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Prebiotic Synthesis in Atmospheres Containing CH_4, CO, and CO_2

I. Amino Acids

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Summary. The prebiotic synthesis of organic compounds using a spark discharge on various simulated primitive earth atmospheres at 25°C has been studied. Methane mixtures contained $H_2 + CH_4 + H_2O + N_2 + NH_3$ with H_2/CH_4 molar ratios from 0 to 4 and $pNH_3 = 0.1$ torr. A similar set of experiments without added NH_3 was performed. The yields of amino acids (1.2 to 4.7% based on the carbon) are approximately independent of the H_2/CH_4 ratio and whether NH_3 was present, and a wide variety of amino acids are obtained. Mixtures of $H_2 + CO + H_2O + N_2$ and $H_2 + CO_2 + H_2O + N_2$, with and without added NH_3, all gave about 2% yields of amino acids at H_2/CO and H_2/CO_2 ratios of 2 to 4. For a H_2/CO_2 ratio of 0, the yield of amino acids is extremely low (10^{-3}%). Glycine is almost the only amino acid produced from CO and CO_2 model atmospheres. These results show that the maximum yield is about the same for the three carbon sources at high H_2/carbon ratios, but that CH_4 is superior at low H_2/carbon ratios. In addition, CH_4 gives a much greater variety of amino acids than either CO or CO_2. If it is assumed that an abundance of amino acids more complex than glycine was required for the origin of life, then these results indicate the requirement for CH_4 in the primitive atmosphere.

Key words: Primitive atmospheres of CH_4, CO, CO_2 – Prebiotic synthesis – Electric discharge – Amino acids

Introduction

There have been many attempts to synthesize organic compounds from CO and CO_2 (for reviews see Rabinowitch 1945; Chittenden and Schwartz 1981). Some specific examples which may be relevant to primitive earth conditions include the early electric discharge synthesis of glycine from CO + H_2 + NH_3 (Löb 1913), the synthesis of formaldehyde and polymers of unknown composition from CO_2 + H_2O + ultraviolet light (Groth and Suess 1938), the synthesis of small amounts of formic acid and formaldehyde from CO_2 + H_2O and 40 MeV helium ions (Garrison et al. 1951), the inability to detect any organic compounds produced from CO_2 + H_2O and a spark discharge (Wilde et al. 1953), the synthesis of HCN and amino acids from various mixtures of CO, CO_2, N_2, NH_3, H_2, and H_2O by an electric discharge (Heyns et al. 1957; Abelson 1955–1956, 1965, 1965–1966; Abelson and Hoering 1965– 1966), the synthesis of formaldehyde, acetaldehyde and glycolic acid from CO, H_2O and ultraviolet light on Vycor and other surfaces (Hubbard et al. 1971), the Fischer-Tropsch type synthesis using CO + H_2 + NH_3 which gives a wide variety of organic compounds in substantial yields (Hayatsu and Anders 1981), the synthesis of aldehydes and alcohols from CO + H_2O + ultraviolet light (Bar-Nun and Hartman 1978), the synthesis of amino acids from H_2O, N_2 and NH_3 using an electric discharge with carbon electrodes (Harada and Suzuki 1977; Yamagata et al. 1981), the synthesis of inorganic compounds such as hydrazine and carbohydrazide in low yield by sparking aqueous $CaCO_3$ and N_2 (Folsome et al. 1981), and the synthesis of cyanate and formic acid from CO_2, H_2, N_2, H_2O mixtures (Yamagata and Mohri 1982; Kawamoto and Akaboshi 1982). However, there has never been a systematic comparison of the compounds produced with various gas mixtures. It was of particular interest to compare the results from CO and CO_2 containing atmospheres with those from the more reduced CH_4 atmospheres, which produce a wide variety of organic compounds, especially amino acids (Miller

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1953, 1955; Ring et al. 1972; Wolman et al. 1972). A spark discharge was used in these experiments because of its probable importance as a source of energy on the primitive earth, its efficiency in organic compound synthesis, and its frequent use in other prebiotic synthesis experiments.

Experimental

The spark discharge apparatus, shown in Fig. 1, was that previously used (Ring et al. 1972; Wolman et al. 1972; Miller 1974). The continuous wave spark generator was a Cenco Model 80721. This spark generator was modified for continuous operation by removing part of its Bakelite covering to allow for air circulation and cooling.

100 ml of either water or 0.05 M NH_4Cl solution was added to the 3 l discharge flask, the air was removed, and the desired gases were added via a vacuum manifold system. The gases were C.P. grade and used without further purification except for the CH_4 which was condensed and distilled. The partial pressures of N_2, CH_4, CO or CO_2 were 100 torr in all experiments except those shown in Fig. 4. The flasks with the NH_4Cl solution were brought to a pH of about 8.7 by adding about 1.0 ml of 1 M NaOH through the stopcock of the flask, with care being taken to insure that no air entered the flask. This gave a pNH_3 of about 0.1 torr. The flask was kept at room temperature, and the spark was run continuously for 48 h.

A gas sample was taken for subsequent gas chromatographic analysis, after which the solution was allowed to remain at room temperature for 48 h so that the amino and hydroxy nitriles would approach their equilibrium concentrations in the aqueous phase. A portion of the solution was then hydrolyzed in 3 M HCl for 20 h, and the remainder of the of the sample was stored in a freezer. The hydrolyzed samples were desalted and the amino acids determined on a Beckman Spinco Model 119 amino acid analyzer.

For the electric discharge experiments measuring the yield of amino acids as a function of the duration of sparking of the gas mixture, two different experimental techniques were used. For the $CH_4 + N_2 + NH_3$ curve (Fig. 3) individual experiments were conducted for each of the indicated periods of sparking time. In the case of the $CO + N_2 + H_2$ curve only one experimental flask was utilized. Aliquots (approximately 3 ml) of the aqueous phase were removed through a vacuum system at the indicated periods of sparking time and were then prepared for amino acid analysis in the usual manner.

The yields of the less abundant amino acids (Table 1) were determined by fractionating a hydrolyzed and desalted aliquot of the products on a Dowex 50W-X8 cation exchange column (15 ml volume), using 1.5 and 2.5 M HCl as eluants. Aliquots of the various fractions were run on the amino acid analyzer. This procedure permitted the estimation of various amino acids in the presence of a large amount of glycine.

The gas phase samples were analyzed by gas chromatography, using an F&M Model 700 gas chromatograph fitted with an external gas storage/injection system and a 1.8 m column containing Spherocarb 80–100 mesh stationary phase. During each analysis the column was operated at 0°C for separation of H_2, N_2, and CO, and then heated to 100°C for elution of CH_4. Identification and quantification of the peaks in the experimental samples was by comparison with a standard gas mixture.

Results

The first point to be made about these experiments is the difficulty of reproducing the results, especially the amino acid yields. These yields typically varied by a factor of two between duplicate experiments and in some cases the variation was greater. Much of this difficulty is due to the variations in power output of the spark generator, which we tried to control by rotating three spark generators among three flasks during the 48 h run. However, this did not entirely solve the problem since the spark intensity was not constant over time with each spark generator. Permitting the aqueous phase to sit for 48 h after sparking allowed some of the aqueous solution chemistry to proceed, especially the formation of amino nitriles. While this length of time was probably adequate for the formation of most of the nitriles, the rate of formation of glycine nitrile is particularly slow with $t_{1/2}$ = 40 days at 25°C (Miller and Van Trump 1981), so it is clear that complete equilibrium was not attained between glycine nitrile and glycolonitrile.

Amino Acid Yields

These are shown in Fig. 2, and are the total amino acid yields based on carbon. There are two series of experiments with each carbon source, those with added NH_4Cl (e.g. $CH_4 + H_2 + N_2 + NH_3$) and those with no added NH_4Cl (e.g. $CH_4 + H_2 + N_2$). The experiments with added NH_4Cl were designed to reflect the requirements for $NH_4{}^+$ in the ocean to ensure the stability of aspartic acid (Bada and Miller 1968) and for the synthesis of amino acids by the Strecker synthesis (Miller and Van Trump 1981). These considerations point to a minimum

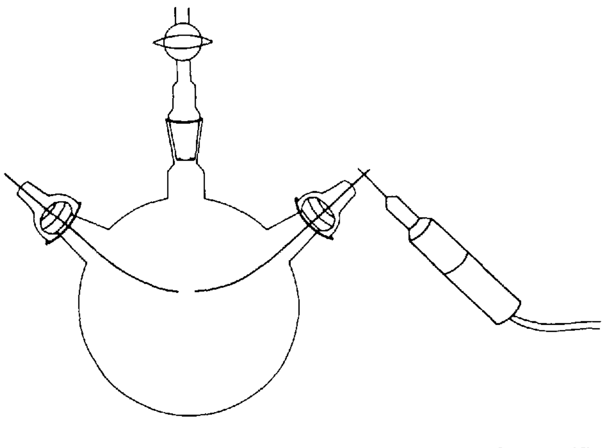


Fig. 1. The spark discharge apparatus. It consists of a modified 3-l flask with two removable tungsten electrodes and a stopcock. The spark generator is shown at the right in contact with one of the tungsten electrodes. The second electrode is usually not grounded. The flask contained 100 ml H_2O or 0.05 M NH_4Cl. The gases were added from a vacuum manifold through the stopcock

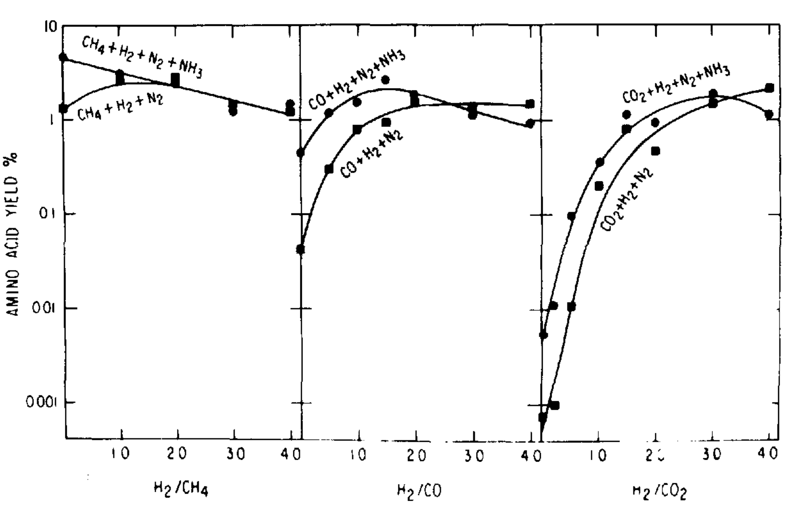


Fig. 2. Amino acid yields based on initial carbon. In all experiments pN_2 = 100 torr, and pCH_4 or pCO, or pCO_2 = 100 torr. For experiments containing NH_3, the spark discharge flask contained 100 ml 0.05 M NH_4Cl brought pH 8.7 so that pNH_3 was 0.1 torr. For experiments not containing NH_3, the flask had 100 ml of H_2O. The flask was kept at room temperature, and the spark generator was operated continuously for 48 h

NH_4^+ concentration of about 10^{-3} M. The maximum NH_4^+ is about 10^{-2} M, since higher concentrations will be absorbed on the clay minerals. The 0.05 M NH_4Cl is somewhat high, but these conditions should favor amino acid synthesis. The gaseous NH_3 could also act as a hydrogen source in the low H_2/CO and H_2/CO_2 experiments. The experiments with no added NH_3 were done because it has been claimed that NH_3 was never present in significant quantities in the earth's primitive atmosphere (Abelson 1966; Ferris and Nicodem 1972; Kuhn and Atreya 1979; Henderson-Sellers and Cogley 1982). In addition it was desired to see how much NH_3 was produced directly in the spark.

The first section of Fig. 2 shows the methane results, with H_2/CH_4 varying from 0 to 4. The yield of amino acids with added NH_3 is 4.7% at H_2/CH_4 = 0, and it drops steadily to 1.4% at H_2/CH_4 = 4. The yields are based on the carbon added as CH_4 [% yield = 100 N (moles of amino acid)/(mole added CH_4), where N is the number of carbon atoms in the amino acid]. The reason for this decline in yield is the lowered yields of both HCN and aldehydes, especially the latter (see Figs. 1 and 2 of following paper). A second set of experiments without added NH_3 gave quite similar results.

The middle section of Fig. 2 shows the amino acid yields for H_2/CO ratios from 0 to 4. One curve shows the results for experiments in which a 0.05 M NH_4Cl solution was added to the flask and the second curve shows the results when no NH_4Cl was included in the aqueous phase. The amino acid yields at a H_2/CO = 0 are 0.44% with added NH_3, and 0.05% without added NH_3. The yields increase at higher H_2/CO ratios and the two curves approach and cross each other. The maximum yield of amino acids in these experiments is 2.7%.

The third section of Fig. 2 shows the amino acid yields for H_2/CO_2 ratios from 0 to 4. The amino acid yield at H_2/CO_2 = 0 is 5×10^{-3}% with added NH_3 and 6×10^{-4}% without added NH_3. These quantities are just above the level of reagent contamination. The yields rise rapidly as the H_2/CO_2 ratio is increased, and again the curves cross at H_2/CO_2 = 3. The maximum yield of amino acids is 2.0%. It is to be noted that while CO_2 is more soluble in water than CH_4 and CO, the amount of CO_2 dissolved was less than 10% of that added. Even in the case of the experiments with added 0.05 M NH_4Cl brought to pH 8.5, less than 10% of the CO_2 dissolved in the aqueous phase. These yields are in general agreement with Abelson's CO_2 experiments (Abelson 1965); the CO experiments can not be compared because quantitative amino acid yields were not determined (Abelson 1955–1956).

The maxima in the amino acid yields could be interpreted in terms of the stoichiometry of the synthetic reaction. However, it is not clear which reaction to use, and the experimental yield curves are not sufficiently well defined to make these comparisons meaningful.

Types of Amino Acids Synthesized

The particular amino acids produced with CO and CO_2 are about the same and quite different from those produced from CH_4. Table 1 gives an analysis for six different gas mixtures. The yields of glycine are not greatly different except for H_2/CO_2 = 0.5, ranging from 0.40% to 1.8%, but glycine is almost the only amino acid found in the CO and CO_2 runs. The only other amino acids found with CO and CO_2 atmospheres are small amounts of alanine and serine and trace amounts of several others. By contrast, the CH_4 experiment contains almost as much alanine and α-amino-n-butyric acid as glycine along with the abundant variety of amino acids previously reported in this type of experiment (Ring et al. 1972; Wolman et al. 1972). The yields of amino acids are somewhat different in these methane experiments from those results previously reported, but the qualitative results are consistant. The amino acids other than glycine are expected to be racemic mixtures as shown previously (Ring et al. 1972; Wolman et al. 1972).

Table 1. Mole ratio of amino acids relative to glycine = 100. The percent yield of glycine based on carbon is given in parentheses. All runs contained no added NH_4Cl except $H_2/CH_4 = 0.0$

Amino acid	$H_2/CH_4 = 0.0$	$H_2/CH_4 = 3.0$	$H_2/CO = 0.5$	$H_2/CO = 3.0$	$H_2/CO_2 = 0.5$	$H_2/CO_2 = 3.0$
Glycine	100 (1.77%)	100 (0.40%)	100 (0.30%)	100 (1.42%)	100 (0.01%)	100 (1.53%)
Alanine	85	101	2.8	2.4	7.0	0.87
α-Amino butyric	18	30	0.01	0.04	< 0.001	0.09
Valine	2.1	1.2	< 0.001	0.005	< 0.001	< 0.001
Norvaline	3.3	1.3	< 0.001	0.01	< 0.001	< 0.001
Aspartic acid	0.4	1.6	0.04	0.09	0.22	0.14
Glutamic acid	1.5	1.5	< 0.001	0.01	0.06	< 0.001
Serine	1.4	3.1	0.08	0.15	0.40	0.23

The amino acid yields from the CO and CO_2 model atmospheres are similar to those obtained from a HCN polymerization (Oro and Kamat 1961; Ferris et al. 1981), where glycine is the major amino acid and only small amounts of alanine, aspartic acid and serine are produced. The mechanism, however, is different since H_2CO was in excess over HCN in these spark discharge reactions and there is essentially no free H_2CO present during an HCN polymerization. Although the products are similar in the two pathways, the spark discharge pathway with CO and CO_2 atmospheres is likely to have been more important on the primitive earth than the HCN polymerization. This is probably also the case with CH_4 atmospheres unless the HCN/H_2CO ratio produced by the various sources of energy was far higher than observed in these experiments.

Time Course of the Reaction

We investigated the amino acid yield as a function of time of sparking for two runs. The results are shown in Fig. 3. The amino acid yield after two days is about 60% of the maximum for the CH_4 experiment and about 80% for the CO experiment. Thus the yields shown in Fig. 2 are not far from those that would have been obtained at very long sparking times.

Effects of CH_4 and CO Partial Pressures

The effect of CH_4 and CO partial pressures on the amino acid yields was investigated in two experiments. In the first experiment pCH_4 was varied from 1.6 to 100 torr, and no H_2 was added. In the second experiment both the H_2 and CO were varied from 2.3 to 100 torr and the H_2/CO ratio was kept at 1.0. Figure 4 shows the percent yields of amino acids as a function of the CH_4 or CO partial pressure. In both cases the yields drop by a factor of about 6 on lowering the partial pressure from 100 torr to 0 torr. The lowest CH_4 point diverges from the curve by a factor of 2.5. This may be due to both the variability of yields obtained in this type of experiment and to the difficulty of accurately measuring partial pressures of CH_4 in the 1 to 5 torr region. It is to be noted that the figures given are percent yields and not absolute yields which would be zero at zero pressure of CH_4 or CO.

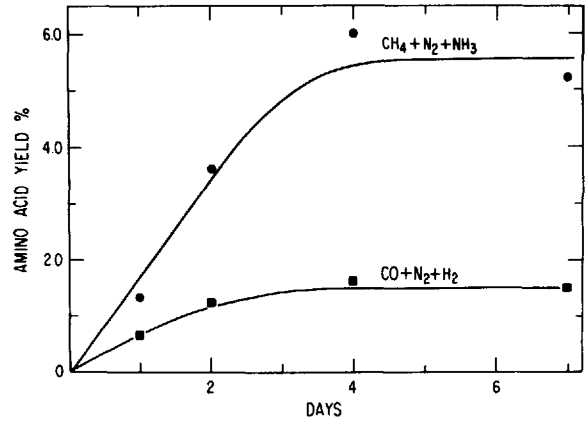


Fig. 3. Amino acid yield as a function of sparking time. The methane experiment contained no added H_2. The CO experiment had $H_2/CO = 1.0$. $pN_2 = 100$ torr

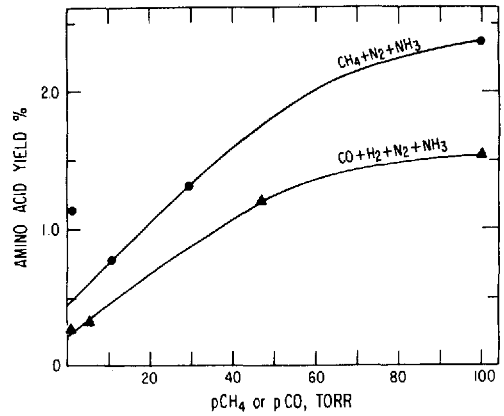


Fig. 4. Amino acid yield as a function of pCH_4 and pCO. The methane experiment had no added H_2. The CO experiment had $H_2/CO = 1.0$. The pN_2 was kept at 100 torr in all experiments

The decrease in percent yield at low pressures may be due to a number of causes. The most important is probably the low amino nitrile concentrations in the low pCH_4 and pCO experiments due to extensive dissociation. In the primitive ocean, the formation and hydrolysis of amino nitriles would increase the yields of amino acids over those observed in these short term experiments, and we would expect that the percent yields of the more dilute solutions would approach those of the more concentrated solutions. A second cause is that most of the energy of the spark is used in dissociating the N_2 rather than the less abundant CH_4 or CO. Thus we would expect that longer sparking times would increase the yields at lower partial pressures of CH_4 and CO.

It is possible that the yield is solely a function of pH_2 and not the H_2/carbon ratios. The yields in the CO experiments do correlate with pH_2, but the extrapolation to zero pH_2 gives the same yield as extrapolating $H_2/CO = 1.0$ to zero pressures. A similar comparison cannot be drawn for the CH_4 data because no H_2 was added to those experiments. The available data do not permit a choice to be made between the H_2/carbon and the pH_2 parameters as the determining factor in the amino acid yield at low partial pressures.

Gas Phase Analysis

At the conclusion of each experiment a sample of the gas phase was obtained through a vacuum line and was subsequently analyzed by gas chromatography. The 100 torr of N_2 initially present in each gas mixture served as an internal standard for calibration of the chromatographic results.

In the CH_4-containing experiments appreciable quantities of methane remained unreacted after two days of sparking, while small amounts of CO were also produced. The amount of CH_4 remaining in the experiments with added NH_4Cl varied from 10% for $H_2/CH_4 = 0$ to 75% for $H_2/CH_4 = 3.0$, with somewhat less CH_4 remaining in the experiments without added NH_3. The amount of CO produced varied from 1.21% to 5.29%.

The results for the CO-containing experiments demonstrated that after two days of sparking only small amounts (from 0.68 to 2.72%) of the initial CO remained in the gas phase at all H_2/CO ratios. Traces of CH_4 (2.5×10^{-2} to 10.7×10^{-2}%) were also detected. The remaining CO can be accounted for as HCN (2 to 10%), H_2CO (2 to 10%), unknown amount of other organic compounds, and CO_2 which was not analyzed for.

In the CO_2-containing experiments it was not possible to determine the quantity of CO_2 remaining in the gas phase at the end of each experiment, because of limitations in the analysis procedure. However, appreciable quantities of CO were detected. The amount of CO produced increased roughly linearly with the H_2/CO_2 ratio. For the experiments without added NH_4Cl the amount of CO detected ranged from 0.022% for $H_2/CO_2 = 0.25$ to 16.4% for $H_2/CO_2 = 4$. For the experiments with added NH_4Cl the range was from 6.14% for $H_2/CO_2 = 0.25$ to 37.2% for $H_2/CO_2 = 4$.

Discussion

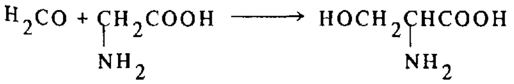
These results have implications as to the earth's primitive atmosphere. In agreement with previous results, CH_4 containing model atmospheres give high yields and good varieties of amino acids. Carbon monoxide containing model atmospheres give good yields of amino acids at most H_2/CO ratios. Even at $H_2/CO = 0$ the amino acid yields, though small, may have been adequate for the accumulation needed for further stages of chemical evolution. However, atmospheric CO is unstable because CO is a relatively reactive gas (Van Trump and Miller 1973). Therefore, high partial pressures of CO are not likely although a low steady state partial pressure would be expected.

The amino acid yields with CO_2 model atmospheres containing small amounts of H_2 are low. When H_2/CO_2 is less than 0.5, the yields of amino acids are so low it is difficult to detect them above the reagent contamination. Yields of this level, even with the available concentration mechanisms, might not permit sufficient accumulation of amino acids to make it plausible for life to arise. The yields with CO mixtures do not fall off as much at low H_2/CO ratios as with the CO_2 mixtures. At H_2/CO_2 and H_2/CO ratios of 1.0 or greater, the amino acid yields are about the same as with CH_4 mixtures. But this raises the problem of maintaining an adequate steady state partial pressure of H_2 on the primitive earth.

If we take a H_2/CO_2 ratio of 2.0 or more as that needed for efficient prebiotic synthesis, then a H_2 mixing ratio of 6×10^{-4} would be needed for the present pCO_2 of 3×10^{-4} atm. It is possible that pCO_2 may have been much higher due to the slow precipitation of $CaCO_3$. High pCO_2 has also been proposed to give an enhanced greenhouse effect (Owen et al. 1979). If we take this increase to be a factor of 10, then the mixing ratios of H_2 and CO_2 would have to be 6×10^{-3} and 3×10^{-3} respectively. A very low exosphere temperature where the Jean's escape mechanism is limiting would allow for such H_2 mixing ratios. However, at the present time the limiting factor on the rate of escape is the diffusion to the escape layer, and this was presumably the case on the primitive earth. The H_2 mixing ratios have been calculated on the basis of diffusion limited escape and various volcanic inputs (Walker 1977). The H_2 mixing ratio is essentially proportional to the volcanic input when the O_2 sources are small. Thus the H_2 mixing ratio would be 2×10^{-5} for the present H_2 flux from volcanoes of 4×10^8 molecules

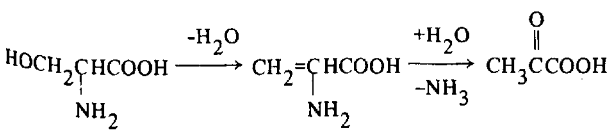
cm^{-2} s^{-1}. The volcano flux would have to be 30 times higher for a CO_2 mixing ratio of 6 x 10^{-4}, and 300 times higher for a CO_2 mixing ratio of 6 x 10^{-3}. It would appear that volcanic activities of this magnitude are too high, but other sources of H_2 should be added to the volcanoes. These include submarine hot springs, H_2 production from diagenesis of organic material in the oceans and sediments, photochemical H_2 production from organic compounds in the atmosphere (this would not, however, result in a net synthesis of organic compounds), photolysis of H_2O in the atmosphere provided a sink for the OH and O_2 was available, and photochemical production of H_2 from water in the presence of suitable electron donors such as Fe^{2+}. The evaluation of these sources is beyond the scope of this paper, but it would seem difficult for these H_2 sources to maintian mixing ratios of 30 to 300 times those produced by present day volcanoes.

Even with an adequate pH_2, there is a problem with using CO and CO_2 atmospheres. From the standpoint of amino acid synthesis the results are quite disappointing – essentially only glycine is produced. If it is assumed that a wide variety of amino acids were needed on the primitive earth for the origin of life, then CO and CO_2 containing atmospheres give a suite of amino acids that is apparently inadequate. The failure may not be as bad as it seems because reactions of glycine can give some of the higher amino acids. For example, glycine reacts reversibly with formaldehyde to give serine (Friedmann et al. 1971).



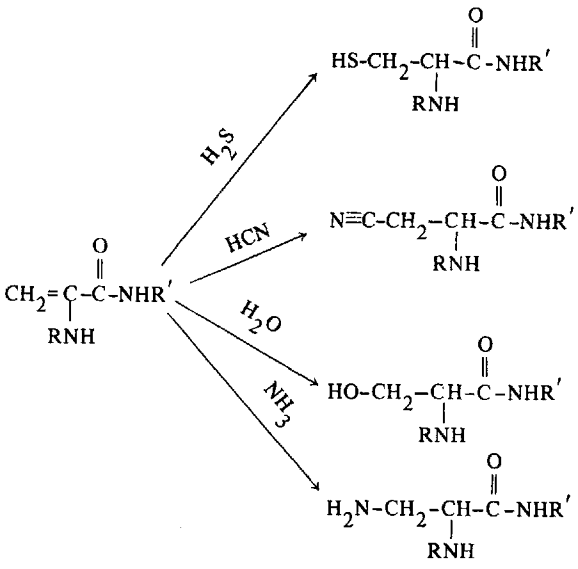
$$H_2CO + \underset{NH_2}{C}H_2COOH \longrightarrow HOCH_2\underset{NH_2}{C}HCOOH$$

and with polyglycine to give serine peptides (Akabori 1959). Serine is converted to pyruvate via dehydroalanine



$$HOCH_2\underset{NH_2}{C}HCOOH \xrightarrow{-H_2O} CH_2{=}\underset{NH_2}{C}HCOOH \xrightarrow[-NH_3]{+H_2O} CH_3\overset{O}{\overset{\|}{C}}COOH$$

Free dehydroalanine is apparently converted to pyruvate too rapidly for nucleophiles to add, but in peptide form it is probably stable enough to add H_2S and HCN to give cysteine and the semi-nitrile of aspartic acid. Sulfur nucleophiles are known to add rapidly to N-acetyl dehydroalanine ethyl ester (Snow et al. 1976). In addition serine is converted to alanine and threonine to α-amino-n-butyric acid in proteins dissolved in the ocean (Bada and Hoopes 1979). The mechanism which involves a reduction or transamination is not clear.



These reactions account for five of the twenty amino acids in proteins. Many different aldehydes and ketones could add to glycine to produce in a few steps the desired amino acids (e.g., acetone for valine and benzaldehyde for phenylalanine), but the source of these aldehydes in a CO or CO_2 atmosphere is not apparent. It is possible that amino acids produced from CO or CO_2 in low abundance (e.g., valine) were selectively concentrated and made available for peptide synthesis. Such concentration mechanisms have not been demonstrated, and in any case would not be needed for the amino acids produced in a CH_4 atmosphere.

One can of course write out many schemes to synthesize any amino acid needed, but such speculations are not useful without direct experimental support. Analogs with known organic reactions are usually invalid when tried in the context of prebiotic conditions. It is to be noted that bacteria exist which make all 20 amino acids as well as the other necessary biochemical metabolites from almost any organic compound. However, this is done by an extended series of enzyme catalysed reactions, and most of these reactions are not prebiotic.

Since we do not know which amino acids were used by the most primitive organisms, we cannot say that glycine and the amino acids formed from it in the primitive ocean were insufficient. Thus CO and CO_2 atmospheres cannot be excluded on the basis of inadequate amino acid yield and variety as long as sufficient H_2 is present. However, a methane atmosphere is much more favorable for the types and yield of amino acids.

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