

PREBIOTIC SYNTHESIS - THE ORIGIN OF LIFE

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"Once upon a time, very long ago, perhaps two and a half billion years ago, under a deadly sun, in an ammoniated ocean topped by a poisonous atmosphere, in the midst of a soup of organic molecules, a nucleic acid molecule came into being that could somehow bring about the existence of another like itself-" and from that, all else did follow.

from--Isaac Asimov  
The Wellsprings of Life

# PREBIOTIC SYNTHESIS - THE ORIGIN OF LIFE

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Ever since he has been capable of free, abstract thought man has pondered the question of his origin and the origin of life in general. The general philosophy concerning an accurate definition of "life" is beyond the scope of this paper. Instead, I will be dealing with the origin of amino acids, which most scientists generally agree are the "building blocks of life" in the universe and so would be the precursors to all higher life forms.

The first recorded ideas on the creation of life use a religious viewpoint to give credit for the creation of life to a god or demi-god. The best example of a religious view on the creation of life is the story of God's creation of the world in six days with life being created on the fifth and sixth days. Using religious reasoning precludes the need to use scientific reasoning which is not necessary to satisfy the needs of a religious man.

The next ideas on the creation of life were from more of a scientific viewpoint and concerned spontaneous generation which deals with the bringing forth of life from inorganic materials. Aristotle, Lucretius, Paracelsus, van Helmont, and William Harvey were all avid supporters of the theory of spontaneous generation. The first person to attempt to disprove the theory of spontaneous generation was the Florentine physician Francesco Redi who conducted experiments in 1668 to prove that flies

actually laid the eggs which caused maggots to grow from rotting meat. In 1683 Antony von Leeuwenhook, with the use of the newly discovered microscope, discovered the existence of microorganisms in the air which served to dispel the theory of spontaneous generation even more. In 1864, Louis Pasteur, by the use of apparatus to sterilize air and the use of S-necked flasks was one of the last modern scientists who gave any real thought to trying to disprove the theory of spontaneous generation. By scientific methodry, Pasteur proved that when sterilized air entered a flask containing a sterilized broth solution there was no spontaneous generation of life and so the microorganisms in the air must have been responsible for what earlier observers thought was spontaneous generation in broth solutions.<sup>1</sup>

The publication of Charles Darwin's Origin of Species in 1859 solved the problem of millions of different species by suggesting the idea that all life evolved from a common basis or ancestor. In his book Worlds in the Making (1908) Svante Arrhenius suggested that life was universal and could be found floating as spores in space. It was one of these spores which landed on Earth to begin life on our planet.<sup>2</sup> The only problem with Arrhenius' theory is that it would still be necessary to explain how the spores originated in the first place.

After Pasteur disproved the theory of spontaneous generation the scientific community, who would not be satisfied with a religious explanation, was left with only one alternative which was that life, whether originally terrestrial or extraterrestrial, originated from some common ancestor. All that was necessary now was to find the common ancestor.

The primitive atmosphere of Earth was composed mainly of inorganic gases which had been spewed forth from volcanoes while the surface of

the planet was abundant with metallic oxides, metallic salts, metal carbonates and carbides, and metallic hydrides.<sup>3</sup> Since all of the compounds present in the Earth's primordial state were considered to be inorganic in nature while the amino acids necessary to life were organic in nature it would be necessary to be able to form organic products from the reaction of inorganic reactants. Frederick Wohler, who in 1828 synthesized urea from ammonium cyanate, laid the basis for modern synthetic organic chemistry<sup>4</sup> and also proved that if correct reaction sequences were discovered it was probably possible to produce the necessary organic constituents for life from the inorganic compounds on the primitive Earth.

In 1928 the British biologist John Haldane was the first to speculate on the nature of the primitive atmosphere. Haldane suggested that the primitive atmosphere was different from the present atmosphere. He said that since coal originates from plant life and plant life gets carbon from carbon dioxide in the air, then before life originated all of the carbon in coal must have been present in air in the form of carbon dioxide. Since oxygen in air is supplied by the same plant-based reactions which absorb carbon dioxide (photosynthesis) then it logically follows that the primordial atmosphere was composed of nitrogen and carbon dioxide and not nitrogen and oxygen as is the present atmosphere. Also, with a lack of oxygen, there would be no ozone which is present in a layer 30 kilometers above the Earth at present. The lack of ozone would permit larger amounts of energy in the form of ultraviolet rays from the sun to reach the Earth and react in the atmosphere.<sup>5</sup> With the lack of oxygen the primitive atmosphere would be reducing in nature.

The present Earthly atmosphere with its lack of ultraviolet rays, its overabundance of oxygen and its overabundance of life would not

permit the reactions of the primitive atmosphere. The following quote from the letters of Charles Darwin seems to agree with the ideas of Haldane.

"It is often said that all the conditions for the first production of a living organism are now present, which could ever have been present. 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 a 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."

The Russian biochemist Alexander Oparin in his first book on the origins of life published in 1928 agreed with Haldane in all respects but one concerning the primitive atmosphere. Oparin thought that the primitive atmosphere contained elemental hydrogen as well as hydrogen in methane, ammonia, and water.<sup>6</sup>

Present day scientists feel that Oparin's idea was the most correct because the sun's ultraviolet radiation could react with water to release oxygen which would react with ammonia and methane to form the nitrogen, carbon dioxide, and water vapor of Haldane's atmosphere. The photosynthetic reactions of plants would then be able to produce the nitrogen, oxygen, water vapor atmosphere of present day.<sup>7</sup>

With all of this information on primitive Earth conditions available the next logical step was to test the theory to see if life could have formed under primitive Earth conditions. The first experiment to test the theories of Oparin and Haldane was conducted by Stanley L. Miller, a graduate student of Harold Urey at the University of Chicago in 1953. Urey, who agreed with the atmospheric composition of Oparin, suggested that Miller use methane, ammonia, and water vapor as the atmosphere of his primitive Earth simulation.

There were several factors which Miller had to decide upon in order to conduct his experiment. These variables included atmospheric composition, temperature, energy source, and time of reaction. The decision to use the methane, ammonia, water vapor atmosphere of Oparin as suggested by Urey was decided upon due to the fact that it could be the basis of the present atmosphere and also of the atmosphere suggested by Haldane as discussed earlier. The reason for the present oxidizing atmosphere as opposed to the suggested reducing atmosphere is generally thought to be the result of the escape of hydrogen from the primitive reducing atmosphere. The rate of escape of gases from a primitive atmosphere is determined by the formula of Jeans<sup>8</sup>

$$L = N \sqrt{\frac{RT}{2\pi\mu}} (1+X)e^{-X} \quad \text{where } X = \frac{GM\mu}{RTa_c}$$

when;

- L= rate of escape in atoms cm<sup>-2</sup> sec<sup>-1</sup>
- N= atoms cm<sup>-3</sup> in the escape layer
- R= gas constant
- T= absolute temperature in escape layer
- $\mu$ = atomic weight of the gas
- G= gravitational constant
- M= mass of the Earth
- a<sub>c</sub> = radius of planet at the escape layer

The Earth's escape layer begins about 600 kilometers above the surface where T= 1500°K. With  $\mu$  being so low for hydrogen and considerably higher for oxygen and nitrogen it follows that a much greater quantity of hydrogen would escape thus leaving the present oxidizing atmosphere. There are two views on the temperature of the primitive Earth at the time of prebiotic synthesis. The first view which considers that the Earth began in an entirely molten state and gradually cooled to its present surface temperature<sup>9</sup> has been replaced by the theory that the surface



temperature of the Earth has remained constant throughout the Earth's history. This constant temperature theory is due to the fact that the surface temperature of the Earth is now determined exclusively by the activity of the sun. Astronomical evidence tells us that there has been no great change in solar activity during the Earth's lifetime and so primitive surface temperatures must have been the same as present surface temperatures.<sup>10</sup>

A chart of energy sources available for organic synthesis on the Earth is found in appendix 1A. The largest source of energy is the sun, however, compounds such as methane, ammonia, and water can only absorb this energy at wavelengths below 2,000 Å which is only a very small fraction of the total available energy. The energy from radioactive decay of uranium, thorium, and potassium is not readily accessible since the elements are contained in rocks. The effects of cosmic rays are considered negligible as are the effects of volcanoes. There have been some reports of shock waves producing good yields in the synthesis of amino acids but these reports are not substantiated. This leaves electric discharges as the primary energy source in prebiotic syntheses. These discharges would come primarily from lightning and the corona discharge from pointed objects. Electric discharges would have occurred near the planet's surface while ultraviolet photochemical reactions would occur in the upper atmosphere and so reactions occurring by electric discharge energy would not run into a problem with rate of transport to the oceans where concentration of products is thought to have taken place.<sup>11</sup>

Since the soup of organic compounds was so dilute it must have had some means of concentration. J.D. Bernal, in 1947, theorized that the fine clay in the oceans provided the means for concentrating the organic compounds in amounts needed for further reaction.<sup>12</sup> The Laboratory of

Chemical Evolution at the University of Maryland at College Park under the direction of Dr. Cyril Ponnampertuma is presently engaged in research on the role of clay in prebiotic synthesis reactions. It would seem, therefore, that the electric discharge would again be the more feasible energy source.

The time of the experimental run was not based on any figures since none were available at the time, this being the first such experiment.

Now that all of the variables have been examined Miller's original experiment will be discussed.

The equipment for Miller's experiment is diagrammed in appendix 1B. A 500cc flask is used to simulate the primitive ocean and it contains all liquids in the system. The 500cc flask is heated just enough so that the liquid contained in it will boil (70-80°C) and cause vapors and gases to be circulated through the system and passed through the spark which is generated across the two tungsten electrodes in the 5-liter flask by a 60,000 volt Tesla coil. The 5-liter flask containing the electrodes simulates the primitive atmosphere where the electric discharges would take place. The gases are then passed through a condenser where they are cooled to about 35°C and return to a liquid state. Any tars or resins will collect in the bottom U-tube while the liquids will flow back into the 500cc flask.<sup>13</sup>

The apparatus was filled with 200ml of water and then all air was evacuated from the system after which 10cm pressure of hydrogen, 20cm pressure of methane, and 20cm pressure of ammonia were added to the system. The water was boiled and the discharge run for a week.<sup>14</sup> Pressure in the system was kept below 1.5 atmospheres in order to keep the glassware from breaking. Methane and ammonia were taken in equal amounts so that appreciable quantities of carbon and nitrogen would

react in the spark. Hydrogen was added to simulate a reducing atmosphere even though it would not be needed after the organic compounds form since they produce hydrogen when they react.<sup>15</sup>

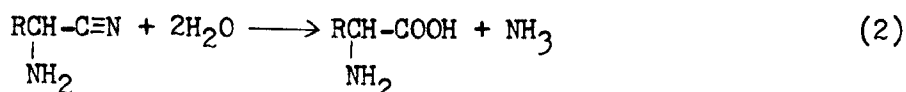
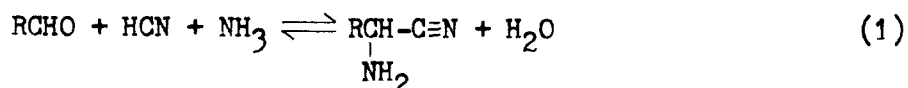
The run time of one week under the given conditions is equal to approximately fifty million years on the primieval Earth.<sup>16</sup>

Analysis of the gases was performed on a gas analyzer and the results are found in appendix 1C while results of a chromatographic analysis of the products from the 500cc flask are found in appendix 1D.

The results in appendix 1D show that only a few relatively simple compounds accounted for a large proportion of the products. Miller had anticipated a mixture containing small amounts of a great variety of compounds.<sup>17</sup> The major products of the reaction were not random organic compounds but instead a number of compounds occurring in living substances.

During another run which lasted for a week Miller determined the concentrations of ammonia, hydrogen cyanide, and aldehydes in the U-tube and the concentration of amino acids in the 500cc flask in order to study the mechanisms of the syntheses. The results of this run are seen in graphical form in appendix 1E.

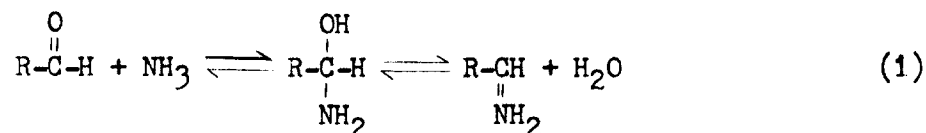
The equations relating the reactions of hydrogen cyanide, aldehydes, ammonia, and water are as follows:



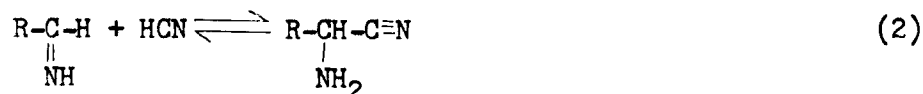
This would account for most of the amino acids formed and also for the

limited variety of products.<sup>18</sup>

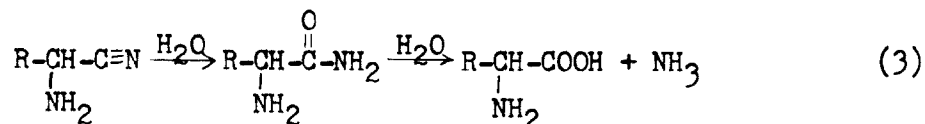
There are two major syntheses of amino acids whose mechanisms are used to explain most of the early work in prebiotic synthesis of simple amino acids. The Strecker synthesis is the oldest organic synthesis of amino acids and is as follows: in step (1) ammonia adds to an aldehyde to form an imine.



Cyanide then adds to the imine in step (2) to yield an aminonitrile.



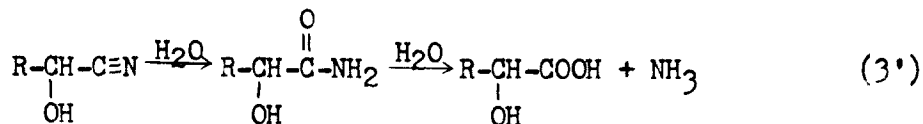
Since steps (1) and (2) are reversible the reaction is completed by step (3) which is the irreversible hydrolysis of the aminonitrile.



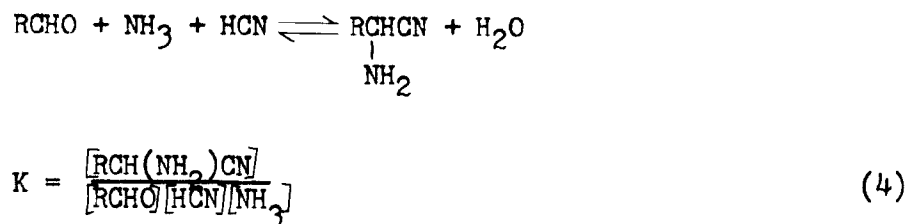
An alternate set of reactions which forms hydroxy-acids is where the cyanide adds to the aldehyde (2') to form a hydroxy-nitrile.



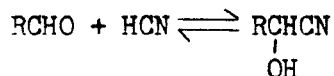
The hydroxy-nitrile is then hydrolyzed to form the hydroxy-acid in (3').



Equilibrium constants for the reaction are as follows:

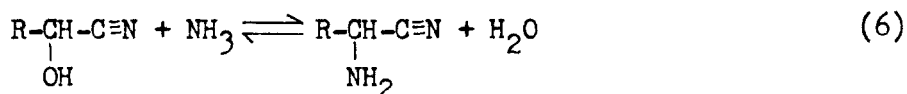


and



$$H = \frac{[\text{RCH(OH)CN}]}{[\text{RCHO}][\text{HCN}]} \quad (5)$$

Therefore, an equilibrium reaction between the hydroxynitrile and the aminonitrile



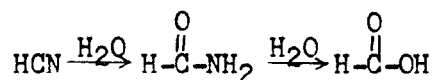
is related by

$$\frac{[\text{RCH(NH}_2\text{)CN}]}{[\text{RCH(OH)CN}][\text{NH}_3]} = \frac{K}{H} \quad (7)$$

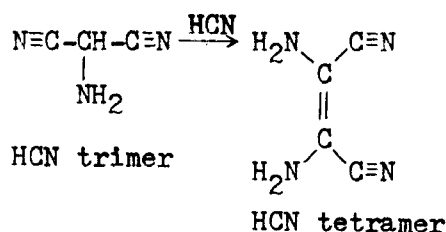
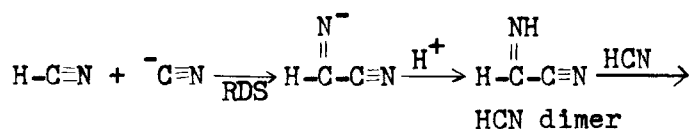
Thus if  $\text{NH}_3$  is large, then the aminonitrile will predominate, otherwise, the hydroxynitrile will predominate. There are no experimental results to check on the rates of steps (3) or (3') but theory favors the hydrolysis of aminonitriles which would lead to the formation of amino acids.

The simple aliphatic aldehydes needed as precursors to the various amino acids are formed by the action of the electric discharge on methane and water vapor.<sup>19</sup>

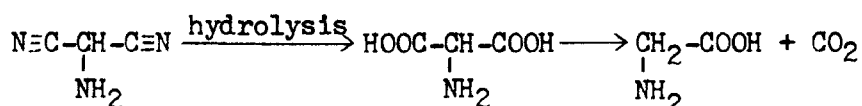
The synthesis of amino acids from hydrogen cyanide is the second major synthesis mechanism for amino acids. It deals with the hydrolysis of hydrogen cyanide to formamide and formic acid at a pH of about 8.0.



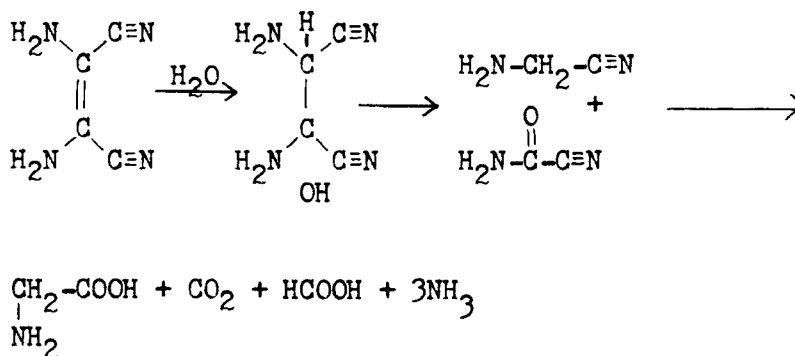
If the pH is closer to 9.0 and the solution is more concentrated, then a sequence of polymerization reactions occurs with the first reaction step seeming to be the rate determining step.



The trimer can now react to form glycine by hydrolysis.



It is also possible for the tetramer to form glycine and in concentrated solutions the tetramer is probably the more important intermediate.<sup>20</sup>



Now that some of the mechanisms and reaction sequences are known it is possible to go back and explain the graphical results of appendix 1E. The concentration of ammonia decreased steadily during the run due to its breakdown into hydrogen and nitrogen in the electric discharge and also due to its use in synthesis reactions such as the Strecker synthesis. The initial rise in concentration of hydrogen cyanide and aldehydes is due to the fact that they are being synthesized in the discharge. After about 25 hours the concentrations of both hydrogen cyanide and aldehydes

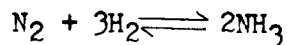
levels off which indicates that they are being replaced as fast as they are being used to form amino acids. After about 125 hours the concentrations of the hydrogen cyanide and the aldehydes begin to fall which indicates that their formation in the discharge is decreasing and so they are not being replaced as fast as they are being used.<sup>21</sup>

The formation of amino acids occurred at a steady rate during the run as long as the concentrations of hydrogen cyanide and aldehydes remained constant. When the concentrations of hydrogen cyanide and aldehydes began to drop after 120 hours the formation of amino acids leveled off and it is probably reasonable to assume that if the graph were extrapolated further the concentration of amino acids would remain constant so long as no extraneous variables were to intervene.

Miller also made several other runs of his experiment under different conditions in order to gather further data which he could relate to his first run. A run similar to the first run was conducted with the addition of ferrous ammonium sulphate in order to take into account the great abundance of iron as both metal and ferrous compounds on the Earth. By the end of the run about 16 percent of the iron had been oxidized to ferric and the results were the same as in run one (appendix 1D) but with slightly different quantitative values.<sup>22</sup>

Using an ozonizer to provide a silent electric discharge instead of a spark gave results similar to run one but with only about 25 percent of the quantitative yields.<sup>23</sup> The decreased yield was probably due to a steady state reaction mixture of gases<sup>24</sup> and also the fact that the voltage used was only 15,000 volts.

Substituting nitrogen for ammonia gave the same results as run one but with slightly lower yields. The substitution of the nitrogen for ammonia is due to the fact that in the reaction:



the equilibrium constant is  $7 \times 10^5 \text{ atm}^{-2}$  at  $25^\circ\text{C}$  and so nitrogen would remain as ammonia instead of  $\text{N}_2$  until the partial pressure of hydrogen dropped low enough to permit its escape into outer space (about  $10^{-2} \text{ atm}$ ).<sup>25</sup>

There have been many successful attempts to duplicate Miller's experiments including that found in appendix 2 which I performed in April of 1977. The results of several duplications of Miller's original experiment are found in appendix 3A as are the results of experiments substituting ultraviolet light (appendix 3B), ionizing radiation (appendix 3C), and intense heat (appendix 3D) for the electric discharge.

It seems to follow that in order for prebiotic synthesis to occur there are really only two conditions to be met. The atmosphere must be anoxygenic and the atoms of carbon, nitrogen, inorganic catalysts, water, etc. which are the building blocks of the "organic" molecules must be present. Beyond these two conditions it seems as if all else is variable and will only result in changes of a particular product or yield.

Appendix 5 contains the reaction sequences that explain the synthesis of several amino acids under possible prebiotic conditions. Although it is not possible to directly synthesize all twenty protein occurring amino acids it is reasonably safe to assume that several sets of conditions occurred on the primitive Earth and the products of earlier syntheses were likely to combine with each other in subsequent reactions. It is by this method that reaction pathways should eventually be worked out for all twenty amino acids.



Most of the work on prebiotic synthesis was done in the 1960's and early 1970's. The more recent work has been centered on four main areas: the search for synthesis mechanisms, the proof of old theories with new information, the presence of organic compounds in meteorites, and the origins of the genetic code as a further step of the synthesis.

With several suspected reaction pathways for prebiotic synthesis it would be necessary to derive a feasible mechanism for each pathway in order to figure out which would most likely have been followed. A mechanism for the condensation of cyanide to HCN oligomers is suggested by Ferris and Edelson who provide data comparing reactions occurring in both reducing and oxidizing atmospheres.<sup>26</sup>

Miller, Urey, and Oró have co-authored a paper which reviews the forms of energy available for both terrestrial and extraterrestrial prebiotic synthesis. The synthesis of amino acids by the electric discharge method gives results both quantitatively and qualitatively comparable to the amino acids found on the Murchison Meteorite.<sup>27</sup>

Cyril Ponnampertuma is currently involved in two lines of research at the University of Maryland at College Park Laboratory of Chemical Evolution. The first area concerns the discovery of amino acids in carbonaceous chondrites which are meteorites that have been found in the snowfields of Antarctica. The meteorites are free from terrestrial contamination and yet contain amino acids and other organic compounds thus proving the extraterrestrial nature of these compounds.<sup>28</sup> The second line of research is involved with the origins of the genetic code from the prebiotic synthesis systems. It has been suggested that the genetic code and its constituent amino acids co-evolved to precede the final selection of proteinous amino acids.<sup>30</sup>

In conclusion, most of the basic work concerning prebiotic synthesis

has been completed and future work will probably continue along the lines of research involved with the further development of the genetic code and higher living systems and the determination of whether or not the appearance of life on the Earth was a one-of-a-kind occurrence or is a common happening in the universe.

APPENDICES

APPENDIX IA

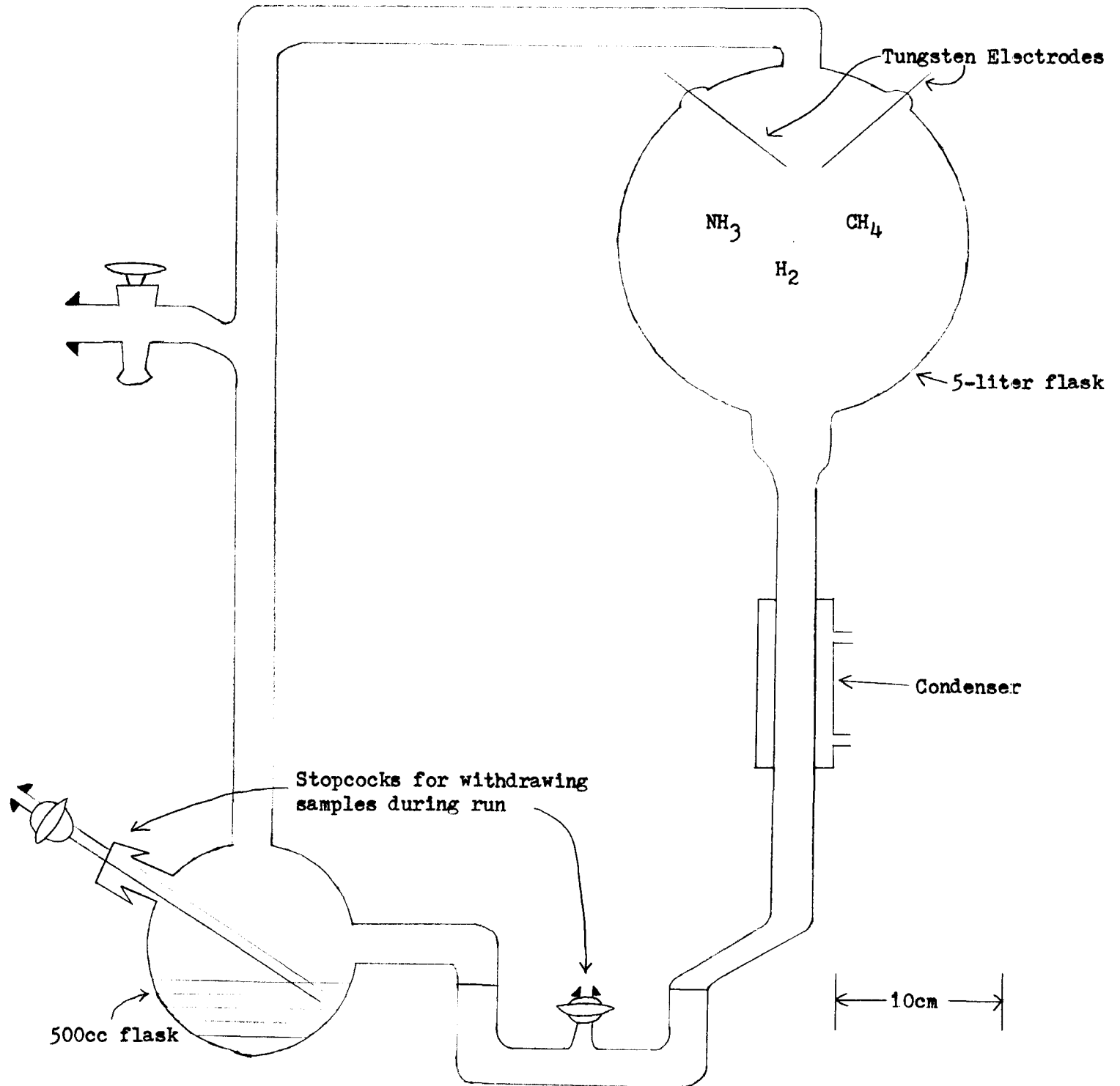
Present Sources of Energy Averaged over the Earth<sup>31</sup>

Source	Energy (cal cm <sup>-2</sup> yr <sup>-1</sup> )
Total radiation from sun	260,000
Ultraviolet light	
< 3,000 Å	3,400
< 2,500 Å	563
< 2,000 Å	41
< 1,500 Å	1.7
Electric Discharges	4
Cosmic Rays	0.0015
Radioactivity (to 1.0 km depth)	0.8
Volcanoes	0.13
Shock Waves	1.1

The value for radioactivity  $4 \times 10^9$  years ago was  $2.8 \text{ cal cm}^{-2} \text{ yr}^{-1}$ .

The energy from shock waves includes  $0.1 \text{ cal cm}^{-2} \text{ yr}^{-1}$  from meteorites and meteors and  $1 \text{ cal cm}^{-2} \text{ yr}^{-1}$  from the shock or pressure wave of a lightning bolt.

Apparatus for the electric discharge synthesis of amino acids<sup>32</sup>  
(Miller 1953)



APPENDIX IC

Gas Analyses<sup>33</sup>

Gas	% present (final)	% present (initial)
H <sub>2</sub>	74.6	20.0
CO	10.0	----
CH <sub>4</sub>	10.4	40.0
N <sub>2</sub>	5.0	----
NH <sub>3</sub>	8.6	40.0
C (as org. cmpds.)	53.0	

Percentage of NH<sub>3</sub> calculated by the formula

$$100P_{\text{NH}_3} / (P_{\text{H}_2} + P_{\text{CO}} + P_{\text{CH}_4} + P_{\text{N}_2})$$

Percentage of C as organic compounds calculated by the formula

$$100(\text{initial } P_{\text{CH}_4} - \text{final } P_{\text{CO} + \text{CH}_4}) / (\text{initial } P_{\text{CH}_4})$$

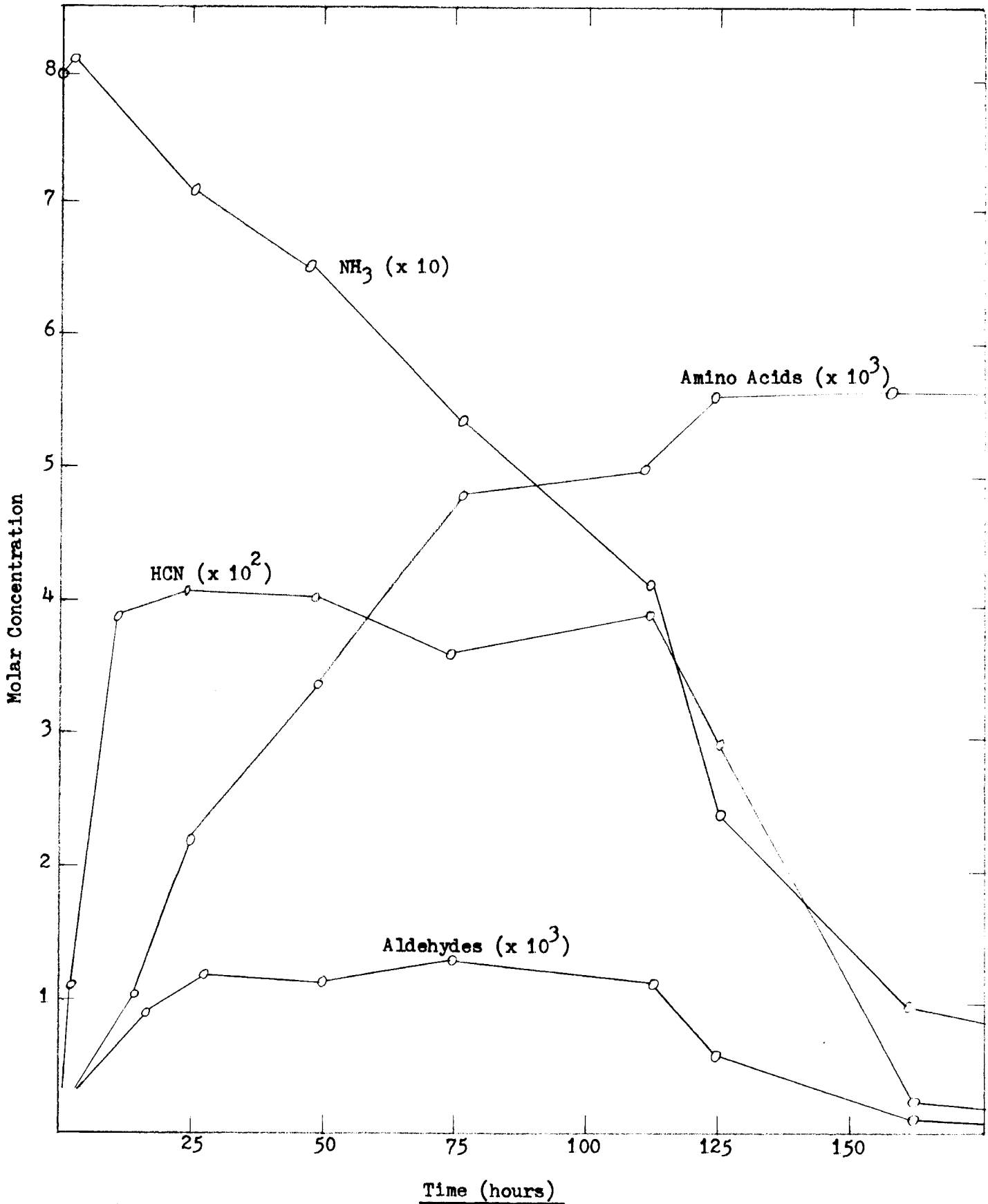
APPENDIX ID

Yields from sparking a mixture of CH<sub>4</sub> , NH<sub>3</sub> , H<sub>2</sub>O , and H<sub>2</sub><sup>34</sup>

Compound	Yield ( $\mu$ M)	Yield (%)
Glycine	630	2.1
Glycolic acid	560	1.9
Sarcosine	50	0.25
Alanine	340	1.7
Lactic acid	310	1.6
N-Methylalanine	10	0.07
$\alpha$ -Amino-n-butyric acid	50	0.34
$\alpha$ -Aminoisobutyric acid	1	0.007
$\alpha$ -Hydroxybutyric acid	50	0.34
$\beta$ -Alanine	150	0.76
Succinic acid	40	0.27
Aspartic acid	4	0.024
Glutamic acid	6	0.051
Iminodiacetic acid	55	0.37
Iminoaceticpropionic acid	15	0.13
Formic acid	2,330	4.0
Acetic acid	150	0.51
Propionic acid	130	0.66
Urea	20	0.034
N-Methyl urea	15	0.051

59 mmoles (710mg) of Carbon was added as CH<sub>4</sub>. The percent yields are based on the Carbon.

APPENDIX IE

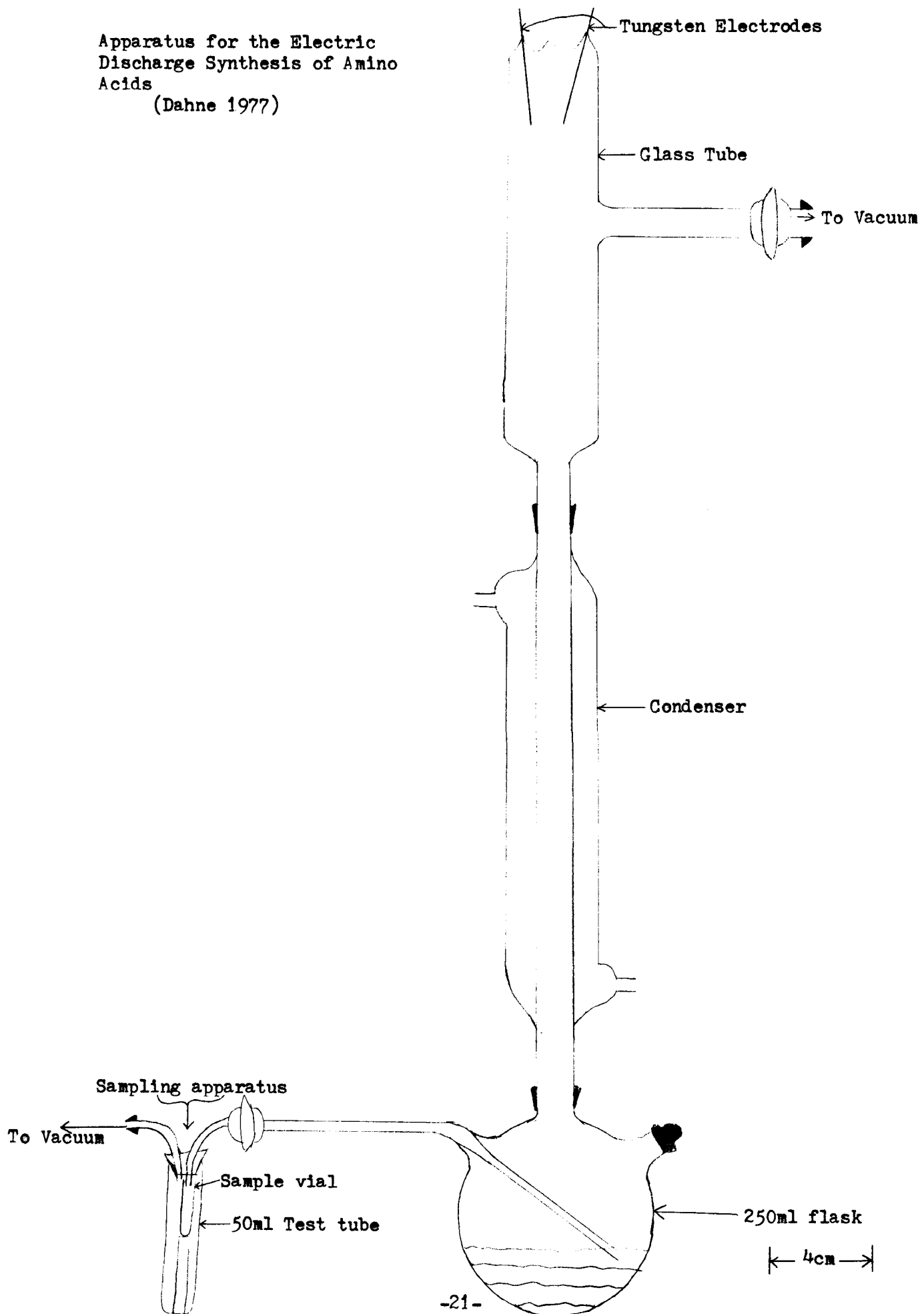


The concentration of ammonia, hydrogen cyanide, and aldehyde in the U-tubes and the concentration of amino acids in the 500ml flask while sparking a mixture of methane, ammonia, water, and hydrogen in the preceding apparatus. 55



APPENDIX 2A

Apparatus for the Electric  
Discharge Synthesis of Amino  
Acids  
(Dahne 1977)



Description of Equipment  
(Dahne 1977)

The equipment which I used to duplicate the experiment of Miller (1953) is diagrammed in Appendix 2A. A 250ml flask is used to simulate the primitive ocean and the liquid in the flask is kept boiling by the use of a heating mantle. The gases were added to the equipment in the following way. Two rubber balloons were filled to a diameter of 7.5 inches, one with methane and the other with ammonia gas. A third balloon was filled to a diameter of 6 inches with hydrogen gas. These proportions were from the report of C.L. Stong (1970). All three balloons were then combined into a single balloon and this balloon was attached to the stopcock at the upper glass tube of the apparatus. The apparatus, having been evacuated of air will now fill with the gases from the balloon. Once the gases have entered the system the system is sealed off. The upper glass tube now represents the gas-filled primitive atmosphere. The tungsten electrodes are connected to a 13,500 volt 0.31 milliamperere transformer to provide the energy for the electric discharge.

Once the apparatus is set up and the run begins, the boiling water will circulate the vapor and gases into the vicinity of the spark where a reaction will occur. The reacted products will then be passed through the condenser and cooled to drop back into the liquid in the flask.

The experiment was run for a week and periodic samples were taken by use of the attached sampling apparatus. The sampling apparatus was a simple vacuum apparatus which pulled liquid from the flask and into a sample vial without contaminating the rest of the liquid.

Results of Electric Discharge Synthesis of Amino Acids  
(Dahne 1977)

This run was actually done as a feasibility study in order to see if it was possible to easily duplicate the efforts of Miller (1953). Although the equipment was sterilized, it is possible that there were still some microorganisms present on the glass. Also, the presence of a rubber stopper in the sampling apparatus could have contributed to the presence of organic compounds.

Taking these error factors into account I still performed a thin-layer chromatographic analysis of the products at the end of a week and compared the results to a previously made set of standards. The results, using ninhydrin as an indicator, showed a definite presence of amino acids and it seemed that there was a predominance of alanine. This is a feasible result due to the fact that one of the most predominant compounds in Miller's final analysis was also alanine.

As was previously stated, this experiment was only done as a feasibility study to get a yes or no answer for the presence of amino acids and to be able to familiarize myself with the equipment. Due to lack of time it does not seem likely that I will be able to attempt a run in order to obtain any actual qualitative or quantitative results.

Production of Amino Acids by the Action of Electric Discharges on Various Simulated Atmospheres<sup>36</sup>

Investigators	Gas Mixture	Products
Miller (1953, 1955)	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> , H <sub>2</sub> O	Simple aliphatic amino acids, fatty acids, and related compounds
Abelson (1956)	CO <sub>2</sub> (CO), N <sub>2</sub> (NH <sub>3</sub> ), H <sub>2</sub> , H <sub>2</sub> O	Simple amino acids
Pavlovskaya and Pasynski (1959)	CH <sub>4</sub> , H <sub>2</sub> O, NH <sub>3</sub> or CH <sub>4</sub> , CO, NH <sub>3</sub>	Simple amino acids
Oró (1963b)	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Simple amino acids, also leucine and valine
Matthews and Moser (1966)	CH <sub>4</sub> , NH <sub>3</sub>	Polymeric material that yields simple amino acids after hydrolysis

Production of Amino Acids by the Action of Ultraviolet Light on Various Simulated Atmospheres<sup>37</sup>

Investigators	Wavelength	Gas Mixture	Products
Groth and Weyssenhoff (1957)	Various Hg lines	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , NH <sub>3</sub> , H <sub>2</sub> O (Hg as sensitizer)	Simple amino acids
Terenin (1959)	1000-2000 Å	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Simple amino acids
Dodonova and Sidorova (1961)	1450-1800 Å	CH <sub>4</sub> , CO, NH <sub>3</sub> , H <sub>2</sub> O	Simple amino acids, also norleucine

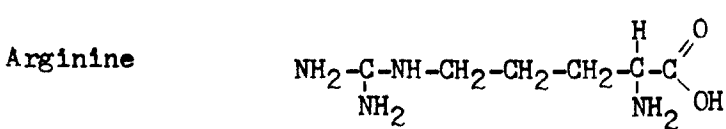
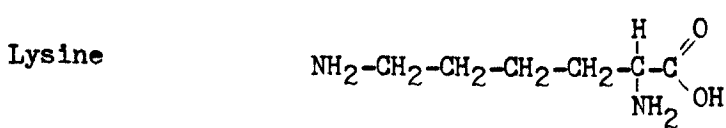
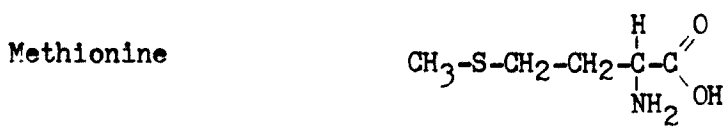
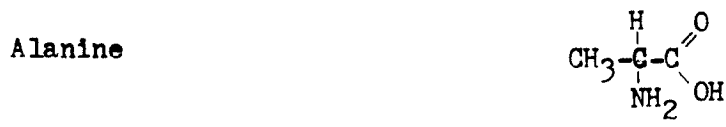
Production of Amino Acids by the Action of Ionizing Radiation on Various Simulated Atmospheres<sup>38</sup>

Investigators	Radiation	Gas Mixture	Products
Dose and Rajewsky (1957)	X-rays	CH <sub>4</sub> , CO <sub>2</sub> , CO, NH <sub>3</sub> , N <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> O	Simple amino acids
Palm and Calvin (1962)	Electrons	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O, H <sub>2</sub>	Simple amino acids
Oró (1963c)	Electrons	C <sub>2</sub> H <sub>6</sub> , N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	Simple amino acids
Choughuley and Lemmon (1966)	Electrons	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O, H <sub>2</sub> S	Simple amino acids, also taurine, cysteic acid (and cystamine)

Production of Amino Acids by the Action of Heat (~1000°C) on Various Simulated Primitive Atmospheres<sup>39</sup>

Investigators	Temperature and Contact Materials	Gas Mixture	Products
Harada and Fox (1964)	900-1100°C silica sand, silica gel	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Glycine, alanine, aspartic acid, glutamic acid, valine, leucine, isoleucine, serine, threonine, proline, tyrosine, and phenylalanine. Also β-alanine, α-aminobutyric acid, and alloisoleucine
Oró (1965)	1100°C no contact material	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Simple amino acids predominate
Taube et al. (1967)	800-1100°C silica	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Same products as those reported by Harada and Fox, 1964. Lysine reported.
Friedmann et al. (1971)	1300°C tungsten wire	NH <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub>	Phenylacetylene and indoles. From these phenylalanine, tyrosine, and tryptophan were produced in subsequent reactions at lower temperatures.

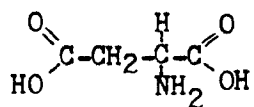
The twenty naturally occurring amino acids <sup>40</sup>



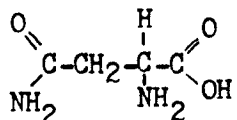


APPENDIX 4  
(continued)

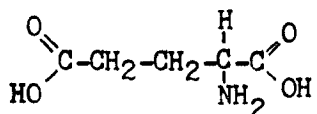
Aspartic acid



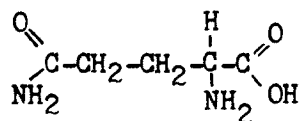
Asparagine



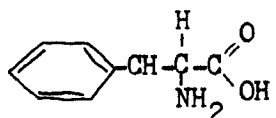
Glutamic acid



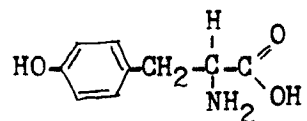
Glutamine



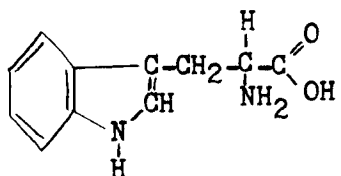
Phenylalanine



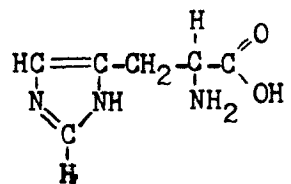
Tyrosine



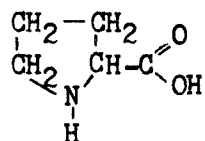
Tryptophan



Histidine

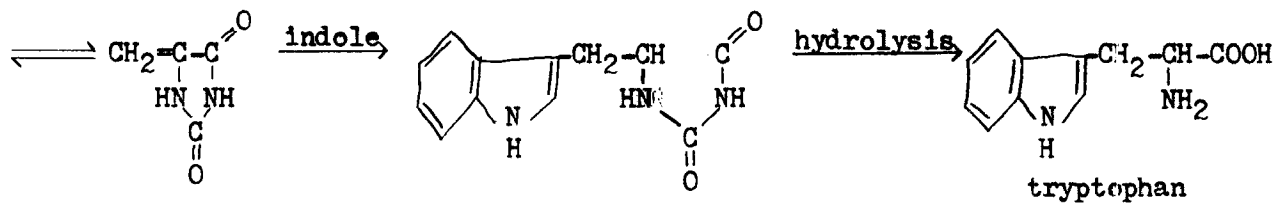
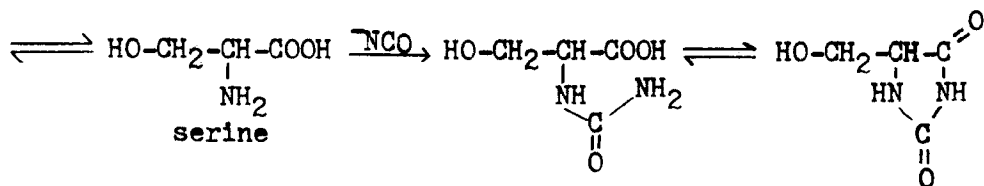
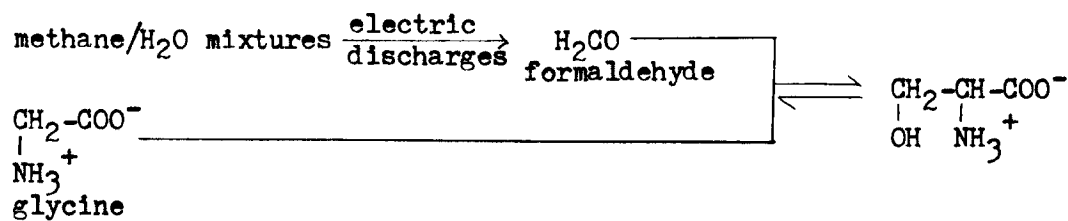
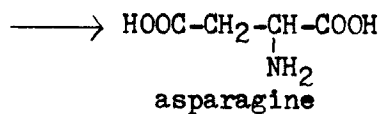
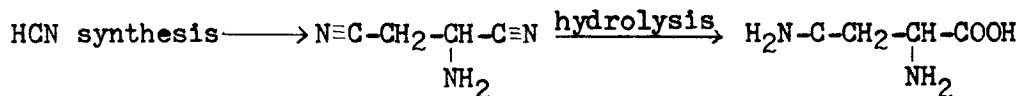


Proline





Synthesis of various amino acids



ENDNOTES

- <sup>1</sup> J. Keosian, "The Origin of Life," Van Nostrand Reinhold Co., New York, 1968, pp. 1-7.
- <sup>2</sup> I. Asimov, "Extraterrestrial Civilizations," Crown Publishers Inc., New York, 1979, p. 151.
- <sup>3</sup> C. E. Folsome, "The Origin of Life-A Warm Little Pond," W. H. Freeman & Co., San Francisco, 1979, p. 44.
- <sup>4</sup> C. Ponnampereuma, "The Origins of Life," E. P. Dutton & Co., Inc., New York, 1972, p. 135.
- <sup>5</sup> Asimov, op. cit., 153.
- <sup>6</sup> A. I. Oparin and S. Margulis, "The Origin of Life," Dover Publications Inc., New York, 1953, p. 248.
- <sup>7</sup> Asimov, op. cit., 154.
- <sup>8</sup> H. C. Urey, "Primitive Planetary Atmospheres and the Origin of Life", Aspects of the Origin of Life, Pergammon Press, Oxford, 1960, pp.8-14.
- <sup>9</sup> V. G. Fesenkov, "Some Considerations about the Primaeval State of the Earth", The Origin of Life on the Earth, 1, Pergammon Press, New York, 1959, pp.9-15.
- <sup>10</sup> F. Clark and R. L. M. Synge, "Proceedings of the First International Symposium on the Origins of Life," Pergammon Press, New York, 1959, pp. 114-115.
- <sup>11</sup> S. L. Miller and L. E. Orgel, "The Origins of Life on Earth," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1974, pp. 55-60.
- <sup>12</sup> Ponnampereuma, op. cit., 25-26.
- <sup>13</sup> S. L. Miller, "Production of Some Organic Compounds Under Possible Primitive Earth Conditions", J. Am. Chem. Soc., 77, 2351-2353(1955).
- <sup>14</sup> S. L. Miller, "A Production of Amino Acids Under Possible Primitive Earth Conditions", Science, 117, 528(1953).
- <sup>15</sup> S. L. Miller, JACS, op. cit., 2353.
- <sup>16</sup> C. E. Folsome, op. cit., 60.
- <sup>17</sup> S. L. Miller and L. E. Orgel, op. cit., 84.
- <sup>18</sup> Ibid, 85.
- <sup>19</sup> Ibid, 88-89.
- <sup>20</sup> Ibid, 92-93.

<sup>21</sup> S. L. Miller, "Formation of Organic Compounds on the Primitive Earth", Aspects of the Origin of Life, Pergamon Press, Oxford, 1960, p. 90.

<sup>22</sup> Ibid, 88.

<sup>23</sup> Ibid.

<sup>24</sup> S. L. Miller, JACS, op. cit., 2353.

<sup>25</sup> S. L. Miller, Aspects of the Origin of Life, op. cit., 88.

<sup>26</sup> J. P. Ferris and E. H. Edelson, "Chemical Evolution. 31. Mechanism of the Condensation of Cyanide to HCN Oligomers", J. Org. Chem., 43(21), 3989-3995(1978).

<sup>27</sup> S. L. Miller, H. C. Urey, and J. Oró, "Origin of Organic Compounds on the Primitive Earth and in Meteorites", Journal of Molecular Evolution, 9, 59-72(1976).

<sup>28</sup> R. K. Kotra, A. Shimoyama, C. Ponnampereuma, and P. E. Hare, "Amino Acids in a Carbonaceous Chondrite from Antarctica", Journal of Molecular Evolution, 13, 179-184(1979).

<sup>29</sup> Personal communications with Dr. Cyril Ponnampereuma at University of Maryland at College Park on December 21, 1979.

<sup>30</sup> J. Tze-Fei Wong and P. M. Bronskill, "Inadequacy of Prebiotic Synthesis as Origin of Proteinous Amino Acids", Journal of Molecular Evolution, 13, 115-125(1979).

<sup>31</sup> S. L. Miller and L. E. Orgel, op. cit., 55.

<sup>32</sup> Ibid, 84.

<sup>33</sup> S. L. Miller, JACS, op. cit., 2354.

<sup>34</sup> S. L. Miller and L. E. Orgel, op. cit., 85.

<sup>35</sup> Ibid, 86.

<sup>36</sup> S. W. Fox and K. Dose, "Molecular Evolution and the Origin of Life," W. H. Freeman and Co., San Francisco, 1972, p.76.

<sup>37</sup> Ibid, 78.

<sup>38</sup> Ibid, 81.

<sup>39</sup> Ibid, 83.

<sup>40</sup> L. E. Orgel, "The Origins of Life: Molecules and Natural Selection," John Wiley and Sons, Inc., New York, 1973, p.37.

<sup>41</sup> S. L. Miller and L. E. Orgel, op. cit., 88-93.

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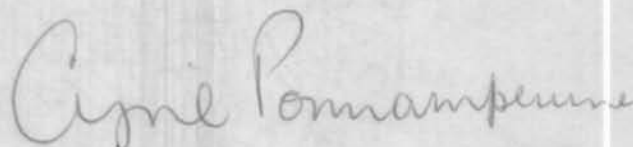
April 23, 1980

Mr. Scott E. Dahne  
c/o Western Maryland College  
Westminster, Maryland 21157

Dear Mr. Dahne:

This is just a brief note to thank you for the copy of  
your paper, PREBIOTIC SYNTHESIS - THE ORIGIN OF LIFE. I enjoyed  
reading it.

Sincerely,



Cyril Ponnampereuma  
Professor of Chemistry  
Director  
Laboratory of Chemical Evolution

sd