THE MECHANISM OF SYNTHESIS OF AMINO ACIDS BY ELECTRIC DISCHARGES*

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The action of electric discharge on a mixture of methane, ammonia, water, and hydrogen was shown to give a significant yield of amino, hydroxy, and aliphatic acids[1,2]. This mixture of gases has been proposed by OPARIN[3] and by UREY[4] as the composition of the earth's atmosphere in its early stages of formation. Two alternative mechanisms were proposed for the synthesis of the amino and hydroxy acids. The first hypothesis was that they are formed by hydrolysis of the corresponding nitriles, and the second hypothesis was that the synthesis takes place directly in the electric discharge. Hydrogen cyanide and aldehydes, which were shown to be direct products of the spark discharge, would react to form amino and hydroxynitriles (Strecker synthesis), and so the principal uncertainty of the correctness of the first hypothesis is whether the boiling ammonium hydroxide can hydrolyze the nitriles to the corresponding acid. It was also important to see if there was sufficient hydrogen cyanide and aldehyde produced in the electric discharge to account for the amino acids found at the end of a run.

Since iron is one of the more abundant elements on the earth, an experiment was performed to compare the organic compounds synthesized in the system with and without added iron. Under reducing conditions part of the iron would be metallic and part as ferrous compounds. The solubility of iron in the ocean would be low because of precipitation of the hydroxide or sulfide, etc. However, there might be surface reactions on the precipitates or catalytic reactions with the ferrous compounds, and it was of interest to see if any of the iron would be oxidized to ferric by products of the electric discharge.

The equilibrium constant for the reaction $N_2 + 3H_2 = 2NH_3$ is $7 \cdot 10^5$ atm.$^{-2}$ at 25°, which predicts that the nitrogen in the atmosphere would be ammonia instead of N_2 until the partial pressure of hydrogen fell below about 10^{-2} atm. by escape into outer space. However, the disruptive effects of ultraviolet light and electric discharges might result in a steady state concentration of ammonia less than the equilibrium value. In order to see which organic compounds would be formed under these conditions, a mixture of methane, nitrogen, hydrogen, and water was sparked.

Several compounds described in the last paper[2] were not then identified, and some of these unknown compounds have now been characterized.

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EXPERIMENTAL

Hydrolysis of amino and hydroxynitriles (Run 4a)

Apparatus No. 1[2] was altered by adding stopcocks in the U-tube and on the 500 ml flask, which permitted withdrawal of samples during the course of the run. This apparatus was filled with hydrogen to 30 cm Hg pressure followed by 4.5 ml of 28% ammonia (corresponding to 25 cm pressure of ammonia), 20 mmoles hydrogen cyanide, 6.1 mmoles formaldehyde, 3.64 mmoles acetaldehyde, and 1.16 mmoles propionaldehyde dissolved in 325 ml water. After boiling for a week the products were analyzed as described previously[2].

Table I shows the yields of compounds from Run 4a. This experiment shows that amino and hydroxynitriles can be hydrolyzed by dilute ammonium hydroxide at 80–100°. The compounds in the table account for 52, 58 and 36 % of the formaldehyde, acetaldehyde and propionaldehyde, respectively. Acetic and propionic acids could not be detected, but formic acid was formed, probably from hydrolysis of the hydrogen cyanide. The aldehydes not accounted for probably formed aldol condensation products.

TABLE I

YIELDS FROM RUN 4a

Acid	*Moles × 10^6*	*Yield %**
Glycine	98	16
Alanine	129	35
α-Aminobutyric	27	23
Glycolic	72	12
Lactic	42	12
α-Hydroxybutyric	15	13
Iminodiacetic	56	18
Imino-acetic-propionic	45	

* The yields are based on the aldehyde added to the apparatus.

Rate of hydrolysis of the aminonitriles (Run 4b)

The previous experiment was repeated using formaldehyde, acetaldehyde, propionaldehyde, *n*-butyraldehyde, *iso*butyraldehyde, and acetone as carbonyls. The cyanide in the U-tube was titrated with $AgNO_3$[5], and samples were withdrawn from the 500 ml flask at various times. From the rate of decrease of the hydrogen cyanide concentration in the U-tube, the rate constant for hydrolysis of hydrogen cyanide (to formic acid) in the system is calculated to be 0.1 h^{-1}. This refers to the rate of hydrolysis in the 500 ml flask at about 90°. The rate of hydrolysis in the apparatus as a whole is 1/2 this figure since only about 1/2 the total hydrogen cyanide was in the 500 ml flask. The amino acid concentrations in the 500 ml flask fractions were estimated by colorimetric ninhydrin analyses[6] after removing the ammonia and checked by quantitative paper chromatography[7]. The rate constant for hydrolysis of the aminonitrile in the 500 ml flask is calculated to be 0.2 h^{-1} from these data.

The amino acid amides

The first step in the hydrolysis of the aminonitrile would be to the amino acid amide. The acids and amino acids of Run 4b were separated from the amides by retention of the former on Dowex-2(OH^-)[8]. The effluent containing the amides was evaporated to dryness, hydrolyzed in 6 *M* HCl (105°, 14 hours), and chromatographed on Dowex-50(H^+)[9]. With the exception of small amounts of valine and norvaline, no amino acids were found in the hydrolysate, indicating that amino acid amides were essentially absent from the apparatus at the end of the run. Paper chromatography of the sample from the 500 ml flask withdrawn after 3 hours of boiling showed no amino acid amides to be present. It is concluded that under the conditions of this experiment the hydrolysis of the amino acid amide is rapid compared to the hydrolysis of the aminonitrile to the amide.

The amino acids from Run 4b were chromatographed on Dowex-50(H^+). The α-amino*iso*butyric acid peak coincides with the alanine peak, but chromatography of this peak on paper separated the compounds. The α-amino*iso*butyric acid spot could barely be detected. It is estimated that less than 0.2 % of the acetone was recovered as α-amino*iso*butyric acid in contrast to a 28 % recovery of the propionaldehyde as α-amino-*n*-butyric acid.

The primary products of the electric discharge

Samples were withdrawn from the U-tube and from the 500 ml flask at various intervals while sparking a mixture of 5 cm Hg pressure hydrogen, 25 cm methane, 25 cm ammonia, and water. The ammonia was titrated to a methyl red endpoint, and the cyanide was estimated by the Liebig method[5]. After removal of the hydrogen cyanide, the aldehydes and ketones were estimated colorimetrically as their 2,4-dinitrophenylhydrazones in methanolic potassium hydroxide[10]. Formaldehyde and acetaldehyde were detected qualitatively with chromotropic acid and *p*-hydroxydiphenyl, respectively[11]. The amino acid concentration was estimated by quantitative paper chromatography[7].

The effect of adding ferrous ammonium sulfate (Run 5)

Apparatus No. 1 was filled with hydrogen, methane, and ammonia to partial pressures of 5, 21 and 20 cm Hg, respectively, followed by 1.5 g of ferrous ammonium sulfate dissolved in 350 ml oxygen-free water. Most of the iron precipitated as the hydroxide, and very little ferrocyanide or ferricyanide was formed since the solution turned only slightly blue. After sparking for a week, samples were withdrawn from the apparatus under conditions that excluded oxygen, and the ferric was read as the thiocyanate at 480 mμ. The total iron in the same sample was estimated after oxidation to ferric. The iron in the apparatus was 16 mole % ferric. The oxidizing agent is not known, but hydrogen peroxide which might be formed in low yield in the discharge is one reasonable possibility. The results of the analysis of the organic compounds are shown in Table II.

Sparking a mixture of methane, nitrogen, water, and hydrogen (Run 6)

The initial pressures of methane, nitrogen, and hydrogen were 20, 14, and 14 cm of Hg, respectively. After sparking for 60 hours the concentration of both ammonia and hydrogen cyanide in the U-tube was about 10^{-2} *M* while the aldehydes were 10^{-3} *M*. After 11 days of sparking the mixture of compounds was analyzed; the yields are shown in Table II.

Polymer

The production of the yellow polymer (tars) varied in the different runs, and seemed to depend on the electrode spacing, exact nature of the spark, etc. At times most of the tars were formed on the electrodes and dissolved in the water that condensed on the electrodes.

A considerable fraction of the tars and most of the amino acids were dialyzed (against distilled water) after 24 hours. Continued dialysis for 48 hours resulted in further tars in the dialysate. The non-dialyzed fraction contained some colloidal silica and a significant fraction of the tars. Hydrolysis of this fraction (6 *M* HCl, 105°, 24 h) followed by paper chromatography showed only a small amount of amino acids present. Whether this small amount of amino acids was "conjugated" as peptides could not be determined. Treatment of a fraction of the run with trichloroacetic acid gave a substantial precipitate. While this is often taken as a test for proteins it is probable that any high molecular weight compound with charged groups would also be precipitated.

Absence of purines and pyrimidines

The mixture of compounds from a run similar to Run 1[2] was evaporated to dryness, and the whole sample was chromatographed on a column of Dowex-50(H^+)[12]. The eluent showed no 260 mμ absorption maximum where the naturally occurring purines and pyrimidines would come, and paper chromatography of the evaporated fractions showed no spots with an ultraviolet lamp. It is concluded that the amount present of any purine was less than $0.2 \cdot 10^{-5}$ moles and of any pyrimidine was less than $0.1 \cdot 10^{-5}$ moles.

Identification of further organic compounds

The yield of some of the compounds was not sufficient to prepare derivatives, and the identifications based only on R_F values cannot be considered definite. The letters in parenthesis refer to the unknown or tentatively identified compounds of ref.[2]. The figures in parenthesis refer to the R_F values with phenol, butanol-acetic acid, and on Dowex-50(H^+) relative to glycine, respectively.

Iminodiacetic acid (C). Iminodiacetic acid was prepared by hydrolysis of nitrilotriacetic acid[13] at 150°. Compound C (0.32, 0.10, 0.59); Iminodiacetic acid (0.33, 0.10, 0.59). The phenylhydantoin of this amino acid melted at 206.0–207.0°, and a mixed melting point with an authentic sample of 3-phenylhydantoin-1-acetic acid, m.p. 206.0–207.0°, was not depressed.

a,a-Imino-acetic-propionic acid (H). This compound was prepared from chloroacetic acid and DL-alanine[14]. Compound H (0.46,0.46, 0.14, 0.61); Imino-acetic-propionic acid (0.47, 0.13, 0.61).

Aspartic acid (A). The aspartic and iminodiacetic acid peaks coincide when chromatographed on Dowex-50(H^+), but chromatography on Dowex-50 in the sodium form[15] separated the two acids, giving the same R_F values as the knowns. Compound A (0.17, 0.18, 0.59); Aspartic acid (0.18, 0.18, 0.59).

Glutamic acid (D). Compound D was thought not to be glutamic acid because it was not held by a weakly basic ion-exchange column[2]. However, further work indicated that this resin did not retain all of the glutamic acid. Compound D (0.32, 0.27, 0.70); Glutamic acid (0.30, 0.27, 0.70).

N-Methylalanine (B_1). DL-N-Methylalanine was prepared from methylamine and DL-α-bromopropionic acid[16]. Compound B_1 (0.90, 0.28, 1.29); N-Methylalanine (0.89, 0.28, 1.27). The phenylhydantoin of Compound B_1 melted at 144.0–145.0°, and a mixed melting point with an authentic sample of DL-3-phenyl-1,5-dimethylhydantoin, m.p. 144.0–145.0°, was not depressed.

Urea and N-methylurea. The weakly basic fractions were examined for urea by paper chromatography[17], and two spots were detected with Ehrlich's reagent. The first gave R_F values of urea (0.77, 0.53), and the second of methylurea (0.90, 0.70). Chromatography of the whole fraction on paper, elution from the paper, sublimation, and recrystallization gave a compound melting at 131.0–132.0°. A mixed melting point with an authentic sample of urea, m.p. 131.0–132.5°, was not depressed. Only the R_F values were obtained for methylurea.

α-Hydroxybutyric acid. The tentative identification is based only on the equal R_F values of the unknown and an authentic sample of α-hydroxybutyric acid when chromatographed on silica.

Succinic acid. Because succinic acid is eluted from the silica with butanol-chloroform at the same point as the peak previously identified as lactic acid, this peak was examined for succinic acid by elution from silica with 25% butanol-benzene[18]. Two peaks were present giving the same R_F values as known succinic and lactic acids. The succinic acid isolated from this chromatography melted at 182.5–185.0°, and a mixed melting point with an authentic sample of succinic acid, m.p. 183.0–185.0°, was not depressed. The previous lactic acid value for Run 1 is corrected in Table II for the succinic acid found to be present in the peak.

RESULTS

Fig. 1 shows the concentrations of ammonia, hydrogen cyanide, and aldehydes in the U-tube and amino acids in the 500 ml flask during the sparking of a mixture of methane, ammonia, water and hydrogen. It is seen that the concentration of ammonia decreased steadily during the run. Some of this decrease is due to formation of amino compounds, but most of the decrease is probably due to decomposition of the ammonia to hydrogen and nitrogen in the discharge. The hydrogen cyanide concentration rose to $4 \cdot 10^{-2}\,M$, and after 120 hours apparently little more was synthesized in the spark. Thereafter the hydrogen cyanide present was hydrolyzed to formic acid or decomposed in the spark. The aldehyde concentration rose to about $10^{-3}\,M$ and declined after 120 hours. The concentration of amino acids rose during the run and leveled off after about 140 hours.

Several repetitions of this experiment gave concentrations of these compounds of the same order of magnitude, but the values were not reproducible in detail. Probably the most important variable that could not be controlled was the operation of the spark.

From these data and the rate constants for hydrolysis of the aminonitriles and hydrogen cyanide estimated in Run 4b, it is possible to calculate the yield of amino acids and formic acid from hydrolysis of the nitriles. The aldehyde concentration in the 500 ml flask was 1/2 the concentration in the U-tube, and 1/2 the aldehyde in the 500 ml flask is assumed to be as aminonitrile since the amino acids and hydroxy acids were formed in about equal amounts. This gives an average concentration of aminonitrile of $2.5 \cdot 10^{-4}\,M$. The length of the run in which most of the amino acids were synthesized was about 120 hours. The concentration of amino acids is given by $\int_0^t k(\text{aminonitrile})dt = 5.8 \cdot 10^{-3}\,M$ or 1.4 mmoles in the 250 ml of solution in the 500 ml flask. The production of formic acid by hydrolysis of hydrogen cyanide is calculated to be 3.6 mmoles using the rate constant for hydrolysis of 0.1 h^{-1} and an average concentration of hydrogen cyanide in the 500 ml flask of $3 \cdot 10^{-3}\,M$ (the hydrogen cyanide was concentrated in the U-tube by a factor of about 10 over the 500 ml flask). These values agree within the experimental error with the observed yields of 1.2 mmoles of amino acids and 2.4 mmoles of formic acid. Thus in the case of the spark discharge the rates of hydrolysis under the conditions of the experiment are sufficient to account for the total yields of amino acids and formic acid observed.

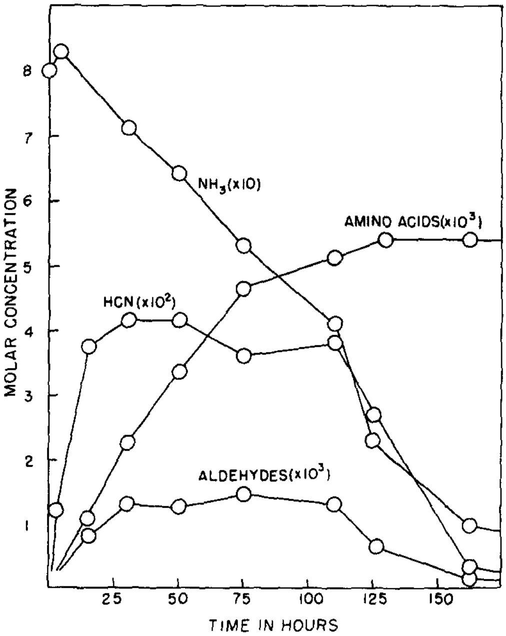

Fig. 1. Concentrations of ammonia, hydrogen cyanide, and aldehydes in the U-tube, and amino acids in the 500 ml flask while sparking a mixture of methane, ammonia, water, and hydrogen.

A similar experiment with the silent discharge (Fig. 3 of ref.[2]) gave concentrations of aldehydes in the same range as with the spark, but the hydrogen cyanide could not be detected with the Liebig titration, and only a weakly positive Prussian Blue test was obtained. The concentration of hydrogen cyanide was therefore only about $10^{-5}\,M$. In the case of the silent discharge the hydrogen cyanide concentration would seem to be too low by a factor of 10 to account for the amount of amino acids and formic acid observed.

The yields of organic compounds for the various runs are shown in Table II. Runs 1 and 3 are the spark and silent discharge, respectively, of the previous paper[2]. Not included in the table is the α-amino*iso*butyric acid estimate for Run 1 of $0.5 \cdot 10^{-5}$ moles. The error is about 10% for entries greater than $20 \cdot 10^{-5}$ moles, while the error may be a factor of two for those less than $2 \cdot 10^{-5}$ moles. The dashes indicate that the compound was present in less than $0.5 \cdot 10^{-5}$ moles. The % yields based on the carbon placed in the system as methane is given in parenthesis for glycine only, and the total yield of the compounds in the table is given in the last entry.

It is seen that the yields from Run 5 differ only slightly from Run 1, and repetition of Run 1 gave similar differences. It is clear then that the addition of ferrous ammonium sulfate gave no marked catalytic effects either in synthesis or in decomposition of the organic compounds.

TABLE II

YIELDS OF COMPOUNDS (MOLES × 10^5)

	Spark *Run 1*	*Silent* *Run 3*	*Fe Run* *Run 5*	*N_2 Run* *Run 6*
Glycine	63 (2.1)	80 (0.46)	65 (2.1)	14.2 (0.48)
Alanine	34	9	10.8	1.0
Sarcosine	5	86	8.8	1.5
β-Alanine	15	4	12.5	7.0
α-Aminobutyric acid	5	1	2.9	—
N-Methylalanine (B_1)	1	12.5	1	—
Aspartic acid (A)	0.4	0.2	0.8	0.3
Glutamic acid (D)	0.6	0.5	0.6	0.5
Iminodiacetic acid (C)	5.5	0.3	11.6	3.9
Imino-acetic-propionic acid (H)	1.5	—	1.6	—
Formic acid	233	149	266	135
Acetic acid	15.2	135	33	41
Propionic acid	12.6	19	22	22
Glycolic acid	56	28	52	32
Lactic acid	31	4.3	10.6	1.5
α-Hydroxybutyric acid	5	1	—	—
Succinic acid	3.8	—	3.8	2
Urea	2	—	4	2
Methylurea	1.5	—	1	0.5
Sum of yields of compounds listed	15%	3%	15%	8%

The synthesis of organic compounds in Run 6 is about 1/3 of Run 1. The lower yield is probably due to the slower hydrolysis of the various nitriles under the less basic conditions than in Run 1. It is clear, however, that amino acids can be synthesized under reducing conditions even if no ammonia is initially present.

THE RATIOS OF PRODUCTS

Further evidence that the synthesis of the amino and hydroxy acids is through the nitrile can be obtained by considering the ratios of products predicted by this mechanism. It was shown previously[2] that if the reaction of the aldehyde, hydrogen cyanide, and ammonia to form the amino and hydroxynitriles is a rapid and reversible equilibrium and if the hydrolysis is a first order irreversible reaction, the ratio of hydroxy acid to amino acid at the end of the run will be

$$R_1 = h_i H_i / k_i K_i (\mathrm{NH_3}).$$

Similarly the ratio of the N-methylamino acid to the amino acid will be

$$R_2 = m_i M_i (\mathrm{CH_3NH_2}) / k_i K_i (\mathrm{NH_3})$$

where H_i, K_i, and M_i are the respective equilibrium constants for the formation of the hydroxy, amino, and methylaminonitrile, and h_i, k_i, and m_i are the respective rates of hydrolysis.

β-Alanine cannot arise from a Strecker synthesis as can the α-amino acids. A reasonable mechanism would be from a Michael addition of ammonia to acrylonitrile, acrylamide, or acrylic acid as proposed previously[2]. One would expect that hydrogen cyanide[19, 20] and methylamine[21] would also add to give, after hydrolysis, succinic acid and N-methyl-β-alanine. N-Methyl-β-alanine was not detected during the analysis

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since it does not react with ninhydrin. The rate of formation of the nitrile of β-alanine and succinonitrile would be $k_{\mathrm{NH_3}}(\mathrm{NH_3})(\mathrm{CH_2{=}CHCN})$ and $k_{\mathrm{HCN}}(\mathrm{CN^-})(\mathrm{CH_2{=}CHCN})$, respectively, where the k's are the rate constants for addition. Assuming that the addition is irreversible and that the nitriles are hydrolyzed by the end of the run, then the ratio of succinic acid to β-alanine will be

$$R_3 = k_{\mathrm{HCN}}(\mathrm{CN^-})/k_{\mathrm{NH_3}}(\mathrm{NH_3}).$$

This treatment is easily generalized to include the additions to acryloamide and acrylic acid. Table III gives the ratios of products for the different runs.

TABLE III

RATIOS OF PRODUCTS

	Spark Run 1	*Silent Run 3*	*Fe Run Run 5*	*N_2 Run Run 6*	*Aldehydes HCN, NH_3 Run 4a*
$\frac{\text{Glycolic}}{\text{Glycine}}$	0.89	0.35	0.80	2.3	0.73
$\frac{\text{Lactic}}{\text{Alanine}}$	0.91	0.48	0.98	1.5	0.33
$\frac{\text{Hydroxybutyric}}{\text{Aminobutyric}}$	1	1	—	—	0.55
$\frac{\text{Sarcosine}}{\text{Glycine}}$	0.08	1.07	0.14	0.11	—
$\frac{\text{Methylalanine}}{\text{Alanine}}$	0.03	1.4	0.09	—	—
$\frac{\text{Succinic}}{\beta\text{-Alanine}}$	0.25	—	0.30	0.29	—
$\frac{\text{Iminodiacetic}}{\text{Glycine}}$	0.09	0.004	0.18	0.27	0.57
$\frac{\text{Imino-acetic-propionic}}{\text{Alanine}}$	0.04	—	0.15	—	0.47

If the ratio hH/kK does not depend on the aldehyde, then equation 1 predicts that R_1 should be the same for the different aldehydes in a given run. Excellent agreement of these ratios is found for the spark discharges (Runs 1 and 5). The agreement is good for the silent discharge except for the hydroxybutyric/aminobutyric ratio, but this ratio is uncertain by a factor of two. In Run 4 the hydrolysis of the amino and hydroxynitriles was necessarily the mechanism for synthesis of the respective acids. There is less agreement of the ratios than with the electric discharges, but the agreement is within the errors of the experiment.

The low yield of α-amino*iso*butyric acid in Runs 1 and 4b is probably due to the instability of the aminonitrile. Hydroxynitriles of ketones are less stable than the hydroxynitriles of aldehydes[22]. Thus the equilibrium constant for the formation of α-hydroxy*iso*butyronitrile from acetone and hydrogen cyanide is only 33, while the constant for the formation of α-amino-*n*-butyronitrile is 1040. While these data are for hydroxynitriles, it can be expected that the aminonitriles formed from ketones would be similarly unstable. Therefore, the acetone would tend to undergo various condensation reactions rather than a Strecker synthesis.

Assuming that mM/kK does not depend on the aldehyde, then R_2 should be the same for a given run, and the data confirm this conclusion. The ratio succinic acid/β-alanine should be proportional to $(CN^-)/(NH_3)$, and R_2 is constant for the three runs reported.

It can be shown that if the concentrations of aldehydes and hydrogen cyanide do not change during the run, then the iminodiacetic/glycine ratio should vary as the product $(HCN)(H_2CO)$. The order of magnitude of this product for Runs 1, 3, 5, 6 and 4 was 10^{-5}, 10^{-8}, 10^{-5} and 10^{-4}, respectively, so the agreement is qualitatively correct. The imino-acetic-propionic/alanine ratio should also vary as $(HCN)(H_2CO)$, and this ratio is the same as the iminodiacetic/glycine ratio for Runs 1, 4a and 5.

The ratios of the various products are in qualitative agreement in all cases and in quantitative agreement (within the experimental error) in most of the cases. The similarity of products in Runs 1 and 4a is striking (except for the expected absence of β-alanine and succinic acid since no acrylonitrile was added), suggesting that the products were formed by the same mechanism. Since the amount of aldehydes and hydrogen cyanide is sufficient to account for the observed yield of amino acids, there can be little doubt that most of the amino and hydroxy acids were formed from the corresponding nitrile. However, these experiments do not exclude the possibility that a small percentage of the amino acids was formed directly in the spark.

While the low yield of hydrogen cyanide would appear to favor some alternative mechanism for the synthesis of the amino acids in the silent discharge apparatus, the similarity of the products and the agreement of the ratios of the products between Runs 1 and 3 would still favor a common mechanism in these two runs. It is possible that some catalyst, perhaps hydrogen peroxide, is aiding in the hydrolysis of the nitriles in the silent discharge case.

The synthesis of the products expected from acrylonitrile (or the amide or acid) and the agreement of the ratios of these products in the different runs provides strong indirect evidence for the synthesis of β-alanine and succinic acid by β-addition, and, in turn, that acrylonitrile or derivatives were synthesized in the electric discharges. It is possible that the acetic and propionic acids could be formed by hydrolysis of the corresponding nitrile and amide. The rate of hydrolysis of acetonitrile is several times faster than hydrogen cyanide in NaOH[23], and nitriles have been synthesized in electric discharges[24]. In analogy with the simpler amino acids, one might expect that the aspartic and glutamic acids were synthesized by a Strecker synthesis from α-cyanoacetaldehyde and β-cyanopropionaldehyde (or the amides or acids). There is no experimental evidence for these aldehydes, but they might be synthesized along with the acrylonitrile in the electric discharge. If cyanate were formed in the electric discharge, then both urea and methylurea would be expected by reaction with ammonia and methylamine (Wöhler synthesis). The direct synthesis of these simple ureas in the electric discharge is also quite reasonable.

DISCUSSION

These experiments indicate that the synthesis of amino acids from methane, ammonia, and water does not require a special set of conditions, but that any process or combination of processes that yielded both aldehydes and hydrogen cyanide would have contributed to the amount of α-amino acids in the oceans of the primitive earth. Electric discharges therefore are not critical for the synthesis of amino acids, and the same results could be expected from ultraviolet light.

Infrared radiation by the polyatomic molecules of the reducing atmosphere would result in a cool atmosphere and ocean rather than the boiling temperatures used in these experiments. However, there might be local areas of high temperature such as volcanos where pyrolytic reactions could take place. Pyrolytic synthesis of hydrogen cyanide has been accomplished under a variety of conditions[25], and aldehydes might be synthesized from hydrocarbons and carbon monoxide by reactions analogous to the Fischer-Tropsch process or the hydroformalation reaction[26].

Hydrolysis of the various nitriles would take place under cool conditions, but more slowly than in these experiments. A quantitative treatment of this problem will not be given here because the values of K, k, and h are not known. The problem is further complicated by catalytic hydrolyses, *e.g.* by hydrogen sulfide.

If the Strecker synthesis was the principal synthesis of amino acids on the primitive earth, then ammonia must have been present in the ocean even though N_2 could be the principal nitrogen species in the atmosphere. This implies that the earth must have been rather reducing, at least 10^{-3} atmospheres of hydrogen, unless one is to assume that the amino acids were formed in limited areas containing reducing conditions.

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SUMMARY

The mechanism of the electric discharge synthesis of amino and hydroxy acids from CH_4, NH_3, H_2O, and H_2 was investigated. Hydrogen cyanide and aldehydes, which are produced in good yield by the spark discharge, react to form amino and hydroxynitriles (Strecker synthesis). The rate of hydrolysis of the aminonitriles formed from the products of the spark discharge is sufficient to account for the total yield of amino acids after a week's sparking. The β-alanine and succinic acid were probably synthesized by addition of ammonia and hydrogen cyanide to acrylonitrile and hydrolysis to the acids. The ratios of products such as hydroxy acid/amino acid and succinic acid/β-alanine can be predicted by considering the equilibria and rates involved, and the agreement of the experimental ratios with the predictions offers further evidence for these mechanisms. The addition of ferrous ammonium sulfate to the spark discharge apparatus did not alter significantly the yields of products, indicating that neither iron nor sulfate produced catalytic syntheses or decompositions. Sparking a mixture of CH_4, H_2O, H_2, and N_2 (instead of NH_3) gave the same products but in lower yield. In addition to the products previously identified, N-methylalanine, iminodiacetic acid, succinic acid, and urea were definitely identified. α,α′-Imino-acetic-propionic, α-hydroxybutyric, aspartic, and glutamic acids, and methylurea were identified by chromatographic R_F values. No purines or pyrimidines could be detected. Some aspects of the synthesis of organic compounds on the primitive Earth are discussed on the basis of these experimental results.

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THE PROPERTIES OF HEMERYTHRIN

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INTRODUCTION

Hemerythrin is the name given by KRUKENBERG[1] to a pigment of the cells of the coelomic fluid of sipunculids and certain other animals. It was originally discovered by DELLE CHIAIE[2] who, working with *Sipunculus nudus*, also found a connection between colour change and oxygenation. However DELLE CHIAIE thought that the dark-coloured pigment was typical of the "venous" and the clear pigment of the "arterialized" blood, while just the reverse is true. SCHWALBE[3] working on *Phascolosoma elongatum* found that the pigment is contained in cells and becomes "burgundy-red" when exposed to the air, whereas RAY-LANKESTER[4] first succeeded in extracting the pigment by hemolysis. This pigment was found by ANDREWS[5] to be a globulin containing iron, but the iron is not bound in a hematin group (GRIFFITHS[6].) MARRIAN gave[7] the first oxygen dissociation curve of the pigment. Hemerythrin from *Phascolosoma elongatum* was crystallized by FLORKIN[8], who reported a maximal binding capacity of one molecule of oxygen for each three iron atoms. Further physical characterization of the pigment comes from the work of ROCHE[9] and ROCHE AND ROCHE[10]. They found that hemerythrin from *Sipunculus nudus* has an isoelectric point of 5.85. They also reported the spectroscopic properties of the pigment and

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