 = 1/2\text{C}_4\text{H}_4\text{N}_2\text{O}_{2a} + 3\text{H}_2\text{O}_{liq} + \text{H}^+$	-	-	-

Notes. Abbreviations: c – crystal, gr – graphite g – gas, liq – liquid, s – solution, a – adsorbed. Thermodynamic potentials (Bulakh A., Bulakh K., 1978, Riabin, Ostroumov, Sweet, 1977). $\lg K_T$ approximate values without regard to H_2O_g . *And so on $+n2CH_2(OH)_{2a}$. **Radical serine.

further study and experimental test, but this study suggests that the adsorption on carbon resolved the some problems of abiogenic synthesis of organic molecules in the origin of life on Earth and above all optical activity of R ribose and S amino acids inherent only to living organisms.

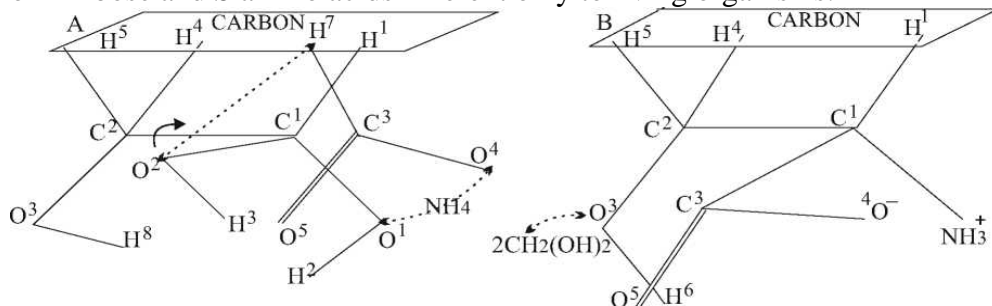


Figure. Structural scheme of S chirality formation in serine (A) and alanine (B, numbered atoms from figure A, having been kept after the reaction) at adsorption on carbon (dotted lines - direction of molecules interaction at the moment of reaction, arc line arrow - direction of the group rotation at C^1).

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