

SYNTHESIS OF ORGANIC COMPOUNDS BY THE ACTION OF ELECTRIC
DISCHARGES IN SIMULATED PRIMITIVE ATMOSPHERES

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In the study of chemical evolution we are interested in the path by which molecules of biological significance could have been formed on the primitive earth in the absence of life. It is generally accepted that the primitive atmosphere of the earth consisted mainly of methane, ammonia, and water. Various forms of energy such as ultraviolet light from the sun, electrical discharges, heat, and ionizing radiation acting on this atmosphere must have given rise to a wide variety of organic substances.

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Table I gives a summary of the sources of energy on the earth's surface today. (1) It is probable, therefore, that solar energy must have made the principal contribution to the synthesis of organic compounds in primordial times. Next in importance are electric discharges, such as lightning and corona discharges from pointed objects. These occur closer to the earth's surface and, hence, would have more effectively transferred the organic matter synthesized to the primitive oceans. This paper describes attempts to simulate some of the reactions which may have taken place on the prebiotic earth, through the action of electric discharges.

While extensive work has been done on the effect of electric discharges on various organic molecules, relatively few experiments have been performed to elucidate its role in chemical evolution. Some of the earliest such investigations were carried out by the chemist Haber. Beutner, in his book entitled "Life's Beginning on the Earth," recalls how Haber performed numerous experiments in which electrical discharges were sent through carbon containing gases like methane, carbon dioxide, etc., with the aim of obtaining sugars. (2) Although traces of some sugars were formed, a large number of various other substances were also synthesized. Haber thus came to the conclusion that by means of electrical discharges through carbon containing gases, "practically any substance known to organic chemistry can be found."

Perhaps the most celebrated experiment in this field was performed by Stanley Miller in Urey's laboratory in 1953. (3) Miller submitted a mixture of methane, ammonia, and water in the presence of hydrogen to electrical discharges from tesla coils. A large number of organic compounds were formed. Among these, four amino acids were identified. Miller postulated two alternative possibilities for the mechanism of synthesis of amino acids. According to the first, aldehydes and hydrogen cyanide are synthesized in the gas phase by the spark. These aldehydes and hydrogen cyanide react in the aqueous phase to give amino and hydroxynitriles. These nitriles are, in turn, hydrolyzed to amino and hydroxy acids. The mechanism is essentially a Strecker synthesis. A second suggestion made was that the amino and hydroxy acids were synthesized in the gas phase by ions and radicals produced in the electrical discharge. Miller's subsequent work has shown that the first mechanism is the one most likely to have produced the amino acids. (4) The rate of production of aldehydes and hydrogen cyanide by the spark and the rate of hydrolysis of the aminonitriles were sufficient to account for the total yield of amino acids.

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In our experimental work, we have endeavored to study the mechanism by which various molecules of biological interest could have been formed by the action of electrical discharges. A series of experiments was outlined in which the starting materials were varied. Four different classes of experiments have been performed: with methane; with methane and ammonia; with methane, ammonia, and water; and with methane and water.

The effect of a semi-corona discharge, a low intensity arc discharge, and a high intensity arc discharge on gaseous methane was first investigated. The current through the discharge was measured by the voltage drop across a resistor with the cell. For the semi-corona discharge, the cell current was 0.4 m. amp, 0.5 m. amp for the low arc, and 10 m. amp for the high arc discharge. Gas chromatography and mass spectrometry were used for the analysis of the end products. Comparative results of the analysis of hydrocarbons up to C₅ are shown in Table II. In the semi-corona most of the methane remained unreacted after a 24-hour discharge. Some ethane and propane were formed. There were small amounts of ethene, propene, and substituted paraffins. In the case of the low and high arcs, ethylene and acetylene were also present.


The analysis of the hydrocarbons from C₆ - C₉ reveals that the semi-corona gave unsaturated substances while the arc discharge gave rise to aromatic compounds. The semi-corona cell yielded a colorless distillate, the gas chromatogram of which was poorly resolved. The high intensity arc gave a yellow fluid, the chromatogram of which had well spaced peaks. Benzene was the most abundant with toluene next in order of magnitude. The peaks from the semi-corona chromatogram were identified by the use of mass spectrometry as: 2,2-dimethyl butane, 2-methyl pentane, 3-methyl pentane, 2,4-dimethyl hexane, 3,4-dimethyl hexane. In figure 1 the chromatogram of the semi-corona discharge products (low) has been superimposed on that from the high intensity arc (high). The results presented here show that the character of compounds in the range of interest appears to be determined by the type of discharge more than by any factor. (5)

We have also examined the composition of the hydrocarbons above C₉ in the products of the semi-corona discharge. The gas chromatogram is very unresolved (Fig. 2). No normals or branched-chain isoprenoid hydrocarbons were identified. Analysis of the mixture by mass spectrometry shows that the compounds are possibly cyclic in structure. (6)

The effect of an arc discharge on anhydrous methane and ammonia was next investigated for two reasons. Firstly, such a study would help us to understand the pathways by which some organic compounds such as amino acids can be synthesized. Secondly, reactions of this type would simulate, to some extent, conditions which may exist on the planet Jupiter.

In this investigation, we have used reaction vessels of about a liter in volume containing an equimolar mixture anhydrous methane and ammonia up to a pressure of 0.5. The electrodes consisted of gold wires about 1 cm apart. A typical reaction lasted for about 15 hours. The current passing through the system was about 0.5 mA. The end products consisted of: (1) gases, (2) a colorless distillate, and (3) a ruby colored residue.

In the present study, our attention was primarily directed to the colorless distillate. The volatile products were vacuum distilled into a U-trap at -78°C and analyzed by gas chromatography (Fig. 3). The fractions corresponding to each peak were collected for subsequent mass spectrometric analysis. The GLC retention time, the mass spectrometric fragmentation pattern, and the NMR spectrum established the



identity of each of the fractions separated by gas chromatography. Ammonium cyanide, methyl cyanide, ethyl cyanide, α -aminoacetonitrile and its C-methyl and N-methyl homologues were identified. The α -aminonitriles on hydrolysis give rise to α -amino acids. These nitriles may provide a reasonable pathway for the origin of amino acids under prebiological conditions.

In some of our discharge experiments, we turned to the question of the origin of monocarboxylic acids under prebiotic conditions. If we assume that pre-existing abiotically synthesized fatty acids were necessary for the functioning of selective membranes, some mechanism must have existed for their formation. The reaction between methane and ammonia appears to provide such a pathway. When a mixture of methane and water exposed to a semi-corona discharge and the end products examined after saponification, the monocarboxylic acids from C_2 - C_{12} were identified. (7)

The volatile acids C_1 - C_8 were examined as their free acids by gas chromatography. A resulting chromatogram is illustrated in Figure 4. The individual peaks were then trapped and their identity confirmed by mass spectrometry. Acids containing seven or more carbon atoms were analyzed as methyl esters. The methyl esters, after chromatography, were examined by mass spectrometry. Of eleven major peaks obtained by gas chromatography (Fig. 5) only one appears as the normal methyl ester. Presumably, the remaining peaks represented branched-chain isomers.

While it is clear that in the case of the longer chain fatty acids several isomers have been produced, only a few of the innumerable possible compounds are realized. A preferential synthesis of some type appears to be favored. Theoretically, the branching of carbon chains, which is favored in free radical reactions, may be repressed by steric restrictions when the lengthening carbon chains are absorbed on monolayers. An attempt to favor the formation of straight chain acids by placing the aqueous phase in close proximity with the discharge zone did not produce any change in our results.

In the study of prebiotic organic synthesis, perhaps the most relevant experiments involve the use of all the main constituents of the presumed primitive earth atmosphere. We have therefore exposed a mixture of methane, ammonia, and water to a discharge from tesla coils simulating lightning on the primitive earth. At the end of a 24-hour discharge, the gas phase analysis has shown that over 90% of the starting methane has been converted into organic compounds. Of this, about 45% is found in the water fraction. 18% of the water soluble material is in the form of cyanide. The formation of cyanide in this reaction is significant in the light of the multiple role played by hydrogen cyanide in organic synthesis. (8)

The analysis of the end products of this reaction by paper chromatography reveals that a large number of organic compounds were formed but none of these corresponded to the commonly occurring amino acids. A certain amount of material appeared at the origin. However, when the reaction products were hydrolyzed with 6N HCl for 24 hours and then analyzed, a large number of amino acids were formed. (Fig. 6). Among those identified are nine which are commonly found in biological materials: glycine, alanine, aspartic, glutamic, threonine, serine, isoleucine, leucine, and phenylalanine. The results obtained by ion exchange analysis were confirmed by gas chromatography. The evidence, thus, points to the fact that the amino acids were already polymerized in the solution of end products. Separation by the use of a biogel-P column gave us a fraction having a molecular weight in the range 186 to about 2,000 and whose 1-dimethylaminonaphthalene-5 sulphonyl chloride (DNS) derivative showed a single band on electrophoresis. When this fraction was hydrolyzed, the amino acids aspartic, serine, glutamic, glycine, and alanine were obtained.

This result is significant in the context of chemical evolution. It has generally been thought, that amino acids had first to be synthesized and then condensed together into a polymer. The synthesis of a polypeptide in an electric discharge experiment reveals that such a sequence of reactions may not have been necessary. If a suitable condensation agent is present the polymer appears to be formed as soon as the acids are synthesized. In our case, the condensation agent is probably hydrogen cyanide. The presence of 18% hydrogen cyanide in the reaction mixture combined with the fact that in previous experiments we have been able to condense bases and sugars with cyanide support this hypothesis.

The different experiments that have been described so far reveal that important biological molecules can be synthesized by the use of a form of energy which existed on the primitive earth. These conditions may be considered to be genuinely abiotic since the materials used are the constituents of the presumed primitive earth atmosphere, the conditions are aqueous, and the form of energy is one that is likely to have occurred on the earth before the appearance of life.

References

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TABLE I

<u>SOURCE</u>	<u>ENERGY</u> (in cal cm ⁻² yr ⁻¹)
Ultraviolet light (2500 Å)	570
Electric discharges	4
Radio activity	0.8
Volcanoes	0.13

TABLE II

	<u>High Arc</u>	<u>Low Arc</u>	<u>Semi-Corona</u>
Total hours of current flow	1.5	40	48
Electrode voltage	1400	2500	9400
Cell current (m. amp)	4.0	0.5	0.3
% Loss CH ₄ /h	6.6	1.1	0.6
End products (%)			
Ethane	32	20	58.8
Propane	2	5.2	36.8
Ethene	32	2.4	1.5
Propene	--	1.9	0.6
Acetylene	27	42.5	0.0

GAS CHROMATOGRAMS

LOW-INTENSITY CELL VS HIGH-INTENSITY CELL

AEROGRAPH A90-P

12' COLUMN 10% OCTOIL-S ON
60-80 MESH CHROMOSORB-W

COLUMN: 130° INJECTOR: 155°

DETECTOR: 160° He = 40 cc/min

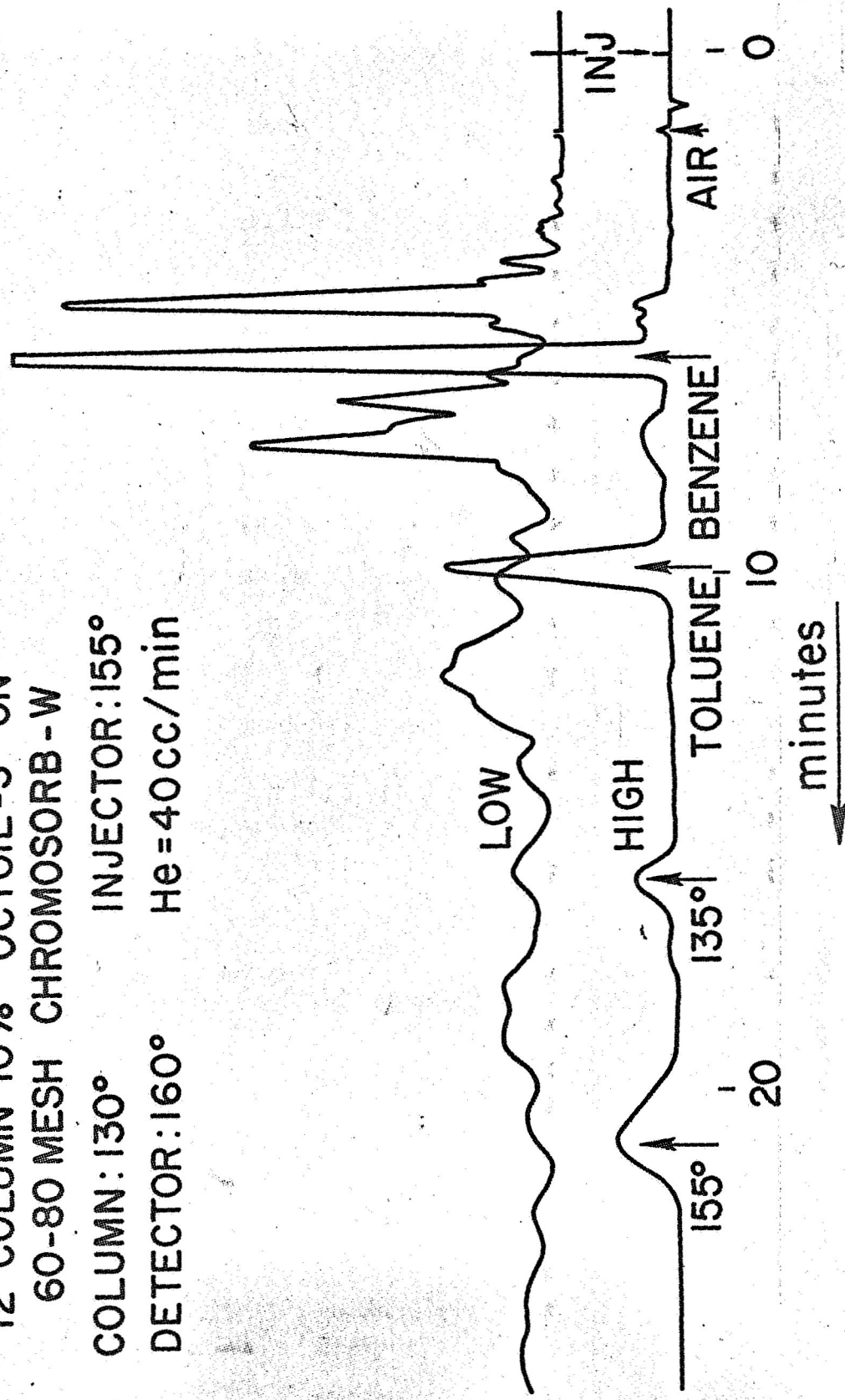


Fig. 1 - Gas chromatograms of semi-corona and arc discharge products C₆ - C₉

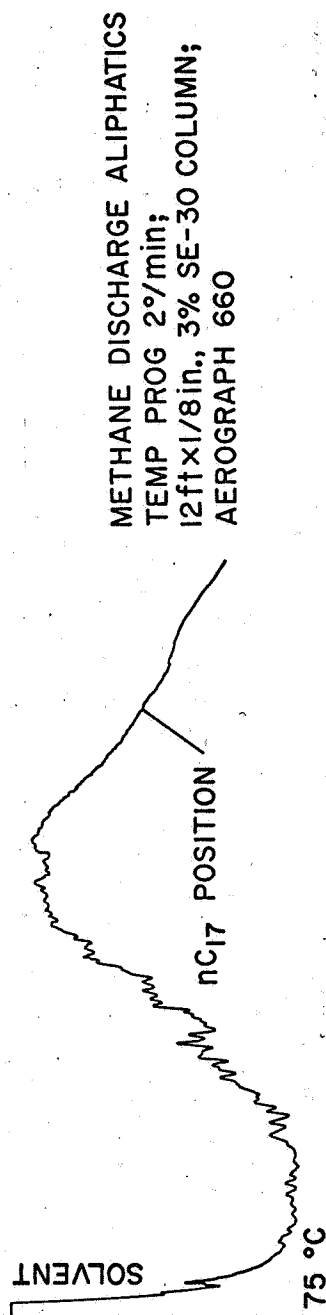


Fig. 2 - Gas chromatogram of semi-corona discharge products above C₉

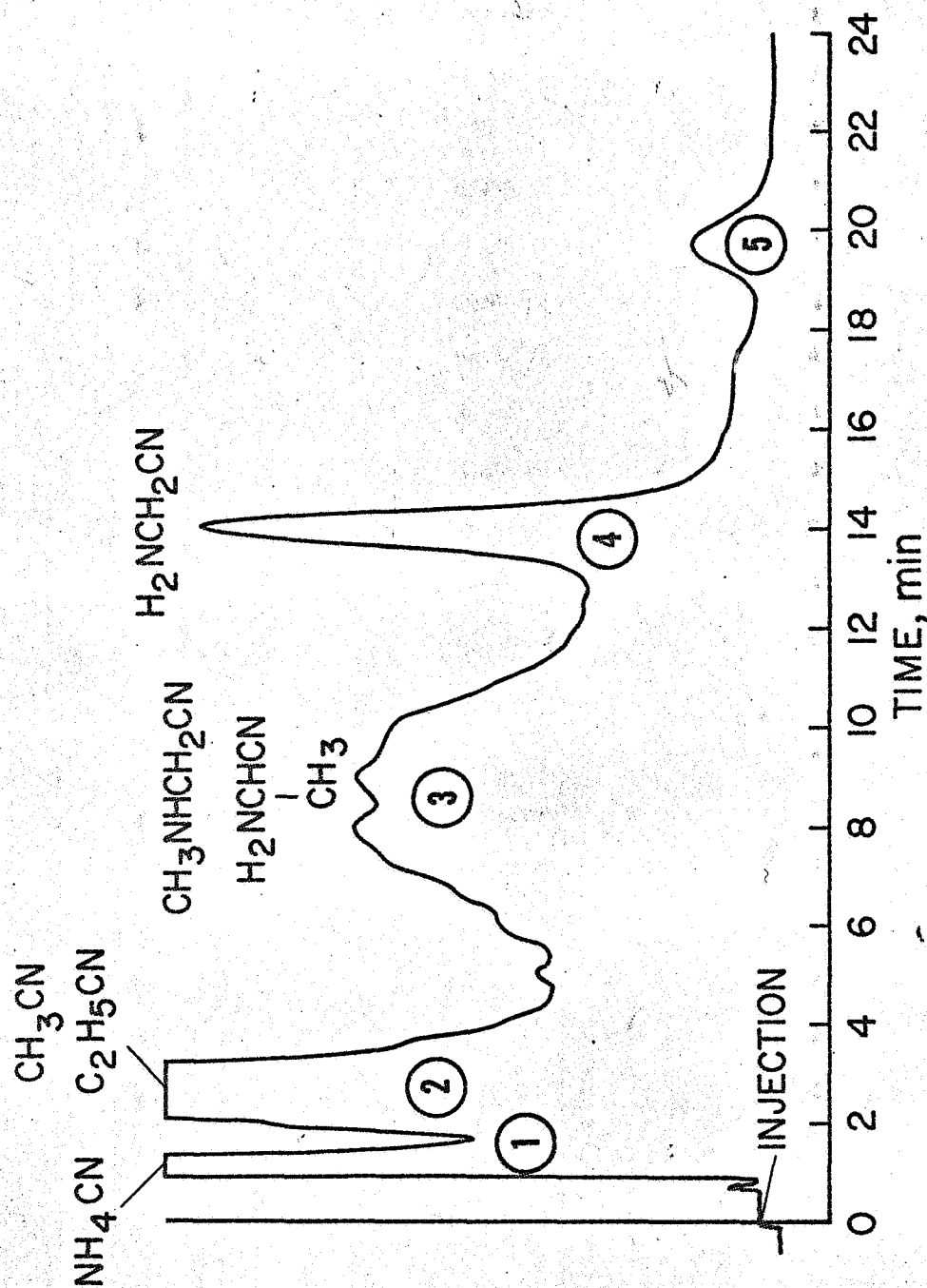


Fig. 3 - Gas chromatogram of colorless distillate from arc discharge through methane and ammonia

VOLATILE FATTY ACIDS

10 ft x 3/16 in; 20% LAC 296 + 2% H₃PO₄
 ON 80/100 MESH CHROMOSORB W; 130°
 ISOTHERMAL; FID; F AND M 609

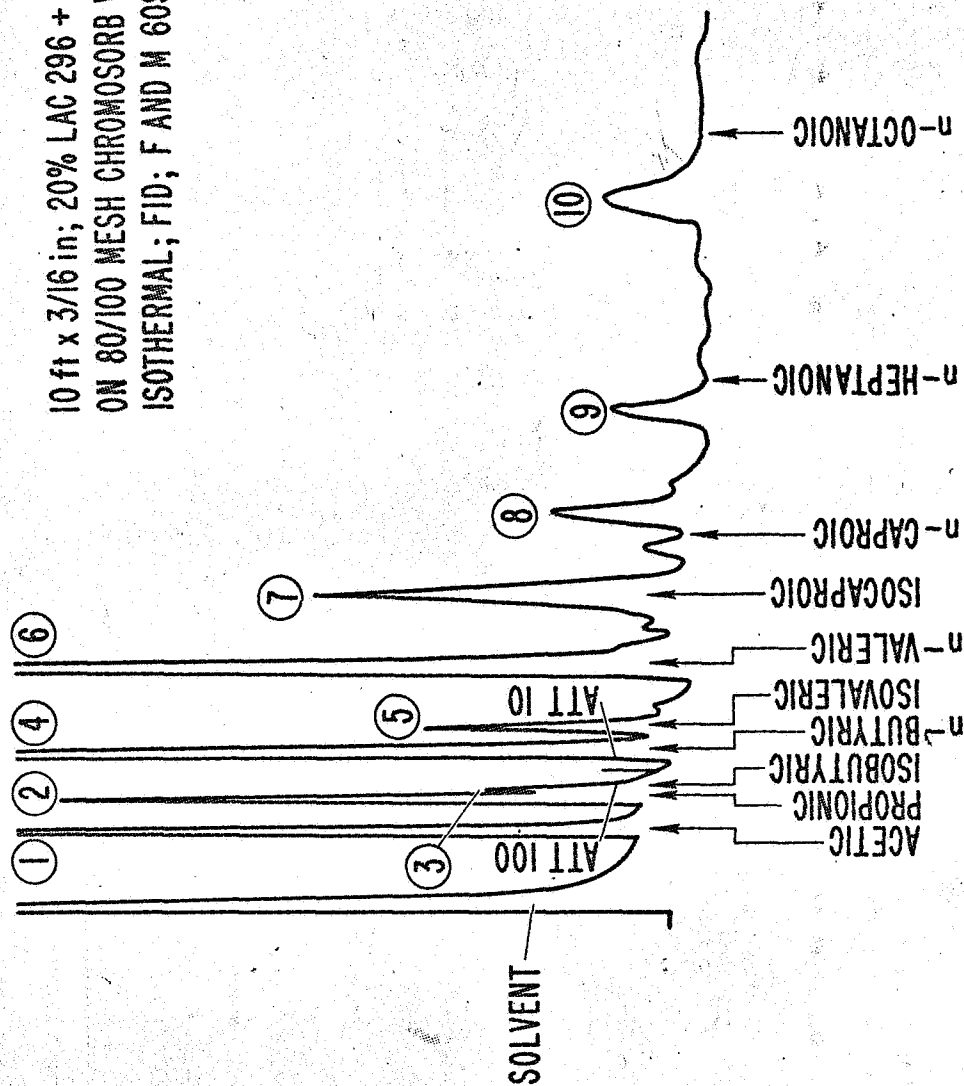


Fig. 4 - Gas chromatogram of volatile fatty acids from a semi-corona discharge through methane and water.

METHYL ESTERS

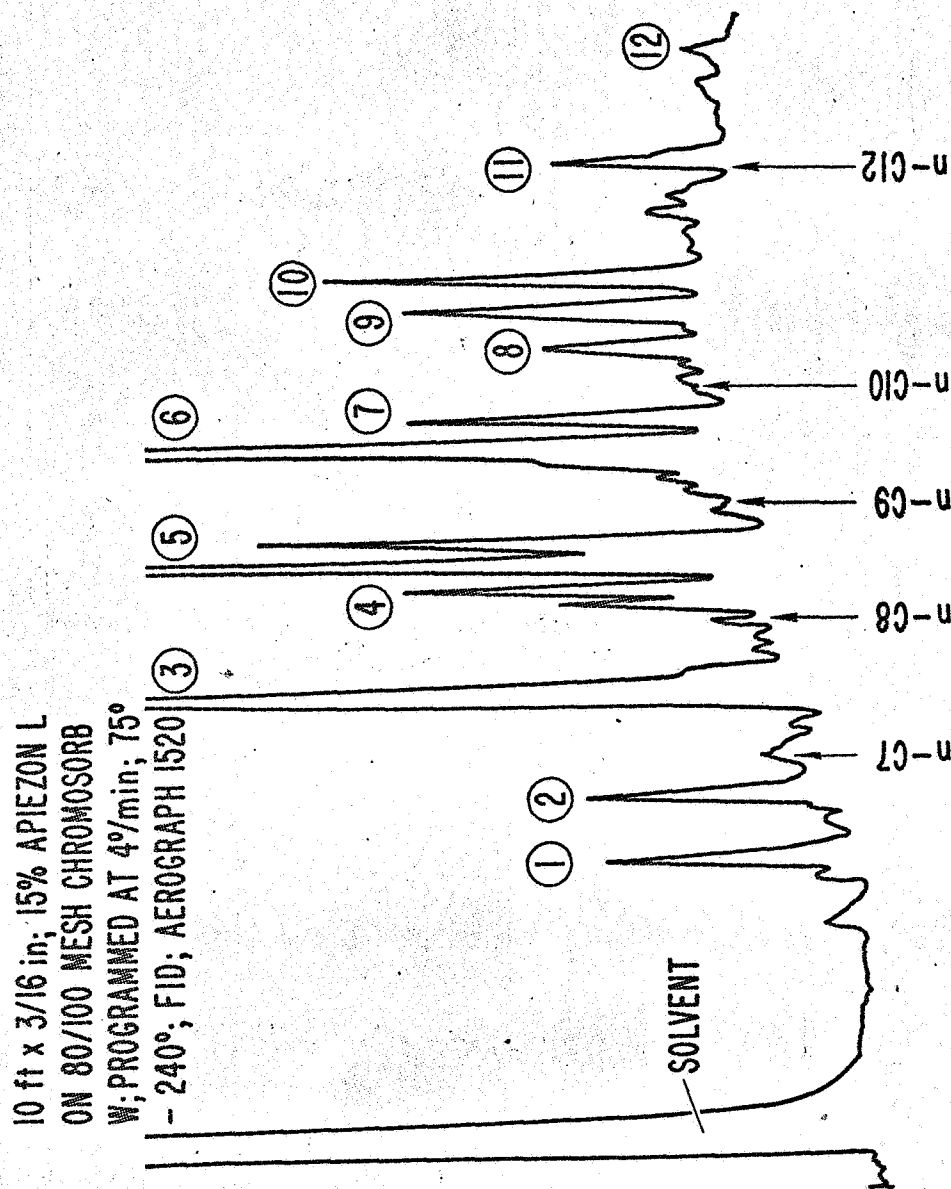


Fig. 5 - Gas chromatogram of methyl esters of higher fatty acids from a semi-corona discharge through methane and water.

AMINO ACIDS FROM A SPARK DISCHARGE ON CH_4 , NH_3 AND H_2O

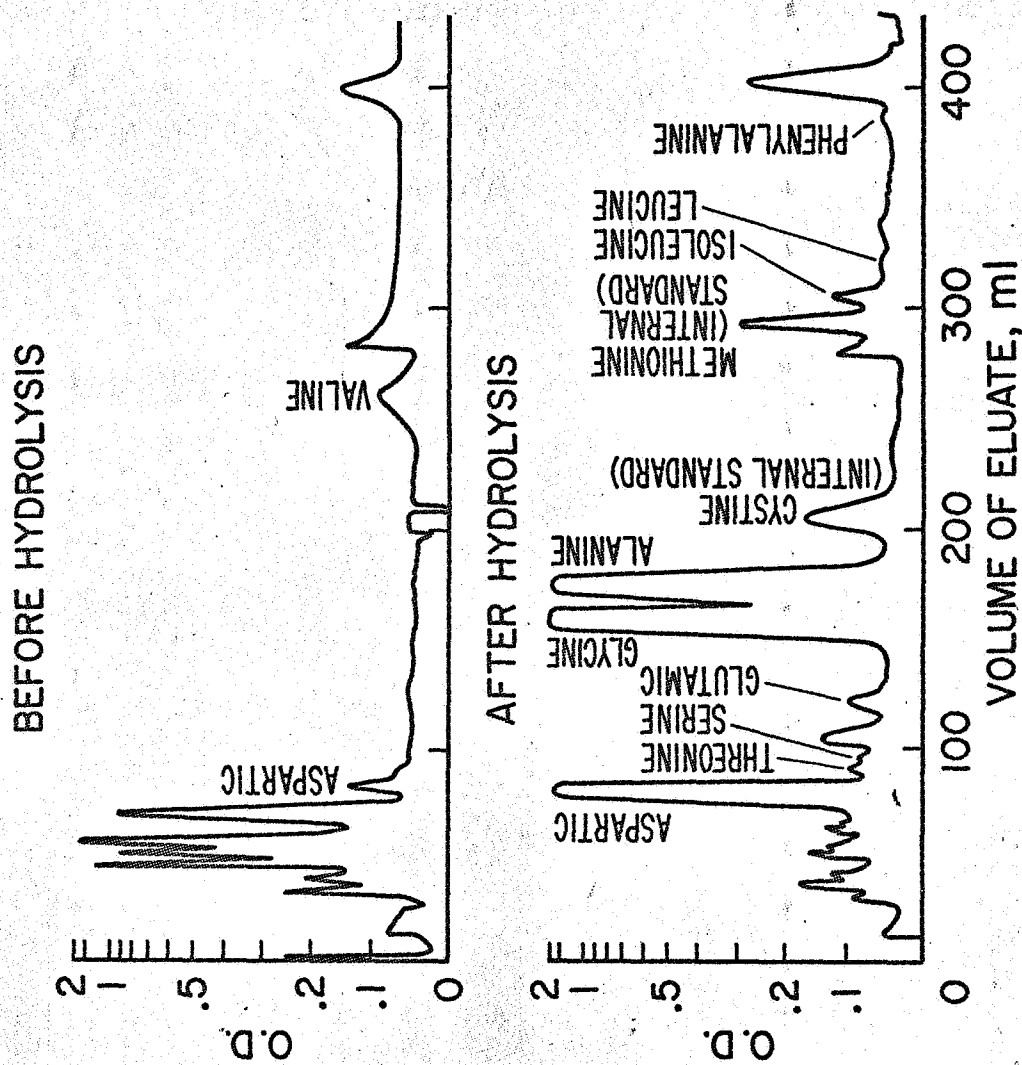


Fig. 6 - Ion exchange separation of amino acids from a spark discharge through methane, ammonia, and water