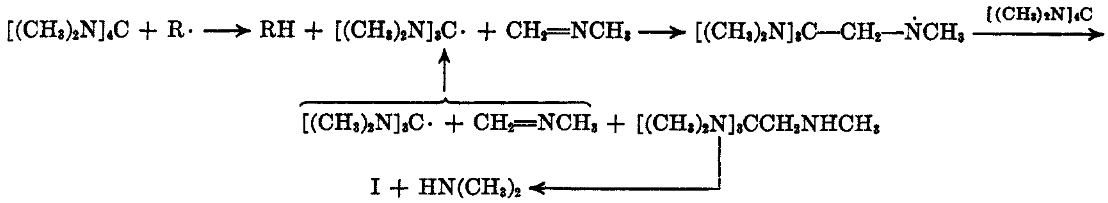
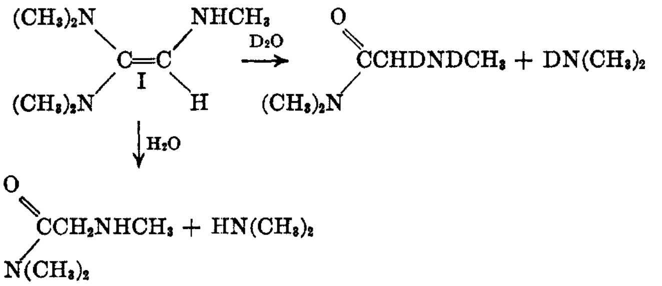
SCHEME I



red spectrum of I is generally consistent with the structure proposed and specifically it exhibits an adsorption at 3500 cm^{-1} for the NH bond.

A powerful chemical confirmation of structure I is obtained on hydrolysis which yields sarcosine dimethylamide[2] and an equivalent of dimethylamine. When the hydrolysis is carried out in D_2O the sarcosine product has a deuterium atom in the α position as expected.



Freshly purified samples of the tetraamine require 15–20 hr at 150° to complete the conversion while samples stored for several months react much more rapidly. This suggests free radical pathways and indeed the addition of a free radical initiator, azobisisobutyronitrile, greatly accelerates the pyrolysis of freshly purified tetraamine. A possible mechanistic scheme is Scheme I.

Experimental Section

Proton nmr spectra were obtained from a Varian Model A-60 spectrometer. Authentic sarcosine dimethylamide was prepared by the method of Waley and Watson.[3]

Pyrolysis of Tetrakis(dimethylamino)methane.—To 5 g of tetrakis(dimethylamino)methane in a 25-ml round-bottom flask was added 0.05 g of azobisisobutyronitrile and the reaction vessel was immersed in an oil bath maintained at 150°. The mixture was kept under a small positive pressure of dry nitrogen throughout the reaction. After 5 hr the reaction mixture was distilled through a small Vigreux column yielding 1.85 g (50%)[4] of tetramethyl(2-methylamino)vinylidenediamine [bp 165–170° (1 atm), $n^{25}D$ 1.4716], which fumes in air.

Anal. Calcd for $C_7H_{17}N_3$: N, 29.4; mol wt, 143. Found: N, 29.3; mol wt, 140 ± 5 (cryoscopy in benzene).

Hydrolysis of Tetramethyl(2-methylamino)vinylidenediamine, I.—To an nmr tube containing 0.1 g of tetramethyl(2-methylamino)vinylidenediamine was added about 1 ml of water. The triamine, at first insoluble, reacts exothermically to give a clear solution of dimethylamine and sarcosine dimethylamide. The nmr spectrum of this solution exhibits singlets at τ 6.57, 7.00, 7.07, and 7.68 in the ratio of 2:3:3:3 [3-(trimethylsilyl)-1-propane sulfonic acid sodium salt internal standard]. The dimethylamine peak appears at τ 7.71 and the above ratio and its relationship to dimethylamine is obtained by nmr spectra made before and after the dimethylamine is removed in a stream of nitrogen. This nmr spectrum of the hydrolysis product was identical with that of authentic sarcosine dimethylamide. When this procedure was carried out using D_2O in place of H_2O the only change in the nmr was the decrease of the τ 6.57 peak. The α-protons of sarcosine dimethylamide do not exchange with D_2O under these conditions.

Registry No.—I, 13958-59-3; tetrakis(dimethylamino)methane, 10524-51-3.

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[2] The sarcosine dimethylamide was not isolated; see Experimental Section.

[3] S. G. Waley and J. Watson, *Proc. Roy. Soc.* (London), **A199**, 499 (1949).

[4] Slightly better yields were obtained when the reaction was carried out in a sealed tube.

Formation of Hydrocarbons in Model Primitive Earth Atmospheres

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While studying the formation of amino acids by electrical discharges in a model primitive earth atmosphere of the Urey[1] type (methane, ammonia, water, and hydrogen), Miller[2] noted incidentally that under certain conditions a considerable quantity of hydrocarbons formed. He did not identify any of them and no one else seems to have followed up this interesting observation.[3]

Electrical discharges in pure methane are well known to produce a horrendous variety of higher hydrocarbons.[4,5] Ponnamperuma and Pering[6] have demonstrated that the hydrocarbon mixture produced by a spark discharge in methane is very similar to the mixture of hydrocarbons present in the ancient Mountsorrel sediment which they therefore suggest is possibly abiogenic in origin. Conceivably such mixtures formed in the *atmosphere* of the primitive earth, although, in the presence of oxygen- and nitrogen-containing gases, the reactive intermediates would tend to be diverted into the synthesis of such end products as amino acids. However, there is at present no necessity for assuming that equilibrium conditions were reached in the primitive earth atmosphere[7] and we thought it would be

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[1] H. C. Urey, "The Planets," Yale University Press, New Haven, Conn., 1952, p 149.

[2] S. L. Miller, *J. Am. Chem. Soc.*, **77**, 2353 (1955).

[3] C. Palm and M. Calvin [*ibid.*, **84**, 2115 (1962)] found ethane, ethylene, and "C_3–C_7 hydrocarbons" in a cursory examination of the gaseous products of electron bombardment of a similar model atmosphere.

[4] For a review, see G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939, p 149.

[5] C. Ponnamperuma and F. Woeller [*Nature*, **203**, 272 (1964)] observed that a change in the type of electrical discharge changed the C_6 to C_9 hydrocarbon products from primarily aliphatic to primarily aromatic.

[6] C. Ponnamperuma and K. Pering, *ibid.*, **209**, 979 (1966).

[7] The amounts of many hydrocarbons, including those found in this work, which would be present in a C–H–N–O system at or near equilibrium at various temperatures and pressures have been computed by R. V. Eck, E. R. Lippincott, M. O. Dayhoff, and Y. T. Pratt, *Science*, **153**, 628 (1966). Whether or not the atmosphere of the prebiological earth ever approached chemical equilibrium is still an open question; A. E. Ringwood [*Geochim. Cosmochim. Acta*, **21**, 295 (1961)] goes so far as to suggest that the surface temperature may have been below 0° 5 billion years ago.

TABLE I

HYDROCARBON FORMATION IN GAS MIXTURES OF METHANE (20 CM), HELIUM (3 CM), AND OTHER COMPONENTS IN 1 HR[a]

			Products, % conversion from methane					
Run	Compn	Temp, °C	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	Total
1	CH_4, He	30	25.0	8.0	8.6	0.62	0.84	43
2	CH_4, He, NH_3[b]	30	6.0	2.0	3.0	0.0	3.9	15
3	CH_4, He, NH_3,[b] ice	−20	1.0	1.6	12.2	0.2	1.2	16
4	CH_4, He, NH_3,[b] H_2O	30	3.5	3.2	5.6	0.15	0.38	13
5[a,c]		50	2.0	0.3	0.8	0.04	0.1	3.2
6[c]		100	0.08	0.05	0.58	0.0	0.04	0.75

[a] Run 5 was sparked for 26 hr. [b] 20 cm. [c] In apparatus H; others in F.

interesting to identify the light hydrocarbons produced by sparking such gas mixtures under various conditions.

Experimental Section

Reactions were run in either apparatus H, a variation of Miller's circulation apparatus described by Heyns, Walter, and Meyer,[8] or in F, a 1-l. round-bottomed flask with tungsten electrodes arranged to produce a spark in the center. A Cenco 97021 Tesla coil was used as the energy source following Miller. In a typical run, distilled water (100 ml) was added and air was replaced with helium[9] by successive evacuations to about 3 cm pressure followed by admission of helium. The pressure was again brought to 3 cm and CP methane (20 cm) added. The apparatus was then brought to the desired temperature and the spark turned on. For the run at −20° the apparatus was placed in a freezing compartment of a refrigerator. In the 50° run, the water was boiled very gently so as to maintain the temperature at about 50° in the vicinity of the spark.

At the end, gas samples of known volume were taken into an evacuated (0.1 mm) infrared microgas cell (path length 10 cm) through a drying tube filled with calcium chloride. The pressure in the apparatus was then brought to ambient by admitting helium if necessary and samples for gas–solid chromatography (gsc) taken through a serum cap. The liquid reaction products were ignored in this study.

Identification and quantitative measurements were made using a 600 × 0.4 cm i.d. copper gsc column, packed with 45–60 mesh activated alumina, at 90° with thermistor detectors and helium as the carrier gas. The hydrocarbon causing each peak was identified by its retention time and confirmed by adding authentic compounds to gsc samples one at a time. For added certainty this process was repeated using a 200 × 0.6 cm i.d. glass column packed with charcoal, on which relative retention times were significantly different. Acetylene was also identified in all of the product mixtures by its characteristic infrared spectrum and its partial pressure was ascertained by quantitative spectroscopy (at 3300 cm^{-1}) using known mixtures as standards. A Perkin-Elmer Model 337 grating infrared spectrophotometer was employed. The amount of unchanged methane was sometimes obtained simultaneously by the same method using one of its lines at about 1335 cm^{-1}. The per cent conversion figures for the other hydrocarbons given in Table I are based on their gsc peak areas relative to acetylene.

Results

Hydrocarbons identified among the products and their retention times in minutes on the alumina column are as follows: ethane (6), ethylene (7), propane (16), propylene (24), and acetylene (30). Resolution was complete and all peaks between 6 and 30 min were identified. Conversions are given in Table I. Hydrogen was another product in all runs, as evidenced by a negative peak at 2.6 min. When the gaseous products of run 3 were gas chromatographed on a silicone rubber column at 70°, small unresolved peaks appeared at times expected for C_4 and C_5 hydrocarbons, but these products were not further investigated. Cyclopropane was sought but not found. Considerable unchanged methane always remained, *e.g.*, in run 3 only 50% of the methane was destroyed.

In our first experiment we approximated Miller's conditions and sparked a mixture like that of run 6, Table I in the circulation apparatus H for 24 hr with the water boiling. Much tarry material was produced and only traces of lower molecular weight hydrocarbons survived. Reducing the time to 1 hr (run 6) we found ethane (0.58%) and very small amounts of other C_2 and C_3 hydrocarbons. When the temperature was reduced to 50° (run 5), more light hydrocarbons survived even for 26 hr, but now the major product was acetylene (2%). No doubt the difference in water vapor pressure in the reaction zone accounts for most of the difference between runs 5 and 6.

While the data obtained in this limited study are too sparse to justify detailed analysis, it is clear from the results of runs 1–4, done in the simple apparatus F, that both water and ammonia reduce the yields of C_2 and C_3 hydrocarbons from methane as was expected. Ammonia and water affect the product distribution strongly, but the only generalization which can be made is that combined yields of C_2 hydrocarbons were always greater than those of C_3 hydrocarbons.

Particularly puzzling is the difference in product distribution between run 3 in which ethane predominates and run 2 in which a more random pattern is found with acetylene the major product. The only known differences are that run 3 at −20° was 50° colder than run 2, which might change the temperature of the spark, and that some water was present in run 3, although the vapor pressure over ice at −20° would seem very low to have such a marked effect.

Thus every hydrocarbon isomer that could have been detected by the method used, with the exception of cyclopropane and propyne, was formed by electrical discharges in these model atmospheres. The presence of water or ammonia decreased the total yield of hydrocarbons and affected the product composition in interesting ways, which cannot be explained at present.

Registry No.—Ethane, 74-84-0; ethylene, 74-85-1; propane, 74-98-6; propylene, 115-07-1; acetylene, 74-86-2.

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[8] K. Heyns, W. Walter, and E. Meyer, *Naturwissenschaften*, **14**, 385 (1957).

[9] These mixtures differ from Miller's[2] in the use of helium in place of hydrogen. Helium was convenient for deoxygenating the apparatus and was no doubt present in the early atmosphere. Hydrogen was formed *in situ* from methane.