POLYAMINO ACID—THE MISSING LINK

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Received 1 July 1978

It is established that simple chemicals, under influences such as electrical discharges, can combine to form such organically important structures as amino acids. Evolutionists have often proposed some such reaction as the beginning of life. However, the amino acids are neither life nor are they sufficient for life. It would be necessary to have them polymerized into polyamino acids. Several schemes for such polymerization have been proposed; but it is shown that there are strong reasons to doubt that any of them ever happened.

One suggestion, in particular, has been that hydrogen cyanide, formed under primitive conditions, polymerized to form complicated molecules which were at least on the way to forming part of living things. However, a closer investigation shows that there is no evidence that the result of the polymerization—if such it be—is the production of molecules of the kinds necessary for life.

Introduction

Since the earliest recorded times, questions concerning the meaning and origin of life have been pre-eminent in the religious and scientific thought of man.[1] For many thousands of years science and mysticism have been intermixed by man in order to rationalize his existence.

An example of such a rationalization was the theory of spontaneous generation. In 1864, however, Pasteur seemingly destroyed the concept of spontaneous generation. While Pasteur's experimentation was aimed at the explication of the evolution of complex biological entities, such as bacteria, original scientific thought concerning the origin of life was not forthcoming for nearly 60 years.

Oparin[2] and Haldane[3] independently theorized that life might have originated in pools of organic matter existing in the primitive ocean. Thus, the concept of spontaneous generation was reborn, albeit on a time scale involving billions of years.

It is claimed by many evolutionists that the atmosphere of the primitive earth did not contain oxygen gas (O_2). In 1929, Russell[4] found that hydrogen is the most abundant element in the universe. Oparin[5] and Urey[6] argued that since the cosmic abundance of hydrogen is so great, the atmosphere of the primitive earth must have been highly reducing.

Synthesis of Amino Acids

The first experimental test of the Oparin-Haldane hypothesis was conducted by Miller in 1953.[7] He subjucted a mixture of methane, ammonia, water and hydrogen to electrical discharge. His isolation of glycine, α-alanine, β-alanine, aspartic acid and α-aminobutyric acid from the reaction solution provided the first experimental support for the Oparin-Haldane hypothesis. Abelson[8] studied the effect of electrical discharge on 20 different gases including hydrogen, ammonia, methane and carbon dioxide. He found that glycine, β-alanine and sarcosine were produced, among other products. Groth and von Weyssenhoff[9] exposed mixtures of methane, ethane, ammonia and water to ultraviolet radiation and identified glycine, alanine, and aminobutyric acid as reaction products. Ionizing radiation,[10] x-rays[11] and heat[12,13] have all been used to produce amino acids under presumed primitive earth conditions.

Synthesis of Polyamino Acids

Polyamino acids are readily prepared under stimulated supposed prebiotic conditions by heating suitable proportions of dry amino acids.[14,15] Such polymers, termed proteinoids, according to the evolutionists, show many properties envisionable as being important in evolutionary processes (for example, catalytic activity, morphogenesis), and they are regarded as models for prebiotic protein.[14]

Temperatures conducive to the removal of nascent water (120° to 200°C) typically have been used in the synthesis of proteinoids, although the polymerizations are known to occur at 60°C in the presence of dehydrating agents.[14] It has been suggested,[16] however, that polyamino acids formed at 120° to 200°C could not have played a major role in evolutionary processes, because such temperatures probably would have occurred only locally on the surface of the prebiotic earth (juxtaposed with much higher, detrimental, temperatures) and would have, on long contact, destroyed any resulting polyamino acids.

Another type of research has shown that peptides and polypeptides can be directly synthesized from α-amino acids under certain conditions. In aqueous ammonia solutions at about 160°C, Oro and Guidry[17, 18] found that up to 18 glycine molecules could be linked together. Glycine precursors such as aminoacetonitrile could be converted to small peptides in aqueous reactions[12] or by heating with clay.[19] Condensing agents that have been postulated to be present in primordial times have also been used. By allowing free α-amino acids to stand in aqueous solutions (acidic) containing cyanamide, Ponnamperuma and Peterson[20] and Steinman, Lemmon, and Calvin[21] obtained tripeptides, while in the absence of water, Schramm and coworkers obtained polypeptides by using phosphorus pentoxide in ether.

The general form of a peptide bond which joins two amino acids is:

$$-\mathrm{NH}-\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$$

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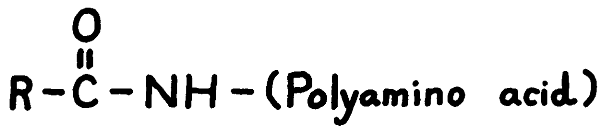
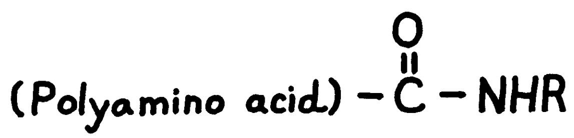
where the carbonyl moiety is from one amino acid, and the amine moiety from the other. The same thermodynamic conditions producing the polymarization could just as easily have brought about the production of an acyl amide bond of any organic acid with the amine of an amino acid, or an amide bond of an amino acid with any organic amine, as follows:

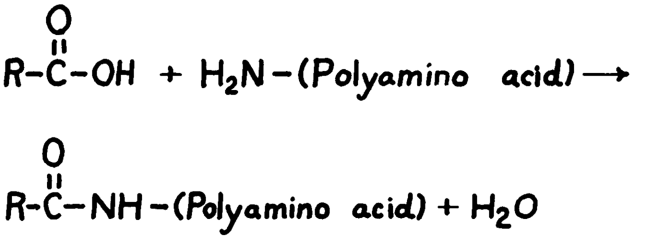


$$R-\overset{O}{\overset{\parallel}{C}}-NH-(\text{Polyamino acid})$$

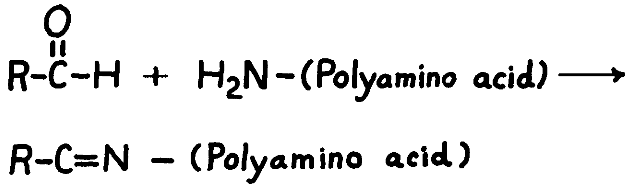


$$(\text{Polyamino acid})-\overset{O}{\overset{\parallel}{C}}-NHR$$

If any of these forms are produced, there will no longer be a possibility of lengthening the polypeptide polymer from the terminal amino group, or from the terminal carbonyl group.[23] Condensation of an aldehyde and carboxylic acid with an amine group, according to the reactions:



$$R-\overset{O}{\overset{\parallel}{C}}-OH + H_2N-(\text{Polyamino acid}) \longrightarrow R-\overset{O}{\overset{\parallel}{C}}-NH-(\text{Polyamino acid}) + H_2O$$



$$R-\overset{O}{\overset{\parallel}{C}}-H + H_2N-(\text{Polyamino acid}) \longrightarrow R-C{=}N-(\text{Polyamino acid})$$

will also prevent further polymerization from the side of the terminal amino group.

It has been shown earlier that polyamino acid polymerization could be done only in a pure system consisting of a reaction mixture of amino acids and the dehydrating agent. A mixture of other acids and amines with amino acids, which should be in a primitive world, has been proven mathematically to fail in polymerization.[23] Besides, the specialized conditions suggested by the model experiments do not have universal appeal[24] since anhydrous locales, high-temperature surface milieu, and acidic oceans or pools are not characteristic of the common view of a young, developing planet. The thermodynamic barrier to spontaneous α-amino acid polymerization is not easily overcome,[25] and indeed seems impassable by any reasonable condensation mechanism.

A completely different sequence of events leading to polypeptide formation has been postulated. This is by condensation of hydrogen cyanide.

Condensation of Hydrogen Cyanide

Hydrogen cyanide is produced in significant amounts when gaseous mixtures containing compounds of carbon, hydrogen and nitrogen are subjected to electrical discharges.[25-30] Cyanide is also formed if other energy sources, such as heat, are used.[31,32] It would appear very likely that hydrogen cyanide would have been formed in the atmosphere supposed to have existed on the primitive earth. This has led many authors to suggest that hydrogen cyanide may have played an important role in terrestrial prebiological chemistry.[28,30,32-34]

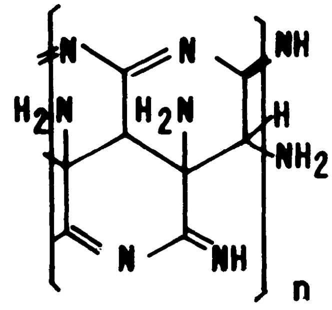
Hydrogen cyanide is known to self-condense to form "polymers". In 1806, Proust[39,40] observed a black solid that precipitated in aged, aqueous solutions of hydrogen cyanide. Boullay[41] called this black solid "azulmic acid", a name still used by some German and French researchers. Gautier[42] believed that this black solid was a "polymer" of hydrogen cyanide.

This "polymer" has also been prepared by irradiating solutions of hydrogen cyanide with radiation derived from radon[43,44] and by electrolysis of aqueous solutions of potassium cyanide.[45] The simplest method of producing the "polymer" is by alkali-induced polymerization of hydrogen cyanide.[46-48] The most commonly used base is ammonium hydroxide. The polymerization has been conducted in non-aqueous solutions as well.[49]

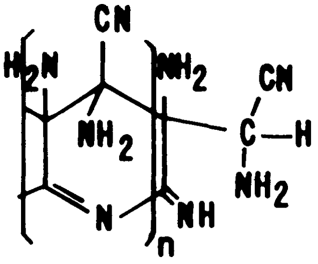
Bedel, in studying the hydrolysis of the "polymer" with alkali found that aminoacetic acid (glycine) and oxalic acid are produced. Volker[49] found the black material derived from hydrogen cyanide to be relatively stable. Decomposition of this material occurred at about 200° liberating hydrogen cyanide, ammonia, carbon dioxide, and left a black residue containing approximately 30% nitrogen. The "polymer" was found to be insoluble in most organic solvents but was partially soluble in mineral acids. The infrared spectra of "polymers" prepared in aqueous solution exhibited a shoulder for the cyano group at 4.5μ but a very well defined peak for the cyano group was observed when the "polymer" was prepared in chloroform solution.

Volker converted the nitrile functionality to an acid by hydrolysis and this was converted to an ester. An imine function, which was readily hydrolyzed, was also reported to be present. Based on limited evidence, Volker proposed the cyclic structure I for the hydrogen cyanide "polymer" obtained from aqueous solutions; and a partially cyclised structure II for the "polymer" obtained from non-aqueous solutions. The cyclic structures I and II were proposed rather than the open-chain structure III on steric arguments. The value of *n* was given as 5-7.

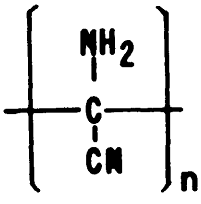
Matthews and Moser[37,38] have shown that when "polymers" produced in these reactions are hydrolyzed in acid, no fewer than 14 amino acids result. The amounts of glycine and ammonia were substantially larger than those of other amino acids. However, large variations were observed in the absolute amounts of each amino acid produced in different samples. It was claimed that hydrolysis of the polymer with water yielded polypeptides which were then cleaved to amino acids with 6*N* hydrochloric acid. In subsequent papers[51,52] the role of iminoacetonitrile, which was stated to possess



I



II



III

carbenoid character, in the formation of the polymer was stressed.

Most research related to the polymerization of hydrogen cyanide has been conducted on relatively concentrated solutions of cyanide (about 1 *M*). It is not expected that such high concentrations of cyanide would have been present in the primitive oceans. Sanchez et al.[56] claimed that dilute solutions of HCN might be concentrated by freezing. It was demonstrated that a frozen solution of 0.01*M* HCN is converted to diaminomaleonitrile more rapidly than one that was not frozen. It was suggested that repetitive freezing and thawing of lakes and oceans containing hydrogen cyanide might have provided a mechanism for the conversion of dilute solutions of cyanide to hydrogen cyanide polymers.

The fact that alkaline solutions of hydrogen cyanide turn brown, and that material precipitates from solution, has been accepted as proof that a "polymer" of hydrogen cyanide is formed.[35,41] This concept has been almost universally accepted even by the most respected researchers in this area.[56]

It should be noted that no polymer has ever been isolated or characterized from these reactions. Molecular weight determinations have indicated a maximal molecular weight range of 500-1000 for undefined products from this system.[49]

Generally, alkaline condensations of hydrogen cyanide are conducted at pH 9.2[56] (the pK_a of hydrogen cyanide is 9.2).[65] If the proposal that polymerization is propagated by condensation of hydrogen cyanide with cyanide anion is accepted,[56] then this reaction is conducted under conditions where the concentrations of monomer and initiator are equal. Under such conditions polymer formation is hardly expected.[65]

How Polyamino Acid was Produced?

Amino acids are liberated when the products of hydrogen cyanide oligomerization are hydrolyzed in acid.[35,38,53,55] This has led many researchers, particularly Matthews, to assert that hydrogen cyanide "polymers" contain peptide linkages. The fact that peptides and proteins are hydrolyzed to amino acids, in acid, does not constitute proof that peptide linkages are existent in this system. Again, it must be emphasized that no compound containing a peptide linkage has been isolated and characterized from the products of this reaction. Despite this fact, Matthews has attempted to rationalize the formation of peptides from hydrogen cyanide "polymerization".[36,37,38,51,52]

Labadie has also studied the cyanide system and was unable to find any indication that peptides were present using pronase, trypsin, or papain digests of reaction solutions. Amino acids were produced upon acid hydrolysis of the hydrogen cyanide polymers.[53-55] Unfortunately, data concerning methodology and controls used in experimentation was lacking or terse. Labadie accepted Volker's proposal for the structure of the material produced by reaction of hydrogen cyanide polymer as a catalytic medium (for example to decarboxylate oxaloacetic acid) and has compared his results to those obtained using enzymes.

Two characteristics of enzyme action are the catalytic effect and specificity of the enzyme. Since we can see (based on electrophoresis and paper chromatography) that the oligomer system is actually composed of a great number of compounds, it is impossible to ascribe any catalytic effect to a specific compound (only small catalytic effects were noted). To discuss specificity with regard to such a system is obviously not possible.[4] It might be that compounds such as ammonium hydroxide, oxalic acid or urea were, in some way responsible for some of the results obtained (in Rensselaer Polytechnic Institute Laboratory, it was identified as products of the oligomerization process)[65] yet one would hardly compare these simple organic molecules with an enzyme.

Although it has proved difficult precisely to characterize the final products of the oligomerization of hydrogen cyanide, a number of compounds have been suggested as possible intermediates in the "polymerization" process.[56] It is generally agreed that the oligomerization reaction proceeds via the initial formation of a dimer of hydrogen cyanide. Matthews first suggested that the dimeric species (IV) shown in Scheme I has the properties of a carbene (VII). He postulated that this carbene dimerized to VI and polymerized to VIII.[35,37,38] It was further suggested that mild hydrolysis of VIII yielded polypeptides, while it was known that vigorous hydrolysis produces amino acids. The reactions leading to the formation of the alkyl substituent (R) of VIII were not discussed in detail and remain nebulous. Scheme I presents the details of Matthews' proposed polymerization sequence.

Discussion and Summary

In recent years great interest has centered on chemical evolution[57-60] and the possible role of hydrogen cyanide in such a process.

While it must be admitted that the nitrile functionality possesses great versatility and capacity for a wide variety of reactions,[61] it should be noted that attempts to ascribe a too specific role to hydrogen cyanide (or any chemical species) in chemical evolution is futile. Argument concerning the course of prebiological synthesis has, in many instances, constituted little more than "a sound and a fury" neglecting the fact that our knowledge of the conditions existent on the primitive earth is, in a large part, speculative. Therefore, results obtained in simulation studies can be only as accurate as the model they seek to represent. Attempts to prove or disprove the role of hydrogen cyanide, or any compound, in the early history of the earth must be viewed with caution and, perhaps, skepticism, in view of the uncertainty involved in constructing a model system and the virtually infinite number of chemical processes that conceivably might have occurred.

All studies related to the evolution of life should meet the criterion of being scientifically valid. The fact that the accumulated knowledge of prebiological conditions is at best fragmentary cannot be considered as an excuse for presenting speculation as fact or desire as dogma. Instead, those standards which apply to chemistry (as one area of scientific endeavor) must be rigidly adhered to when simulation studies are conducted. It is unfortunate that much has been written concerning prebiological synthesis which has no experimental foundation.

It may be that the failure of experiment to maintain pace with theory was born of the great desire of primitive earth chemists to seek a connection between biomonomers, of the type synthesized by Miller,[7] and complex bipolymers, such as proteins and polynucleotides, which molecular biologists have implicated as having import in the nature and function of life.[62] Indeed, the fact that molecular biology (born in large part as a result of the work of Crick and Watson)[63] became a viable field at almost the same time that Miller's work served to stimulate interest in chemical evolution, almost inevitably led researchers in the latter discipline to formulate prebiological sequences leading to the formation of proteins (since amino acids seemed to be more accessible than purines or pyrimidines in simulation experiments). For example, many researchers have concluded that "polymeric" forms of hydrogen cyanide may have served as a link between biomonomers and peptides and eventually proteins on the primitive earth.[35,38] Experimental data presented in this paper have shown that this theory is not correct.

References

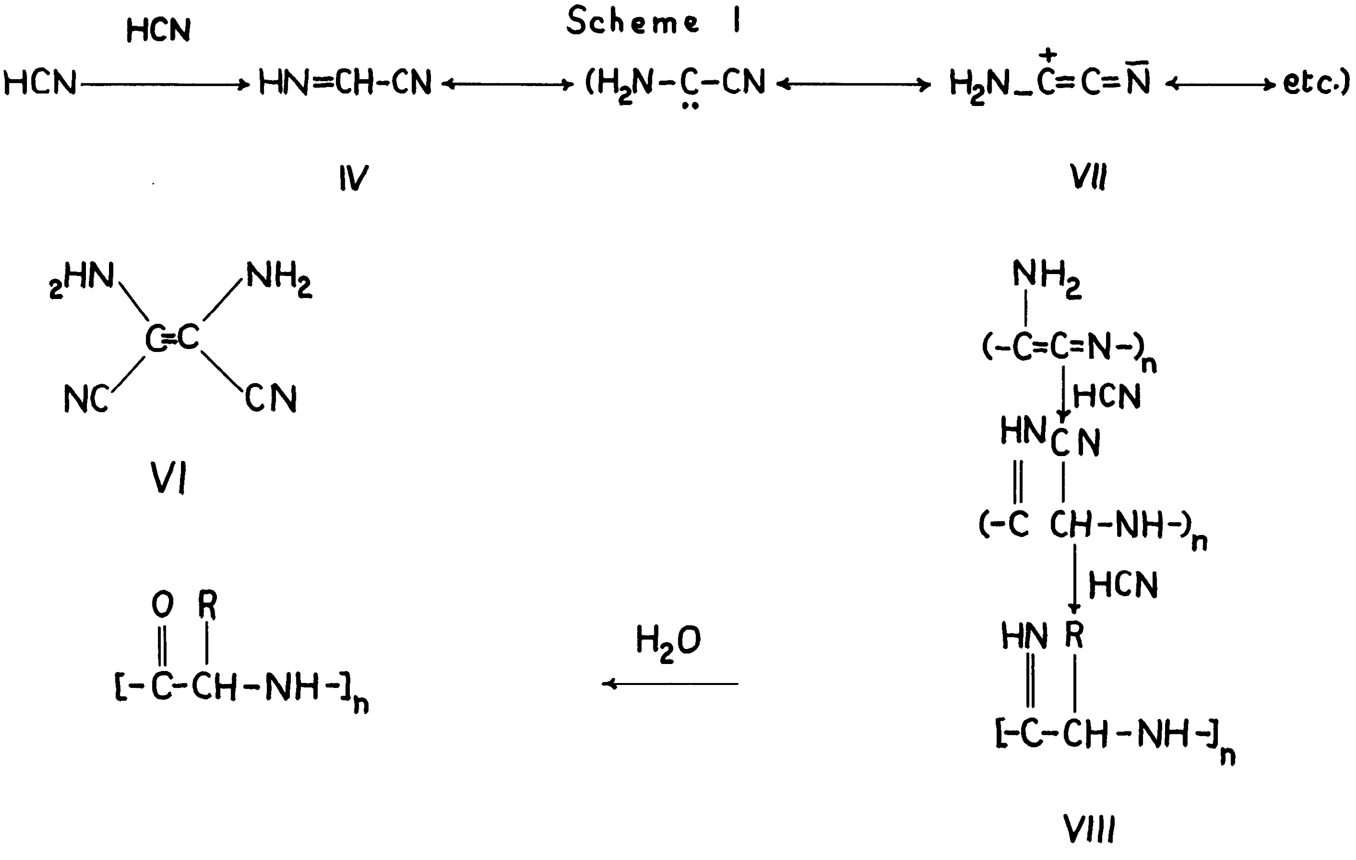
[1] Genesis in The Holy Bible, New Scofield Reference Edition, C. I. Scofield, Editor, Oxford University Press, 1967.

[2] Oparin, A. I., 1924. *Proiskhozhdenie zhizni.* Moskovski Rabochii, Moscow.

[3] Haldane, J. B. S., 1929. *Rationalist annual,* 148.

[4] Russel, Henry Norris, 1929. On the composition of the Sun's atmosphere. *Astrophysical Journal* 70 (1): 11-82.

Scheme I



[5] Oparin, A. I., 1953. Origin of life. Second English edition. Dover, New York. P. 101.

[6] Urey, H. C., 1952. The planets: their origin and development. Yale University Press.

[7] Miller, Stanley L., 1953. A production of amino acids under possible primitive Earth conditions. *Science* 117 (3046): 528-529.

[8] Abelson, P. H., 1955-1956. Paleobiology. Carnegie Institute of Washington Yearbook. No. 53, p. 171.

[9] Groth, W., and H. von Weyssenhoff, 1960. Photochemical formation of organic compounds from mixtures of simple gases. *Planetary and Space Science* 2(2/3): 79-85.

[10] Ponnamperuma, Cyril, and Katherine Pering, 1966. Possible abiogenic origin of some naturally occurring hydrocarbons. *Nature* 209 (5027): 979-982.

[11] Dose, K., and B. Rajewsky, 1957. *Biochimica et Biophysica Acta* 25, 225.

[12] Fox, S. W., and K. Harada, 1960. The thermal copolymerization of amino acids common to protein. *Journal of the American Chemical Society* 82 (13): 3745-3751.

[13] Harada, Kaoru, and Sidney W. Fox, 1964. Thermal synthesis of natural amino-acids from a postulated primitive terrestrial atmosphere. *Nature* 201 (4917): 335-336.

[14] Fox, S. W., and K. Dose, 1972. Molecular evolution and the origin of life. San Francisco.

[15] Saunders, Mary A., and Duane L. Rohlfing, 1975. Inclusion of nonproteinous amino acids in thermally prepared models for prebiotic protein. *Biosystems* 6 (2): 81-92.

[16] Horowitz, N. H., and S. L. Miller. *Prog. Chem. Org. Nat. Prod.* 20, 423. See also Miller, S. L., and L. E. Orgel, 1974. the origin of life on the Earth. Prentice-Hall. P. 145.

[17] Oro, J., 1963. *Ann. N.Y. Acad. Sci.*, 108, 464. See also Reference 23, p. 137.

[18] Guidry, R. L., 1962. Thermal synthesis of polypeptides in aqueous systems. Ph.D. dissertation, University of Houston.

[19] Akabory, S., 1957. (in) Proceedings of the first international symposium on the origin of life on the Earth. Moscow. P. 189.

[20] Ponnamperuma, Cyril, and Etta Peterson, 1965. Peptide synthesis from amino acids in aqueous solution. *Science* 147 (3665): 1572-1574.

[21] Steinman, Gary, Richard M. Lemmon, and Melvin Calvin, 1965. Dicyandiamide: possible role in peptide synthesis during chemical evolution. *Science* 147 (3665): 1574-1575.

[22] Schramm, G., H. Grotsch, and W. Pollman. 1962. *Agnew. Chem. Intl. Ed.* 1, 1.

[23] Trop, M., and A. Shaki, 1974. Is molecular evolution of proteins possible? *Creation Research Society Quarterly* 11 (1): 28-29.

[24] Sagan, C., 1965. (in) Origin of prebiological systems. Academic Press. Pp. 375-377.

[25] Blum, H. F., 1962. Time's arrow and evolution. Harper and Bros., New York.

[26] Miller, Stanley L., 1955. Production of some organic compounds under possible primitive Earth conditions. *Journal of the American Chemical Society* 77 (9): 2351-2361.

[27] Miller, S. L., 1957. *Biochimica et Biophysica Acta* 23, 480.

[28] Sagan, Carl, and Stanley L. Miller, 1960. Molecular synthesis in simulated reducing planetary atmospheres. (abstract). *Astronomical Journal* 65 (9): 499.

[29] Levy, E. M., and C. A. Winkler, 1962. The kinetics of the reaction of active nitrogen with ethylene. *Canadian Journal of Chemistry* 40 (4): 686-691.

[30] Grossenbacher, K. A., and C. A. Knight, 1965. (in) The origins of prebiological systems, edited by S. W. Fox. Academic Press, New York. Pp. 173-186.

[31] Palm, Christof, and Melvin Calvin, 1962. Primordial organic chemistry I. Compounds resulting from electron irradiation of $C^{14}H_4$. *Journal of the American Chemical Society* 84 (11): 2115-2121.

[32] Harada, K. and S. W. Fox, 1965. In Reference 30. pp. 187-201.

[33] Oro, J., 1965. In Reference 30, pp. 137-171.

[34] Ponnamperuma, C., 1965. In Reference 30, pp. 221-242.

[35] Lowe, C. V., M. W. Rees, and R. Markham, 1963. Synthesis of complex organic compounds from simple precursors: formation of amino acids, amino-acid polymers, fatty acids and purines from ammonium cyanide. *Nature* 199 (4890): 219-222.

[36] Kliss, Robert M., and Clifford N. Matthews, 1962. Hydrogen cyanide dimer and chemical evolution. *Proceedings of the U.S. National Academy of Science* 48 (8): 1300-1306.

[37] Matthews, Clifford N., and Robert E. Moser, 1966. Prebiological protein synthesis. *Proceedings of the U.S. National Academy of Science* 56 (4): 1087-1094.

[38] Matthews, C. N., and R. E. Moser, 1967. Peptide synthesis from hydrogen cyanide and water. *Nature* 215 (5107): 1230-1234.

[39] Proust, J. L., 1806. *Ann. Chim. Rec. Mem.* 60, 225.

[40] Proust, J. L., 1807. *Gehlen's J. Chem. Physik* 3, 384.

[41] Boullay, 1830. *Ann. Chim. Phys.* 43 (2): 273.

[42] Gautier, A., 1830. *Ann. Chim. Phys.* 17 (4): 103.

[43] Lind, S. C., and D. C. Bardwell, 1925. The chemical effects in ionized organic gases. *Science* 62 (1610): 422-424.

[44] Lind, S. C., D. C. Bardwell, and J. H. Perry, 1926. The chemical action of gaseous ions produced by alpha particles VII. Unsaturated carbon compounds. *Journal of the American Chemical Society* 48 (6): 1556-1575.

[45] Schmidt, Hans, and Hasso Meinert, 1957. *Electrolysen von Cyaniden I. Electrolysen von Cyaniden in wassrigen Losungen. Z. Anorg. Allg. Chem.* 293 (3-4): 214-227.

[46] Gautier, A., 1869. *Ann. Chim. Phys.* 17 (4): 156.

[47] Lewcock, W., 1918. *Pharmae J.*, 47, 50.

[48] Michael, A., and H. Hilbert, 1909. *Ann. Chem.* 364, 64.

[49] Volker, T., 1960. *Polymere Blausaure. Angew. Chem.* 72 (11): 379-384.

[50] Bedel, M. Cu., 1923. *Comptes Rendus* 76, 168.

[51] Matthews, C. N., R. E. Moser, and A. R. Claggett, 1968. Peptide formation from diaminomaleonitrile (HCN tetramer). *Tetrahedron Letters* no. 13, 1599-1603.

[52] Matthews, C. N., R. E. Moser, and A. R. Claggett, 1968. Peptide formation from aminomalonitrile (HCN trimer). *Tetrahedron Letters* no. 13, 1605-1608.

[53] Labadie, M., R. Jensen, and E. Nenzel, 1967. *Bull. Soc. Chim. Biol.* 49, 673.

[54] Labadie, M., G. Cohere, and C. Brechenmacher, 1967. *Compt. Rend. Soc. Biol.* 161, 1689.

[55] Labadie, Michael, Raymond Jensen, and Eugene Nenzel, 1968. *Recherches sur l'evolution pre-biologique III. Les acides azulmiques noirs formes a partir du cyanure d'ammonium. Biochemica et Biophysica Acta* 165 (11): 525-533.

[56] Sanchez, Robert A., James P. Ferris, and Leslie E. Orgel, 1967. Studies in prebiotic synthesis II. Synthesis of purine precursors and amino acids from aqueous hydrogen cyanide. *Journal of Molecular Biology* 30 (2): 223-253.

[57] Ponnamperuma, C., and N. W. Gable, 1968. Space Life Sciences 1, 64.

[58] Hulett, H. R., 1969. Limitation on prebiological synthesis. *Journal of Theoretical Biology* 24 (1): 56-72.

[59] Lemmon, Richard M., 1970. Chemical evolution. *Chemical Reviews* 70 (1): 95-109.

[60] Fox, S. W., K. Harada, G. Krampitz, and G. Mueller, 1970. *Chemical and Engineering News.* 22 June, p. 70.

[61] Rappoport, Z., 1970. The chemistry of the cyano group. Interscience Publishers, New York.

[62] Watson, J. D., 1970. Molecular biology of the gene. Second edition. W. A. Benjamin, Inc., New York.

[63] Watson, J. D., and F. H. C. Crick, 1953. A structure for deoxyribose nucleic acid. *Nature* 171 (4356): 737-738.

[64] Izatt, Reed, James J. Christensen, Russel T. Pack, and Rees Bench, 1962. Thermodynamics of metal-cyanide coordination. I. pK, $\Delta H°$, and $\Delta S°$ values as a function of temperature for hydrocyanic acid dissociation in Aqueous solutions. *Inorganic Chemistry* 1 (4): 828-831.

[65] Donner, D., 1972. The possible role of hydrogen cyanide in chemical evolution. Ph.D. dissertation, R. P. I., Troy, New York.