THE ATMOSPHERE OF THE PRIMITIVE EARTH AND THE PREBIOTIC SYNTHESIS OF AMINO ACIDS

STANLEY L. MILLER

Dept. of Chemistry, University of California, San Diego, La Jolla, Calif. 92037, U.S.A.

Abstract. The atmosphere of the Earth at the time of its formation is now generally believed to have been reducing, an idea proposed by Oparin and extensively discussed by Urey. This atmosphere would have contained CH_4, N_2 with traces of NH_3, water and hydrogen. Only traces of NH_3 would have been present because of its solubility in water. UV light and electric discharges were the major sources of energy for amino acid synthesis, with electric discharges being the most efficient, although most other sources of energy also give amino acids.

The first prebiotic electric discharge synthesis of amino acids showed that surprisingly high yields of amino acids were synthesized. Eleven amino acids were identified, four of which occur in proteins. Hydroxy acids, simple aliphatic acids and urea were also identified. These experiments have been repeated recently, and 33 amino acids were identified, ten of which occur in proteins, including all of the hydrophobic amino acids.

Methionine can be synthesized by electric discharges if H_2S or CH_3SH is added to the reduced gases. The prebiotic synthesis of phenylalanine, tyrosine and tryptophan involves pyrolysis reactions combined with plausible solution reactions.

Eighteen amino acids have been identified in the Murchison meteorite, a type II carbonaceous chondrite, of which six occur in proteins. All of the amino acids found in the Murchison meteorite have been found among the electric discharge products. Furthermore, the ratios of amino acids in the meteorite show a close correspondence to the ratios from the electric discharge synthesis, indicating that the amino acids on the parent body of the carbonaceous chondrites were synthesized by electric discharges or by an analogous process.

1. Introduction

The atmosphere of the primitive Earth at the time of its formation is now generally believed to have been reducing, an idea proposed by Oparin (1938) and extensively discussed by Urey (1952). This atmosphere is sometimes spoken of as a methane, ammonia, water and hydrogen atmosphere, but most of the nitrogen was probably molecular nitrogen and only traces of ammonia would have been present. Ammonia is very soluble in water and would be largely as NH_4^+ in the primitive ocean, if the pH of the ocean was about 8 as it is at present (Miller and Urey, 1959). The partial pressure of ammonia was not likely to have been much greater than 10^{-5} atm. This is based on an ocean of pH 8 and the fact that the NH_4^+ concentration could not have been much more than 0.01 M because of the absorption of NH_4^+ by clay minerals (Sillén, 1967; Bada and Miller, 1968). Although 10^{-5} atm was a small percentage of the primitive atmosphere, this value corresponds to a significant concentration of NH_4^+ and NH_3 in the ocean, and this dissolved ammonia would have played an important role in the prebiotic synthesis of organic compounds. On the other hand, if the partial pressure of NH_3 in the atmosphere drops much below 10^{-6} atm, the NH_3 and NH_4^+ in the ocean will be to low to obtain amino acids by a Strecker synthesis and aspartic acid will be unstable with respect to deamination to fumaric acid (Bada and Miller, 1968).

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An atmosphere of this type is thermodynamically stable in the presence of sufficient hydrogen, and only extremely small amounts of organic compounds would be present at thermodynamic equilibrium. However, various sources of energy can produce activated molecules (e.g. HCN and aldehydes) which would have reacted in the primitive ocean to produce biologically interesting organic compounds. The major source of energy in the atmosphere is UV light, with electric discharges being the next most abundant source. Most prebiotic experiments have used electric discharges because of their convenience, and they may have been the most important source of energy because of their efficiency, especially for the synthesis of hydrogen cyanide.

In the first prebiotic synthesis of amino acids and other organic compounds by electric discharges (Miller, 1953, 1955, 1957a, b), the discharge apparatus was designed to circulate the gases past the electrodes in a five liter flask and to condense the discharge products into a 500 ml flask about half-filled with water. The water was boiled in the 500 ml flask and the spark run for a week. The results of this experiment gave the yields in Table I. The yields of amino acids from this experiment appear to be the highest obtained in any prebiotic experiment of this type, even though no attempt was made to maximize the yields.

A great deal of effort was taken to properly identify the compounds. Most of the compounds in the table were positively identified by obtaining a melting point of a suitable derivative and showing that the mixed melting point with an authentic sample was not depressed.

It was shown that most if not all of the amino and hydroxy acids were produced by the Strecker and cyanohydrin synthesis from the corresponding aldehyde.

$$\mathrm{RCHO + HCN + NH_3 \rightleftarrows RCH(NH_2)CN + H_2O}$$

$$\mathrm{RCH(NH_2)CN + 2H_2O \rightarrow RCH(NH_2)COOH + NH_3}$$

$$\mathrm{RCHO + HCN \rightleftarrows RCH(OH)CN}$$

$$\mathrm{RCH(OH)CN \rightarrow RCH(OH)COOH}$$

The formation of the nitriles is a reversible reaction, while the hydrolysis of the nitrile, first to the amide and then to the acid, is irreversible. It should be noted that no acid hydrolysis step was used in these experiments; the nitriles were hydrolyzed to the amide and acid by the basic conditions of the boiling ammonia solution in electric discharge apparatus.

The Strecker synthesis can account for the synthesis of the α-amino acids and α-

TABLE I

Yields from sparking a micture of CH_4, NH_3, H_2O and H_2: 59 *m*mole (710 mg) of carbon was added as CH_4. The percent yields are based on the carbon

Compound	Yield (μmole)	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
α-Amino-n-butyric acid	50	0.34
α-Aminoisobutyric acid	1	0.007
α-Hydroxybutyric acid	50	0.34
β-Alanine	150	0.76
Succinic acid	40	0.27
Aspartic acid	4	0.024
Glutamic acid	6	0.051
Iminodiacetic acid	55	0.37
Iminoacetic-propionic acid	15	0.13
Formic acid	2330	4.0
Acetic acid	150	0.51
Propionic acid	130	0.66
Urea	20	0.034
N-Methyl urea	15	0.051
Total		15.2

hydroxy acids. The β-alanine and succinic acids were probably derived from acrylonitrile (Miller, 1957a).

$$NH_3 + CH_2=CH-CN \rightarrow H_2N-CH_2-CH_2-CN \rightarrow H_2N-CH_2-CH_2-COOH$$

$$NC^- + CH_2=CH-CN \rightarrow NC-CH_2-CH_2-CN \rightarrow HOOC-CH_2-CH_2-COOH$$

The addition of HCN to acrylonitrile appears to be irreversible, but it is not clear whether this is the case for NH_3.

2. Prebiotic Synthesis of the Hydrophobic Amino Acids

In these first experiments, the only hydrophobic amino acids that could be identified were glycine, alanine, α-amino-n-butyric acid, and α-aminoisobutyric acid. Subse-

quently, the prebiotic synthesis of the higher aliphatic amino acids was claimed, for example, by the action of electric discharges on $CH_4 + NH_3 + H_2O$ (Grossenbacher and Knight, 1965; Czuchojowski and Zawadzki, 1968; Oró, 1963; Ponnamperuma *et al.*, 1969; Matthews and Moser, 1966), by heating $CH_4 + NH_3 + H_2O$ to 900–1200° (Harada and Fox, 1964; Taube *et al.*, 1967), and by the action of shock waves on CH_4, C_2H_6, NH_3, and H_2O (Bar-Nun *et al.*, 1970). The amino acids were identified only by an amino-acid analyzer (Grossenbacher and Knight, 1965; Czuchojowski and Zawadzki, 1968; Oró, 1963; Matthews and Moser, 1966; Harda and Fox, 1964; Bar-Nun *et al.*, 1970), only by paper electrophoresis (Taube *et al.*, 1967), or only by gas chromatography (Ponnamperuma *et al.*, 1969). However, these techniques are not sufficient by themselves to identify an amino acid.

The synthesis under prebiotic conditions of aspartic acid, glutamic acid, serine, threonine, and proline have been reported in a number of prebiotic experiments, but they have not been properly identified (except for aspartic acid (Oró, 1968)). The synthesis of these amino acids (except proline) has also been reported from the polymerization of HCN (reviewed by Lemmon, 1970), but again without proper identification. A prebiotic synthesis of threonine should also yield allothreonine, but this amino acid has never been reported. In addition, several investigators have reported the appearance of a large peak at the isoleucine position on the amino-acid analyzer (Grossenbacher and Knight, 1965; Oró, 1963; Ponnamperuma *et al.*, 1969; Matthews and Moser, 1966; Fox and Windsor, 1970). The identification of this peak as isoleucine has been questioned (Oró, 1963; Fox and Windsor, 1970). It is evident that this compound cannot be isoleucine, since a corresponding peak for alloisoleucine is not observed.

It seemed likely that part of the reason for the low yield of the higher aliphatic amino acids in the first experiment was the high partial pressure of water near the spark. Therefore, the spark discharge experiments were repeated using lower temperatures and also lower pressures of ammonia (Ring *et al.*, 1972; Wolman *et al.*, 1972).

The electric discharge flask was patterned after that of Oró (1963) and is shown in Figure 1. One hundred ml of 0.05 M NH_4Cl was added to the flask, the flask evacuated, and sufficient NH_3 was added to bring the pH to 8.7. The partial pressure of NH_3 was calculated to be 0.1 mm. Methane (200 mm) and N_2 (80 mm) were then added, and the spark discharge was run for 48 hr. The tesla coil was the same kind as previously used (Miller, 1955). The temperature of the flask remained between 20 and 25°. The aqueous solution, presumably containing the amino nitriles rather than the amino acids (Miller, 1957), was hydrolyzed with 3 M HCl for 24 hr, desalted, and evaporated to dryness. The dried sample was hydrolyzed again with 3 M HCl in order to open the lactam rings of glutamic acid, α,γ-diaminobutyric acid, and α-hydroxy-γ-aminobutytic acid that may have been formed during the desalting. Seven similar runs were combined. A sample of the desalted amino acids was then run on the amino-acid analyzer (Dus *et al.*, 1967). The chromatogram is shown in Figure 2.

In order to separate the various amino acids, the combined runs were chromatographed on a column (38.5 × 2.2 cm) of Dowex 50, in the hydrogen form, and eluted

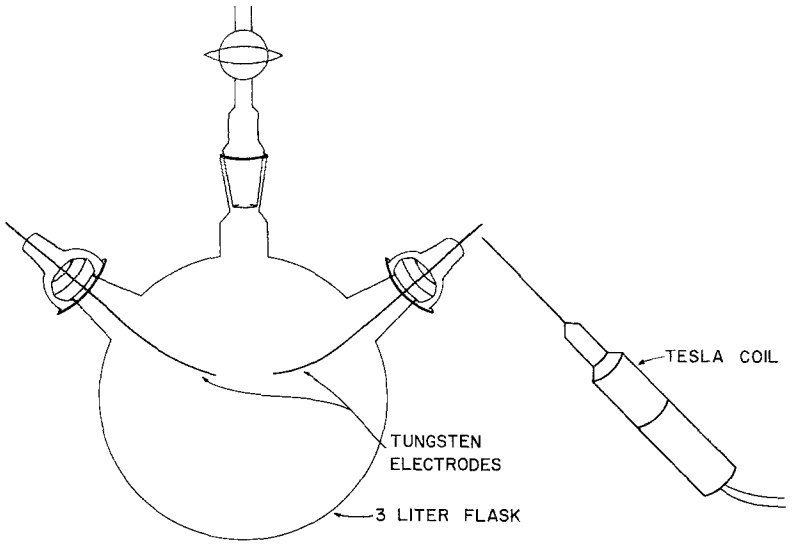


Fig. 1. Electric discharge apparatus used to synthesize amino acids at room temperature (after Oró, 1963).

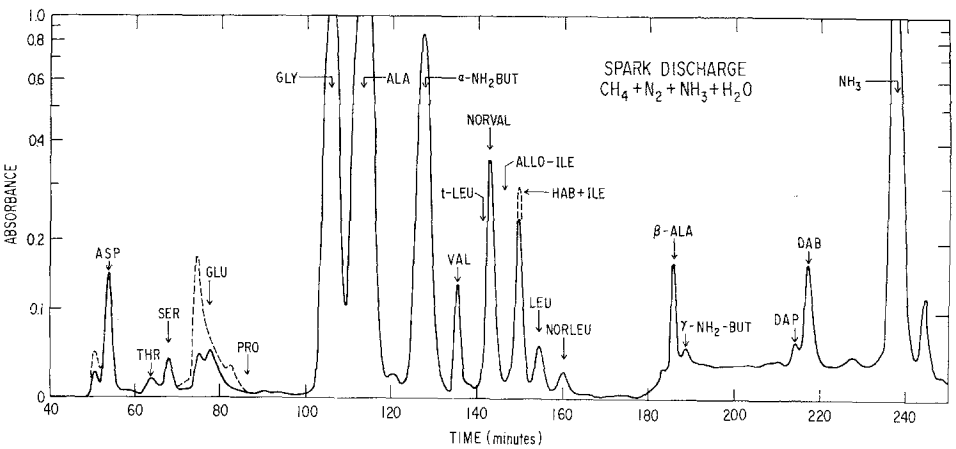


Fig. 2. Amino acid analyzer chromatogram of the desalted amino acids after the electric discharge synthesis. The arrows show the elution time of the indicated amino acids but this is not the basis for their identification. The peak labeled valine, norvaline (norval), allisoleucine, leucine and norleucine (norleu) contain between 50 and 80% of the indicated compound; most of the peaks labeled HAB + + Ile is α-hydroxy-γ-diaminobutyric acid; DAB is α, γ-diaminobutyric acid; DAP is α,β-diaminopropionic acid. The dashed line shows the increase in color on heating the column eluent and ninhydrin for 30 min instead of the usual 8 min; the color yield of proteins amino acids is not changed by the additional heating, but N-substituted amino acids give substantial increases in color yield.

with HCl (Wall, 1953) (400 ml of 1.5 M HCl, 700 ml of 2.5 M HCl, 400 ml of 4.0 M HCl, and 600 ml of 6.0 M HCl). Eighteen fractions were collected and evaporated to dryness in a vacuum desiccator; each fraction was quantitated on the amino-acid analyzer. The results of these analyses are shown in Table II. Those amino acids given only approximate values in the table were either not completely separated from inter-

TABLE II

Yields from sparking CH_4 (336 μmole), N_2, and H_2O with traces of NH_3

	μmole		μmole
Glycine	440	α, γ-Diaminobutyric acid	33
Alanine	790	α-Hydrocy-γ-aminobutyric acid	74
α-Amino-n-butyric acid	270	α, β-Diaminopropionic	6.4
α-Aminoisobutyric acid	~ 30	Isoserine	5.5
Valine	19.5	Sarcosine	55
Norvaline	61	N-Ethylglycine	30
Isovaline	~ 5	N-Propylglycine	~ 2
Leucine	11.3	N-Isopropylglycine	~ 2
Isoleucine	4.8	N-Methylalanine	~ 15
Alloisoleucine	5.1	N-Ethylalanine	< 0.2
Norleucine	6.0	β-Alanine	18.8
tert-Leucine	< 0.02	β-Amino-n-butyric acid	~ 0.3
Proline	1.5	β-Amino-isobutyric acid	~ 0.3
Aspartic acid	34	γ-Aminobutyric acid	2.4
Glutamic acid	7.7	N-Methyl-β-alanine	~ 5
Serine	5.0	N-Ethyl-β-alanine	~ 2
Threonine	~ 0.8	Pipecolic acid	~ 0.05
Allothreonine	~ 0.8		

Yield based on the carbon added as CH_4. Glycine = 0.26%, Alanine = 0.71%, total yield of amino acids in the table = 1.90%.

fering amino acids on the amino-acid analyzer (e.g. threonine and allothreonine) or did not react with ninhydrin (e.g. N-ethyl-β-alanine). These amino acids were estimated by the areas of the peaks found on gas chromatography of the N-trifluoroacetyl-sec-butyl esters.

The identity of each amino acid was based on gas chromatography-mass spectrometry, that is, when the elution time and the mass spectrum of an unknown and of known standards were identical. These identifications were supported by the elution times of the known and unknown on the Dowex 50 column and on the amino-acid analyzer.

In addition to confirming the identity of the unknown, the gas-chromatographic analysis showed that each of the amino acids (except for isovaline, α-hydroxy-γ-aminobutyric acid, α,γ-diaminobutyric acid, and aspartic acid that do not form two peaks on the colums used) were racemic within the experimental error (45–55% D-isomer). This result shows that there was no significant contamination from reagents or dust during the separation process. This conclusion applies particularly to the proline,

where the yield was sufficiently low that contamination was a reasonable possibility.

It was particularly interesting to find that the amino acid which has the same elution time as isoleucine on the amino acid analyzer is α-hydroxy-γ-aminobutyric acid. The aldehyde precursor of this is β-aminopropionaldehyde. The Strecker amino acid of this aldehyde is α,γ-diaminobutyric acid, which was found among the electric discharge products. Similarly, both isoserine and α,β-diaminopropionic acid were found, the aldehyde precursor of which is aminoacetaldehyde.

The results in Table II show that there is no selective synthesis of the branched-chain amino acids that occur in proteins. Indeed, the yield of norvaline is three times that of valine, although the yield of norleucine is 50% that of leucine and that of (isoleucine + alloisoleucine). Therefore, the occurrence of glucine, alanine, valine, isoleucine, and leucine in proteins, but the absence of α-amino-n-butyric acid, norvaline, alloisoleusine, and norleucine, cannot be understood on the basis of the yields from this type of synthesis.

The absence of *tert*-leucine in this synthesis may be due to the instability of its amino nitrile or its precursor aldehyde (pivaladehyde). Two aliphatic amino acids with both α hydrogens substituted, α-aminoisobutyric acid and isovaline (α-amino-α-methyl-n-butyric acid) were found. The six-carbon amino acids of this class were not looked for. The relatively low yield of α-aminoisobutyric and isovaline may be due to the instability of the corresponding aminonitrile, as has been discussed elsewhere (Miller, 1957a).

The yield of proline is quite low – seven times lower than leucine. A yield this low suggests that an electric-discharge synthesis of this type was not the only source of proline on the primitive Earth.

The yield of 5- and 6-carbon amino acids is substantially lower than the glycine, alanine, or even the α-amino-n-butyric acid. The mole ratios of glycine:alanine:α-aminobutyric acid:(valine + norvaline):6-carbon amino acids are 100:180:60:18:6. There is some variation in these ratios in different experiments, with the same conditions and spark source. The reason for the lower yields of the 5- and 6-carbon amino acids is not clear. When the temperature was lowered to 0° during the sparking, the yields of the 5- an d6-carbon amino acids were not increased, nor did the use of ethane instead of methane increase the yields.

It seems unlikely that the amino acids that were important in prebiotic polypeptides were present in the primitive ocean in about equal concentrations. Several mechanisms would have been available to concentrate certain amino acids in prebiotic polypeptides. One possible mechanism would have concentrated the sea water in a lagoon by evaporation until the amino acids were partially precipitated, and then synthesized peptides with the precipitated amino acids. The process would have concentrated the 5- and 6-carbon amino acids, since they are less soluble than glycine, alanine, and α-amino-n-butyric acid. The concentration of the higher aliphatic amino acids could also have occurred by adsorption on suitable mineral surfaces.

Peptide bonds of the 5- and 6-carbon amino acids are more stable to hydrolysis than those of glycine and alanine. This stability has been correlated with the 'rule of 6'

(Whitfield, 1964), and it has been suggested that the relative rates of hydrolysis generated sequences of peptides in the primitive ocean that were hydrolytically stable (Nicholson, 1970). The same considerations would predict that the higher aliphatic amino acids would concentrate in the peptides of a primitive ocean.

These considerations make it plausible that the yields of the 5- and 6-carbon amino acids obtained in this type of experiment would have been adequate for prebiotic peptide synthesis.

3. Prebiotic Synthesis of Methionine

Methionine might be considered 'too complex' an amino acid to be synthesized in significant yield in an electric discharge reaction because of the large number of possible isomers. However, the large yields of α-hydroxy-γ-aminobutyric acid and α,γ-diaminobutyric acid obtained in the above experiments, raised the possibility that acrolein was the precursor. In the presence of CH_3SH, NH_3, and HCN, acrolein might give methionine (Van Trump and Miller, 1972).

We therefore sparked a mixture of CH_4, N_2, H_2S, H_2O, and a trace of NH_3 and found that methionine was synthesized in 0.03% yield based on the H_2S (2×10^{-4}% based on the carbon). The yields of glycine and alanine in the same experiment were 0.068 and 0.104%, respectively based on the carbon.

It seemed likely that the limiting factor in this methionine synthesis was the formation of the thiomethyl group. We therefore sparked a mixture of CH_4, N_2, H_2O, CH_3SH, and a trace of ammonia and obtained 0.23% methionine. In a similar experiment, a mixture of CH_4, N_2, H_2O and a trace of NH_3 was sparked, and the CH_3SH was added at the termination of the sparking. This gave an 0.63% yield of methionine, based on the sulfur.

The methionine in these experiments was separated from the other amino acids by the amino-acid analyzer without the use of ninhydrin. The methionine peak, which contained norvaline and allisoleucine, was desalted and rerun on the analyzer, with the use of only the pH 3.28 citrate buffer. This procedure separated the methionine from the norvaline and alloisoleucine, and allowed quantification. The methionine peak was converted to the N-tri-fluoroacetyl-D-2-butyl ester and chromatographed on a 50-m gas chromatographic capillary column with OV-225 as a stationary phase. The mass spectrum and gas chromatography retention time of this unknown derivative agreed with the mass spectrum and retention time of an authentic sample of DL-methionine.

Acrolein was shown to be a product of the action of a spark discharge on a mixture of CH_4 and H_2O by means of an acrolein-specific fluorescent assay with m-aminophenol (Alarcon, 1968). The yield of acrolein was 0.04%, based on the methane. An alternate spectrophotometric assay with 4-hexylresorcinol (Cohen and Altshuller, 1961), a method which is sensitive to both acrolein and propiolaldehyde, gave a combined yield of 0.11%. A propiolaldehyde yield of 0.07% is in agreement with the results of Dowler *et al.* (1970).

On the basis of these results we propose the following model for the prebiotic synthesis of methionine.

$$\left.\begin{array}{l} CH_4 + H_2O \xrightarrow{\text{spark}} CH_2{=}CH{-}CHO \\ CH_4 + H_2S \xrightarrow[\text{or spark}]{\text{UV}} CH_3SH \end{array}\right\} \rightarrow CH_3S{-}CH_2{-}CH_2{-}CHO$$

$$\xrightarrow[HCN]{NH_3} CH_3S{-}CH_2{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CN \xrightarrow{\text{hydrolysis}} CH_3S{-}CH_2{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH$$

A model experiment was conducted to determine whether methionine could be synthesized from acrolein under the dilute conditions expected in the primitive ocean, a reaction which is effective using high concentrations (Smith, 1962). A mixture of acrolein (8×10^{-4} M), HCN (4×10^{-3} M), NH_3 (2.5×10^{-3} M), and CH_3SH (5×10^{-4} M) was added to a deaerated solution of NH_4Cl (7.5×10^{-3} M, final pH 8.7) and the solution was kept for 28 days. The mixture was hydrolyzed with 3 M HCl, desalted, hydrolyzed again with 3 M HCl, and quantitated on the amino-acid analyzer. The yields were 15% methonine, 0.5% glutamic acid, 0.5% α,γ-diaminobutyric acid, and 13% α-hydroxy-γ-aminobutyric acid, based on the added acrolein. The same experiment omitting the CH_3SH gave 1.5% glutamic acid and 0.8% α,γ-diaminobutyric acid. These results show that CH_3SH adds to acrolein in preference to NH_3 or HCN under the conditions of the experiment. The relative yields of the amino acids in the primitive ocean would depend on the concentrations of CH_3SH, HCN, and NH_3 as well as the temperature and hydrolytic conditions.

It appears likely that acrolein was a key intermediate in prebiotic amino acid synthesis, being a precursor not only of methionine but also of glutamic acid, homocysteine, homoserine, α,γ-diaminobutyric acid, and α-hydroxy-γ-aminobutyric acid (Figure 3).

The results from these low temperature electric discharge experiments are extremely encouraging. Table II shows that 10 of the 20 amino acids in proteins are obtained. Asparagine and glutamine can be included, since they would be obtained as hydrolysis products of the nitriles or from aspartic and glutamic acids under polymerization conditions. Methionine is obtained in the same experiment if H_2S or CH_3SH is added

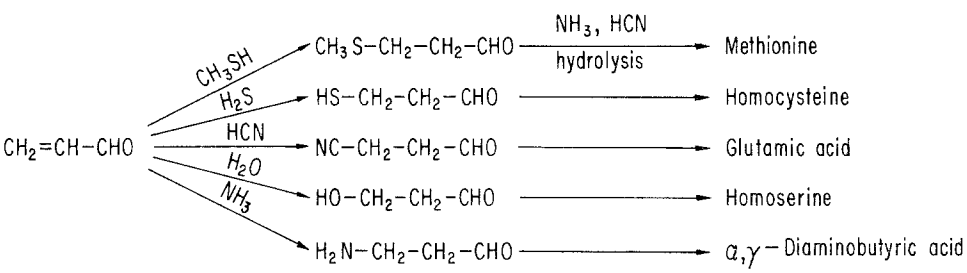


Fig. 3. Previotic synthesis of amino acids from acrolein.

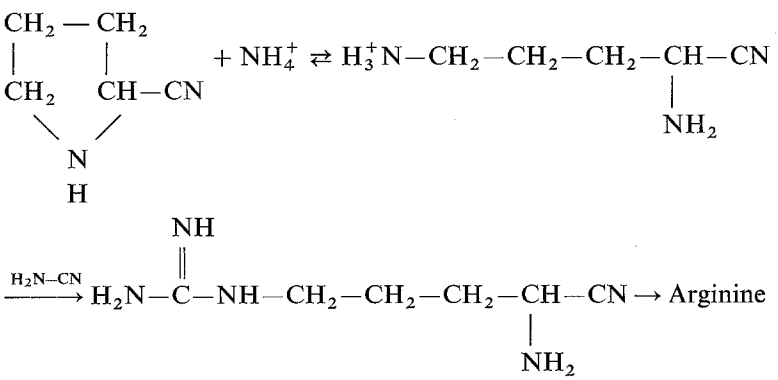
TABLE III

Relative abundances of amino acids in the Murchison meteorite and in an electric discharge synthesis. Mole ratio to glycine (= 100): 0.05–0.5, *; 0.5–5, **; 5–50 ***; > 50, ****.

Amino acid	Murchison meteorite	Electric discharge
Glycine	* * * *	* * * *
Alanine	* * * *	* * * *
α-Amino-n-butyric acid	* * *	* * * *
α-Aminoisobutyric acid	* * * *	* *
Valine	* * *	* *
Norvaline	* * *	* * *
Isovaline	* *	* *
Proline	* * *	*
Pipecolic acid	*	< *
Aspartic acid	* * *	* * *
Glutamic acid	* * *	* *
β-Alanine	* *	* *
β-Amino-n-butyric acid	*	*
β-Aminoisobutyric acid	*	*
γ-Aminobutyric acid	*	* *
Sarcosine	* *	* * *
N-Ethylglycine	* *	* * *
N-Methylalanine	* *	* *

to the gas mixture. Cysteine is obtained by the action of UV on a mixture of methane ethane, ammonia water and hydrogen sulfide (Sagan and Khare, 1971; Khare and Sagan, 1971). The prebiotic synthesis of phenylalanine, tyrosine and tryptophan involves the combination of pyrolysis and plausible solution reactions (Friedmann and Miller, 1969; Friedmann *et al.*, 1971). This adds up to 17 of the 20 amino acids in proteins.

The synthesis of proline and pipecolic acid implies the synthesis of arginine and lysine if they arise from the nitrile,



The nitrile of proline is quite stable relative to ornithine nitrile, but if the nitriles react with cyanamide, the open chain compound should be stable, leading to arginine. Similarly the homolog of proline nitrile, pipecolic acid nitrile, would lead to lysine through homoarginine. However, the details of these reactions need to be worked out.

Only histidine has not been synthesized under prebiotic conditions and properly identified.

4. The Murchison Meteorite

On September 28, 1969 a type II carbonaceous chondrite fell in Murchison, Australia. Surprisingly large amounts of amino acids were found by Kvenvolden *et al.* (1970, 1971). The first report identified seven amino acids (glycine, alanine, valine, proline, glutamic acid, sarcosine and α-aminoisobutyric acid), of which all but valine and proline had been found in the original electric discharge experiments. The most striking are sarcosine and α-aminoisobutyric acid. The second report identified 18 of the amino acids present of which nine had previously been identified in the original electric discharge experiments, but the remaining nine had not. Oró *et al.* (1971) have confirmed the results of Kvenvolden *et al.* (1970, 1971).

At that time we had identified the hydrophobic amino acids from the low temperature electric discharge experiments described above, and therefore we examined the Dowex 50(H^+) samples for the non-protein amino acids found in Murchison. We are able to find all of them.

There is a striking similarity between the products and relative abundances of the amino acids produced by electric discharge and the meteorite amino acids. Unfortunately, there are only a few quantitative values (Cronin and Moore, 1971) for the meteorite amino acids, but we have estimated their relative abundances from the published gas chromatography data (Kvenvolden *et al.*, 1971). Table III compares the results.

The most notable difference between the meteorite and the electric-discharge amino acids is the pipecolic acid, the yield being extremely low in the electric discharge. Proline is also present in relatively low yield from the electric discharge. The amount of α-aminoisobutyric acid is greater than α-amino-n-butyric acid in the meteorite, but the reverse is the case in the electric discharge. The amounts of aspartic and glutamic acids in the meteorite are comparable, but there is five times as much aspartic acid as glutamic acid in the electric discharge.

We do not believe that reasonable differences in ratios of amino acids detract from the overall picture. Indeed, the ratio of α-aminoisobutyric acid to glycine is quite different in two meteorites of the same type, being 0.4 in Murchison and 3.8 in Murray (Cronin and Moore, 1971).

One would expect quantitative differences between the meteorite composition and the electric-discharge products, even if the mechanism of formation in the two cases were identical. Thus cyanoacetylene, which is synthesized by sparking CH_4 and N_2, is probably the major precursor of aspartic acid, but the yield of cyanoacetylene is decreased by the addition of small amounts of NH_3 to the CH_4+N_2 mixture (San-

chez *et al.*, 1966). Therefore, local differences in the NH_3 partial pressures on the parent body of the carbonaceous chondrites would result in substantial differences in the aspartic acid concentration if the amino acids were not completely mixed on the parent body. Temperature differences can also affect the yields. For example, the stability of α-aminoisobutyronitrile is quite sensitive to temperature and cyanide concentration, while α-amino-n-butyronitrile, being more stable is not particularly sensitive to these factors. Also there is the possibility that the amino acids in Murchison may have been decarboxylated or otherwise destroyed to different extents in the time since they were synthesized.

The very close correspondence between the amino acids found in the Murchison meteorite and those produced by an electric discharge synthesis, both as to the amino acids produced and their relative ratios, suggests that the amino acids in the meteorite were synthesized on the parent body by means of an electric discharge or analogous processes. Electric discharges appear to be the most favored source of energy but sufficient data are not available to make realistic comparison with other energy sources. In any case, it is unlikely that a single source of energy synthesized all of the organic compounds either on the parent body of the carbonaceous chondrites or on the primitive Earth. All sources of energy would have made their contribution, and the problem is to evaluate the relative importance of each source.

Our ideas on the prebiotic synthesis of organic compounds are based largely on the results of experiments in model systems. So it is extremely gratifying to see that such synthesis really did take place on the parent body of the meteorite, and so it becomes quite plausible that they took place on the primitive Earth.

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