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PRIMORDIAL ORGANIC CHEMISTRY
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Christof Palm and Melvin Calvin

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PRIMORDIAL ORGANIC CHEMISTRY

I. COMPOUNDS RESULTING FROM ELECTRON IRRADIATION OF $C^{14}H_4$

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Abstract

C^{14}-labeled methane, together with a number of other presumed primordial gases of the earth's atmosphere, has been subjected to electron bombardments. The products formed have been examined by paper chromatography, ion exchange chromatography, mass spectrometry, and ultraviolet light spectrophotometry. A number of minor molecules have been specifically identified, and urea has been found as a major component in the absence of added phosphine; the formation of urea is inhibited by added phosphine. Most of the products can be accounted for as discrete molecules, even though they are as yet unidentified.

Introduction

We have extended our experiments with ionizing irradiation (5 Mev electrons from a linear accelerator) on supposed primitive gas mixtures, containing certain compounds of carbon, hydrogen, oxygen and nitrogen.[1-4]

1. W. M. Garrison, et al., Science, 114, 461 (1951).
2. C. Palm and M. Calvin, in University of California Radiation Laboratory Report, UCRL-9519, Jan. 31, 1961, p. 30.
3. M. Calvin, Ann. Intern. Med. 54, 954 (1961).
4. M. Calvin, Condon Lectures, 'Chemical Evolution', Oregon State Board of Higher Education, in press, 1961.

Chemical evolution has been suggested as the process preceding biological evolution.[5,6] Although little is known with certainty about the atmosphere of

5. M. Calvin, American Scientist, 44, 248 (1956).

6. M. Calvin, Evolution, 13, 362 (1959).

primitive earth, it is generally assumed that reducing atmospheric conditions prevailed at that time.[7,8] Ever since mixtures of simple gases which were con-

7. H. Urey, in Handbuch der Physik, S. Flugge, ed. Springer, Berlin (1959), Vol. 52.

8. H. Holland, Am. Geophys. Union Trans., 1961, p. 29.

sidered as simulating primordial conditions were irradiated in 1951[1] and sparked in 1953[9,10], the results have given rise to further experiments and more factual

9. S. L. Miller, J. Am. Chem. Soc. 77, 2351 (1955).

10. S. L. Miller and H. C. Urey, Science, 130, 245 (1959).

basis for discussions of chemical evolution. Not only have mixtures of simple gases like H_2, CH_4, CO, CO_2, NH_3, and H_2O been exposed to varied sources of energy, but also some more 'evolved' compounds which had been found or were assumed to be involved in these first experiments.

Beta emission, notably from potassium-40, might have contributed a small part to the overall spectrum of available energy sources four to five billion years ago.[11] Its connection with the possibly catalyzing mineral surfaces

11. A. J Swallow, Radiation Chemistry of Organic Compounds, Pergamon Press, Ltd., London (1960), p. 244.

make it particularly interesting. Electron irradiation also proves to be a convenient energy source. So far, only two brief mentions of electron irradiation for this purpose exist.[12] The reasons for irradiating H_2, CH_4, NH_3, and H_2O rather

12. T. Hasselstrom and M. C. Henry, Science, 125, 350 (1957).

than CO, H_2, and H_2O shall not be discussed here beyond the assumption of H_2 in the primitive atmosphere. It should be emphasized, however, that the irradiations presented here can only help to understand chemical evolution, not necessarily reproduce it.

The number of identified compounds formed by primordial chemistry is still very limited. They account for only a small fraction of all the organic matter produced in these experiments. The large variety of reactions and compounds has truly been a limitation in this chemistry of products derived largely from CH_4, H_2, NH_3, H_2O, and energy. Too few compounds are formed in amounts easily susceptible to ordinary analysis. For this reason, the use of carbon-14 labeled CH_4 is stressed here as it will allow more detailed analysis of the fate of carbon.

The formation of amino acids has been well established in primordial chemistry.[9,10,13-16] One of the main incentives of the present work has been to

13. J. Oró, A. P. Kimball and F. Mover, Arch. Biochem. Biophys. 85, 115 (1959).
14. J. Oró and S. S. Kamat, Nature, 190, 442 (1961).
15. B. Frank, Chem. Ber. 93, 446 (1960).
16. T. G. Pavlovskaya and A. G. Pasyuki, Int. Union of Biochemistry Symp. Ser. Vol. 1, 'The Origin of Life on the Earth', Pergamon Press, Ltd., London (1960), 151.

contribute to the discussion on the still unsolved problem of how readily heterocyclic bases, i.e., purines and pyrimidines, might be formed in such systems. So far, none of these have been reported to be found in reactions involving compounds of complexity no greater than H_2, CH_4, H_2O, and NH_3 (N_2, CO, CO_2).[17] It was only

1 S. L Miller, ibid, 126.

during the progress of the present investigations that evidence appeared that by heating a concentrated aqueous solution of NH_4CN, adenine and 4-aminoimidazole-5-

carboxamide are formed.[18,19] Also, malic acid and urea, together with poly-

18. J. Oró and A. P. Kimball, Abstracts ACS Mtg., Sept. 1960. Division of Biological Chemistry, Abstract 68, Page 25C. J. Oró, Nature, 191, 1193 (1961).

19. J. Oró, Biochem. Biophys. Res. Comm, 2, 407 (1960). J. Oró and A. R. Kimball, Arch. Biochem. Biophys., 93, 166 (1961).

phosphoric acid, have been reported to yield uracil by a thermal reaction.[20]

20. S. W. Fox and K. Harada, Science, 133, 1923 (1961).

The value of a demonstration of the synthesis of purines and pyrimidines from simple gases lies in their fundamental function. Fox stresses the continuity of his systems,[20] yet the continuity is limited by the polyphosphoric acid and the temperature. The concentrations and the immense variety of competing reactions which will occur in a more natural mixture must also be considered.

Since some generalizations have resulted from the electron irradiations which were carried out here, these will first be reported in the present paper. The more specific question concerning the possible formation of purines and pyrimidines will be published elsewhere.[21]

21. C. Palm and Melvin Calvin, to be published.

Experimental

Composition of irradiated systems

All the gas mixtures to be irradiated consisted of CH_4 ($C^{14}H_4$) and NH_3 in comparable amounts (20-30 cm Hg), small amounts of H_2 (0-5 cm Hg), and H_2O vapor present over a liquid phase dependent upon temperature (Table 1). An attempt was made to detect possible surface catalysis. The influence of reduced phosphorus was also determined.

TABLE I

Composition of Reaction Mixtures

Experiment No.	M16*+	M25	M26	M28	M30	M20+	M22	M27	M31
CH_4 press., cm Hg	27	30.75	25.55	35.45	32.45	42	30.6	38	28.2
C^{14} activity, mc	1.4	1.155	0.89	2.34	4.31	0.93	1.18	2.705	4.71
H_2 press., cm Hg	5.0	5.2	4	1.9	4.15	5.0	0.2	2.2	2
NH_3 press., cm Hg	20*	20	20	20	20	30	20	18	20
H_2O ml liquid	17	18	20	20	18	20	13	18.4	
Olivine, gmm	3	1.95	1.3	1.35					
$(NH_4PO_3)_x$ mg						1000	100	100	
PH_3 press., cm Hg							3.4	2.8	1.03
Temperature of H_2O, °C.	30	80	80	80	80	30	80	80	80
Time of irrad., hrs.	2	2	4	2	2	2	2	2	2
Total energy absorbed, ergs	10^{11}	10^{11}	2×10^{11}			10^{11}	10^{11}		
Activity in aqueous phase, after irradiation, μc	78	14	47	27.1	49.3	15.3	33	33.5	68.5
Percent conversion from original $C^{14}H_4$	5.55	1.21	5.28	1.16	1.14	1.65	2.84	1.24	1.45

* 20 cm of N_2 also have been present.

\+ Flask volume 657 ml, all others 810 ml.

To one series of experiments, a powdered silicate, olivine [$(Mg,Fe)_2SiO_4$] was added. Olivine is widely distributed in the solar system, witness the stony meteorites, particularly the carbonaceous chondrites.

In a second series of experiments, phosphorus compounds were added to the mixture to be irradiated. The important role which phosphorus compounds have in biological systems today suggests that they entered chemical evolution early. A polymer phosphate, $(NH_4PO_3)_x$, was added to the aqueous phase and to correspond to the presumed reducing conditions, phosphine (PH_3, P_2H_6) was used. $(NH_4PO_3)_x$ was obtained from Kurrol Salt $(NaPO_3)_x$ [22] by exchange in ammonia. Its asbestos

22. Handbuch der Prap. anorg. Chemie, G. Brauer, ed., F. Enke Verlag, Stuttgart (1959), p. 393, 426.

phenotype indicates the stringlike molecular structure. Phosphine, obtained by hydrolysis of Ca_3P_2[22] is a convenient way to introduce more soluble reduced phosphorus compounds.

Apparatus and Irradiation procedure

For the irradiation experiments a sealed Pyrex glass tube of the dimensions indicated in Figure 1 (A) was used. The end of the tube consisted of a thin (0.1 mm) ball-shaped window through which the electrons entered the vessel. For irradiation the tube was kept in a horizontal position, the exit window of the linear accelerator being slightly smaller than the diameter of the tube. A modification (B) was used in later experiments (Experiments M22-M31). The bottom well can be heated to reflux the water and thus increase the partial pressure of water vapor. At the same time, most of the nonvolatile compounds formed during the experiment are washed down and out of the actual irradiation zone. The well was protected by a lead cover during irradiations.

The irradiation was carried out with 5 mev electrons.[f] The linear

[f] The linear accelerator was maintained and operated by William Everette of the Lawrence Radiation Laboratory, to whom we are extremely grateful.

accelerator delivered 30 pulses/sec, each pulse lasting 6 μsec. The integrated dose rate was 9 μamps. Assuming a Feather relationship for the energy loss per electron inside the gaseous mixture, it could be calculated that the total dose was approximately 0.5 - 1×10^{11} erg within two hours. No attempt was made to evaluate the exact dose rate with a chemical dosimeter.

The reaction tube was filled and opened at a manifold. Precautions were taken to avoid contamination of chemical or biological origin. The tube was cleaned with hot cleaning solution and subsequently heated on a steam bath for two to four hours at 125°C. It was then attached to the manifold and evacuated to less than 100 microns pressure while heating with a blue flame. Any solid catalysts were added at this time. As the olivine came from natural sources, it was also cleaned before use in cleaning solution.

The evacuated flask was then cooled with dry ice and the previously boiled water condensed into it. If phosphines were used, they were evolved from Ca_3P_2 in the attached water flask and transferred, together with the water, at the temperature of liquid nitrogen. The Ca_3P_2 may be brought in contact with the water only after evacuation of the manifold. This can be achieved by keeping it in a small pivoted flask connected to the water supply. The manifold was then re-evacuated and the $C^{14}H_4$ introduced from a storage flask. Additional amounts of CH_4 and H_2 were supplied in analytical grade from cylinders. They were added while the water was still frozen. The NH_3 was put in rapidly after the water had melted and it could not be measured accurately. Before the addition of each gas, the manifold and tubing were alternately evacuated and swept to avoid contamination by oxygen.

The reaction tube was then sealed and irradiated. The irradiation took place at temperatures of ~30°C as the tube, and especially the window, were cooled by an air stream. In experiments M22 and later, however, the bottom well was heated to ~80°C in order to allow refluxing of the water at the corresponding pressures.

As can be seen from the compilation in Table I, several different runs have been carried out. The data refer mainly to the amounts and pressures of compounds used. In general, the gases were supplied to a total pressure of less than 1 atm. At 30°, the partial pressure of water amounts to 32 mm Hg; at 80° C to 355 mm Hg.

Analytical methods

In general, the analysis of both types of reaction solutions, with and without phosphorus compounds, was performed in the same manner. In the first experiments in which carbon-14 was not used it became obvious that the amounts of products synthesized would hardly allow general analytical methods to be used. The crude residue, for example, showed ninhydrin-positive reactions, but in only one case could several separated spots be detected after paper chromatography. Carbon-14 was therefore used in activities shown in Table I. Since many compounds are formed, the radioactivity applied at the origin of a two-dimensional chromatogram must be at least 5×10^5 dpm per 100 γ crude products.

For analysis, the irradiated tubes were connected to the manifold, the seal opened and the gases collected in a storage flask. There was only one cursory examination for their composition in the mass spectrometer. Besides the original gases small amounts of $N_2(CO)$, CO_2, C_2H_6, C_2H_4, O_2 and C_3-C_7 hydrocarbons were found in approximately this quantitative order. The irradiated phosphine-containing mixtures had reacted so that no self-ignition occurred. The reaction solutions were then removed and stored in air, though care was taken to keep the solutions stoppered and refrigerated between analyses.

The colorless, or occasionally slightly yellow, solutions have a putrefied odor. A camphorlike smell could also be detected. The odor was particularly unpleasant when C_2 hydrocarbons were used. Because of the excess NH_3 the pH was always over 11.

An aliquot portion of the aqueous phase was removed and evaporated to dryness *in vacuo*. This was done in an inverted U-shaped tube in order to trap volatile material. The C^{14} content of the original solution and the condensate was determined.[f] The total activity was assumed to represent conversion of

[f] All activities were measured by liquid scintillation counting.

$C^{14}H_4$ to higher molecular weight material. The difference between the total activity and that found in the condensate was assumed to represent compounds non-volatile under alkaline conditions. Any solubility of $C^{14}H_4$ in the aqueous phase was disregarded. The conversion data are compiled in Table I. The amounts of non-volatile residue by weight were always slightly higher than those calculated from the radioactivity conversion. We assume this to be due mainly to dissolved silicates from the glass tube.

a. Paper chromatography

After the distribution between volatile and non-volatile compounds was determined, the residue could be redissolved in water and aliquot portions were chromatographed on Whatman No. 1 or No. 4 filter paper in order to obtain radioautographs. The following solvent systems have been used: phenol-water (PH, 1470:604)[f] and n-propanol-ammonia-water (PA, 6:3:1)[f] descending in the first direction and, generally, n-butanol-propionic acid-water (BP, 375:180:245)[f]

[f] The numbers correspond to solvent volume ratios. PH is phenol-water; PA is propanol-ammonia, and BP is butanol-propionic acid.

descending in the second dimension. Examples of radioautographs for each type of reaction mixture are given in Figure 2. They substantiate the idea that numerous compounds result from the irradiation of mixtures of simple gases.

It should be emphasized that in addition to the well-defined separated spots there is a background of radioactivity over most of the chromatogram. This activity increases with the R_f value. Thus, in addition to polymerized material many compounds of small yields are indicated, and only part of them will be concentrated enough in the succeeding fractionations to become distinguishable.

No special ultraviolet absorption was observed on or in the paper. When it was sprayed with ninhydrin, positive reactions were seen only for two spots in the phosphine series (and this only for the acid solvent pair PH-BP). Since the papers could be spotted with about 100 γ of carbonaceous material, the two tests (ultraviolet and ninhydrin) could only indicate yields above 1%.

b. Ion exchange resins

The next step in the separation and concentration of the compounds in the smaller fractions was the use of ion exchange resins. This was first done in an exploratory way as indicated in schemes 1 and 2 for experiments M16 and M22.

1. Separation Scheme for M16*

reaction solution

↓ evaporate

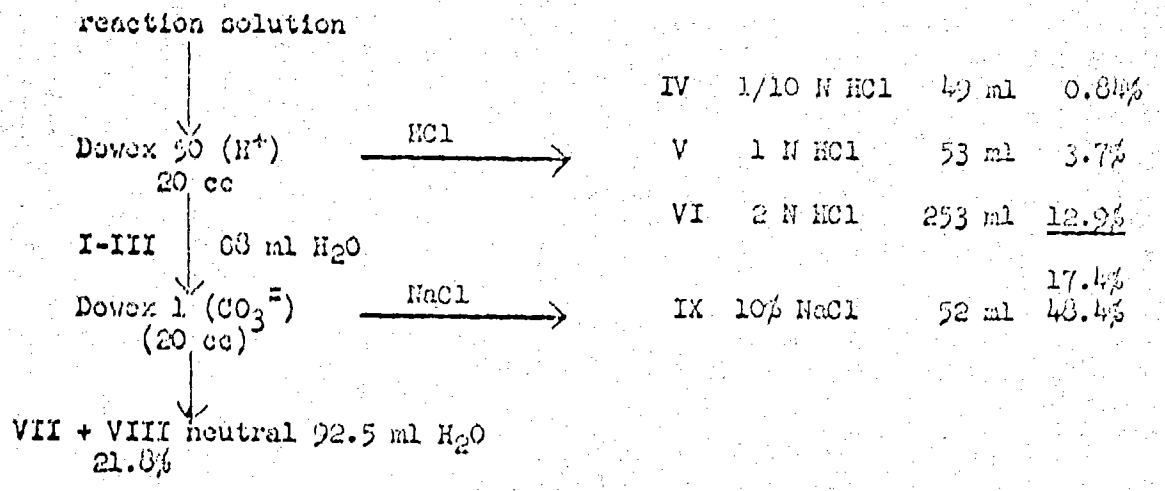
Dowex 50 (H^+) (25 cc) —HCl→

volatile			34.85%
V-VII	1/10 N HCl	60 ml	13.82%
VIII-IX	1 N HCl	40 ml	0.86%
XII	2 N HCl	135 ml	14.95%
			29.63%

↓

Acids + neutral components
I - IV, 80 ml H_2O
33.4%

2. Separation Scheme for M22



* The Roman numerals identify particular fractions; the percentages are of total converted $C^{14}H_4$.

For M16, in contrast to M22, the original solution was first evaporated, then the whole was passed through a cation exchange resin Dowex 50 (H^+). The bases were eluted with increasing molarities of hydrochloric acid. In M22 the aqueous effluent of the acids and nonionic compounds was further separated over the anion exchange resin Dowex 1 ($CO_3^=$). Experiment M20 which had included $(NH_4PO_3)_x$ at the start, but no phosphine, was passed through only Dowex 1 in order to obtain bases free of $PO_4^=$ as effluent.

Chromatograms of the concentrates of every fraction were then prepared. Figure 3 shows those of experiments M16 II, VI and XII, M22 VI and IX, and the basic and neutral fraction of M20. The general distribution of basic, acid and neutral fractions will be discussed below with more data from experiments M27-M31. Yet one other marked difference between the olivine and phosphine-containing experiments becomes obvious here. The dominating compound in the olivine experiments (M16) (Figure 2) appears in the basic fraction upon elution with 0.1 N HCl. It is ninhydrin-negative. In Experiment M22 (containing PH_3), elution with 2 N HCl produced two major compounds in the basic fraction chromatographically similar

to the one from M16. These are the ninhydrin-positive compounds mentioned earlier. They are strikingly different from the dominant base from M16 on chromatography in propanol-ammonia (P,A) since they are volatile under these conditions. The main compound of M20 is identical with that of the olivine experiments and not volatile from P,A.

The principal radioactivity in M16 and M20 could be shown to be due to urea by (a) nitrous acid reaction, (b) cochromatography with unlabeled urea, (c) digestion with urease to produce $C^{14}O_2$. The two major basic compounds (5.1 and 3.1%) in the phosphine experiment M22 are thought to be amines or alkanol amines from their volatility in alkaline systems, though no nitrous acid or periodate reaction could be confirmed. The high urea content in the olivine experiments (18% of total in M16, 30% in M25, 5% in M28) was so striking that a special effort was made to confirm it in M22. No urea was found there, either by cochromatography or by dilution analysis via the urea nitrate.

The acid and neutral fractions were not further analyzed at this point, though two major compounds (13.4% and 8.1%) are easily distinguishable in the acid Fraction IX of experiment M22. (Figure 3)

c. Other methods

Paper cochromatography was undertaken with a few amino acids and acids added to the basic and acid fractions of experiments M16 and M22. The presence of glycine (0.19%), Alanine (0.39%), and lactic acid was confirmed in M16. Glycine (0.04%), alanine (0.18%), aspartic acid (0.04%), and lactic acid (0.99%) were found in experiment M22. The positions of these spots are indicated in Figure 3.

Dilution analysis was used to evaluate the HCN content in experiment M22 as HCN can be considered a very important intermediate.[23] A known amount of

23. See, for example, J. Oró, Nature, 190, 389 (1961).

carrier KCN was added and precipitated as AgCN together with an aliquot of the original solution. After the specific activity had been determined, the AgCN was dissolved in 10% NH_4OH, filtered, and reprecipitated by acidifying. Determining the specific activity each time, this process was repeated two additional times. After the second reprecipitation, the specific activity stayed constant. The CN^- content was thus determined to be about 0.45%. A corresponding evaluation of CN^- in the acid fractions of M27 and M28 reveals their CN^- content to be 0.4% and 2.14%, respectively, of the total organic compounds.

A first attempt by paper cochromatography was then made in order to estimate the limits of a possible formation for adenine and 4-aminoimidazole-5-carboxamide. While the ultraviolet spectra of the unfractionated mixtures and also those of the basic fractions had not yielded any specific absorption other than a general increase below 4000 Å, it could be concluded from the data with the whole basic fraction of M22 that an upper limit exists of 0.2% for adenine and 0.1% for 4-aminoimidazole-5-carboxamide among the basic compounds. This estimate will be more thoroughly described later.[21]

Analysis of experiments M27-M31

Runs M27 through M31 were performed in order to obtain more material for analysis. Again, only the general results are included here, since the principal examination was for purine and pyrimidines.

The reaction mixtures of M27 and M28 were separated into basic, acid and neutral fractions in the following way: Aliquot amounts (10 ml each) were evaporated to near dryness and then placed on top of an ion exchange column, Dowex 50 (H^+) (25 ml). The acids and nonionic materials were washed off with water, the bases eluted with 3 N HCl. The acids were then separated from the neutral compounds by washing through a Dowex 1 (OH^-) (25 ml) column and were

eluted by 5% Na_2SO_4 (see Table II).

In runs M30 and M31, a quite different method of fractionation was used, namely, ion exchange chromatography. This method, following a procedure by Crampton, et al.[24] has the advantage of separating, in one run, the bases

24. C. F. Crampton, I. R. Frankel, A. M. Benson, and A. Wade, Anal. Biochem. 1, 249 (1960).

uracil, thymine, guanine, cytosine, 4-aminoimidazole-5-carboxamide, and adenine. Making use of an automatic fraction collector and an automatic ultraviolet absorption recorder, it was possible by aliquot counting to correlate the C^{14} activity with the distribution of these bases. For this purpose the resin consisted of 105 ml Dowex 50-X2, 200-400 mesh, arranged in a column 60 cm high and 1.5 cm diameter. Elution was achieved at 25°C with a gradient of 0.2 N to 1.0 N. Ammonium formate buffer, pH 4, from a 500 ml mixing chamber.

The superimposed traces of both the C^{14} activity from the reaction mixture and the measured UV absorption from the added bases (at 260 mμ) are given in Figure 4. The elution point of urea is also indicated.

At first the ion exchange elution diagrams appear to present a convenient method of comparison for varied experiments in primordial chemistry, but this can be done only with some reservations.

Figure 5 shows the chromatograms of fraction 64 in each of the above runs. Although general differences in the elution diagrams are apparent, one might expect that the composition of corresponding fractions would be comparable. The chromatograms of corresponding fractions reveal that although there are indeed major components, these are not identical, and in addition there are a multitude of others. At this point the evidence obtained from the diagrams cannot be carried beyond their obvious difference in acid-base distribution, as will be stressed below. Even though urea is known to occur in run M30 but not in M31, this would

TABLE II

Distribution of volatiles, bases, acids, and nonionics*

Without PH_3	volatile	basic	acid	neutral
M16	34.85	29.6	33.4	
M28	37.4	31.9	18.25	8.65
M30	23.5	45.4	20.55	10.6
With PH_3				
M22**	17.3	17.4**	48.4**	21.8**
M27	17.0	7.64	63.1	3.5
M31	25.65	18.4	53.34	2.64

* in % of C^{14} in the aqueous reaction solution.

** the volatile fraction was not evaporated prior to fractionation, but determined separately.

be hard to recognize from the elution diagrams alone.

The first ten fractions can be further separated on a Dowex 1 column for acid and nonionic compounds. Table II includes all of the data on the distribution of basic, acid and nonionic fractions obtained by all methods. They are arranged according to their initial phosphine content.

Except for the separations in M30 and M31 which are normalized, it is seen that the fractions do not add up to 100%. This results from a holdback on the columns and is considered due mainly to polymerized material. Nevertheless, it was possible through C^{14} activity to account for nearly all the CH_4 converted in terms of the compounds formed and to relate them to certain fractions. This had not been achieved in experiments reported heretofore.

One difference becomes obvious when the runs with and without phosphine are compared. The distribution of bases and acids is inverted. The meaning of the higher content of volatile compounds in the olivine runs is not so clear, as these have not been analyzed. From experiment M22 it appears that the volatiles are mainly netural compounds. Hydrocarbons and alcohols would not have been retained under the ammoniacal conditions of evaporation.

In order to obtain a general view of what compounds might possibly be contained in the nonvolatile neutral fractions of M30 and M31, a one-dimensional chromatogram was run together with the products of a $Ca(OH)_2$ condensation of formaldehyde.[25,26] This condensation yields mixtures of aldoses and ketoses.[26]

25. R. Mayer and L. Yaetsko, Liebigs. Ann. Chem. 635, 145 (1960).

26. Unpublished experiments by R. Ferrier.

In Figure 6 the approximate range for the various sugars is indicated by their carbon number. The possibility exists that carbohydrates in the triose to hexose range may be formed by electron irradiation.

Discussion

Many of the possible reactions of primitive mixtures have been discussed before.[3-20, 27,28] The formation of urea in large amounts in one of the irradiated

27. S. W. Fox, K. Harada, and A. Vegotsky, Experientia, 15, 81 (1959).
28. S. W. Fox, Science, 132, 200 (1960).

systems here, with none found in a second system, is noteworthy. Because of the 1,3 nitrogen position, urea is used in pyrimidine synthesis and its possible importance in primitive uracil formation was pointed out recently.[20]

We suggest the synthesis of urea by the reaction[29]

$$HCN + {}^{\bullet}OH\ (H_2O_2) \longrightarrow HOCN$$

$$HOCN + NH_4OH \longrightarrow (H_2N)_2CO + H_2O$$

29. D. Manson, J. Chem. Soc. 91, 1449 (1907).

It is possible that phosphine, or other highly reduced phosphorus compounds, are able to scavenge OH radicals and therefore prevent the formation of urea. From this it follows that urea should be formed upon irradiation of aqueous HCN, and, indeed, this could be confirmed.[2]

Perhaps the most astonishing result which appeared in this initial examination is the fact that very nearly all, that is over 95%, of the material which has reacted under this set of conditions has been accounted for in terms of discrete and distinct compounds as indicated by the paper chromatographic examination of the products. One might have expected a more or less continuous spectrum of polymeric material as a result of indiscriminate free radical and ionizing synthesis, but this does not appear to be the case.

As yet, we have identified only a few of these compounds, but we are proceeding with the identification of others. It may be expected that as the

number of identified chemical species increases, a pattern of chemical transformation under the influence of electron bombardment (as well as other high energy sources) will emerge which will help us in the reconstruction of possible modes of primordial organic synthesis, both with the electron beam and with other energy sources such as electric discharge and ultraviolet light; these latter two processes have heretofore been considered as the principal energy sources in primordial syntheses.