and the alcohol removed from the filtrate. The residue was distilled to give 5.6 g. (51%) of the desired VIII.

Anal. Calcd. for $C_{11}H_{13}OF_7$: C, 44.89; H, 4.42; F, 45.24. Found: C, 45.06; H, 4.70; F, 45.39.

Acknowledgment.—The financial support of the Hooker Chemical Corporation is gratefully acknowledged.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,[1a] UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Primordial Organic Chemistry. I. Compounds Resulting from Electron Irradiation of $C^{14}H_4$

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RECEIVED OCTOBER 25, 1961

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.[2-4]

Chemical evolution has been suggested as the process preceding biological evolution.[3-6] Although little is known with certainty about the atmosphere of primitive earth, it is generally assumed that reducing atmospheric conditions prevailed at that time.[7a,b] Aqueous CO_2-containing ferrous ion and hydrogen was irradiated with accelerated α-particles in 1951.[2a,8] Mixtures of CH_4, NH_3, H_2O and H_2 were sparked in 1953.[9a,b] The results have given rise to further experiments and more factual 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[10] 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 over-all spectrum of available energy sources four to five billion years ago.[11] Its connection with the possibly catalyzing mineral surfaces 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 irradiation of H_2, CH_4, NH_3 and H_2O rather than CO_2, N_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.[9a,b,13-16] One of the main incentives of the present work has been to 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 during the progress of the present investigations that evidence appeared that by heating a concentrated aqueous

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(1) (a) The preparation of this paper was sponsored by the U. S. Atomic Energy Commission. (b) Permanent address: Laboratory of Inorganic Chemistry, University of Munich, Munich, Germany.

(2) (a) W. M. Garrison, *et al.*, *Science*, **114**, 461 (1951); (b) 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, University of Oregon Press, 1961. A history and documentation of this idea is to be found here.

(5) M. Calvin, *Amer. Scientist*, **44**, 248 (1956).

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

(7a) H. C. Urey in "Handbuch der Physik," S. Flugge ed., Springer, Berlin, 1959; H. C. Urey, *Proc. Natl. Acad. Sci.*, **38**, 251 (1952); H. C. Urey, "The Planets," Yale University Press, New Haven, Conn., 1952.

(7b) H. Holland, *Amer. Geophys. Union Trans.*, 29 (1961).

(8) There exists a body of early work on the ultraviolet and sensitized ultraviolet irradiation of aqueous solutions of CO_2 directed by the effort to simulate photosynthesis in simple systems. This work (of Baly and of Bauer; for a review see E. I. Rabinowitch, "Photosynthesis," Vol. I, p. 81) was done before the modern methods of analysis were available and led to no definitive result in the present context as defined in ref. 1.

(9) (a) S. L. Miller, *J. Am. Chem. Soc.*, **77**, 2351 (1955); (b) S. L. Miller and H. C. Urey, *Science*, **130**, 245 (1959).

(10) For example, X-rays were used by Dose and Rajewsky (*Biochim. Biophys. Acta*, **25**, 225 (1957)).

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

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

(13) J. Oró, A. P. Kimball and F. Moser, *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. Pavloskaya 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.

(17) S. L. Miller, ref. 16, p. 126.

TABLE I

COMPOSITION OF REACTION MIXTURES

Experiment	M16[a,b]	M25	M26	M28	M30	M20[b]	M22	M27	M31
CH_4 press., cm.	27	30.75	25.55	35.45	32.45	42	30.6	38	28.2
C^{14} activity, mc.	1.4	1.15	0.89	2.34	4.31	0.93	1.16	2.70	4.71
H_2 press., cm.	5.0	5.2	4	1.9	4.15	5.0	0.2	2.2	2
NH_3 press., cm.	20[a]	20	20	20	20	30	20	18	20
H_2O, ml. liquid	17	18	20	20	18	20	13	18.4	
Olivine, g.	3	1.95	1.3	1.35					
$(NH_4PO_3)_x$, mg.						1000	100	100	
PH_3 press, cm.							3.4	2.8	1.03
Temperature of H_2O, °C.	30	80	80	80	80	30	80	80	80
Time of irradn., hr.[c]	2	2	4	2	2	2	2	2	2
Activity in aq. phase, after irradn., μc.	78	14	47	27.1	49.3	15.3	33	33.5	68.5
Convn. from orig. $C^{14}H_4$, %	5.55	1.21	5.28	1.16	1.14	1.65	2.84	1.24	1.45

[a] 20 cm. of N_2 present in addition to the NH_3. [b] Flask volume 657 ml., all others 810 ml. [c] Rate of energy absorption is $\sim 0.5 \times 10^{11}$ ergs/hr.

solution of NH_4CN, adenine and 4-aminoimidazole-5-carboxamide are formed.[18,19] Also, malic acid and urea, together with polyphosphoric acid, have been reported to yield uracil by a thermal reaction.[20]

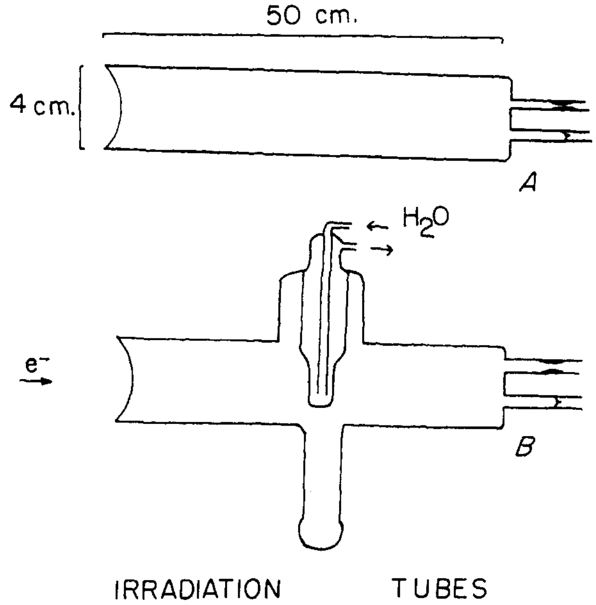

Fig. 1.—Irradiation tubes.

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 discussed elsewhere.[21]

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. press.), small amounts of H_2 (0–5 cm. press.), and H_2O vapor present over a liquid phase, its pressure dependent upon temperature (Table I). An attempt was made to detect possible surface catalysis. The influence of reduced phosphorus was also determined.

To one series of experiments, a powdered silicate, olivine [$(Mg,Fe)_2SiO_4$] was added to simulate somewhat the mineralogical base of the carbonaceous chondrites. It will appear that we have no reason to suppose as yet that its presence has affected the results reported herein.

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 suggested that they entered chemical evolution early. A polymer phosphate, $(NH_4PO_3)_x$, was added to the aqueous phase and a reduced phosphorus compound, phosphine (PH_3, P_2H_6) was also tried. $(NH_4PO_3)_x$ was obtained from Kurrol salt $(NaPO_3)_x$[22] by exchange in ammonia. Its asbestos phenotype indicates the string-like 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 Fig. 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 non-volatile 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.[23] The linear accelerator delivered 30 pulses/sec., each pulse lasting 6 μsec. The integrated dose rate was 9 μamp. Assuming a Feather relationship for the energy loss per electron inside the gaseous mixture, it could be calculated that the total dose was approximately $0.5–1 \times 10^{11}$ 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 2 to 4 hours at 125°. It was then attached to the manifold and evacuated to less than 100 μ pressure while heating with a blue flame. Any solid catalysts were added at this time. As the olivine came from natural sources, its surface 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

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(18) J. Oró and A. P. Kimball, Abstracts American Chemical Society Meeting, Sept., 1960, Division of Biological Chemistry, Abstract 68, p. 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).

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

(21) C. Palm and M. Calvin, in University of California Radiation Laboratory Report UCRL-9900, p. 51.

(22) "Handbuch der Prap. anorg. Chemie," G. Brauer, ed., F. Encke Verlag, Stuttgart, 1959, pp. 398, 426.

(23) The linear accelerator was maintained and operated by William Everette of the Lawrence Radiation Laboratory, to whom we are extremely grateful.

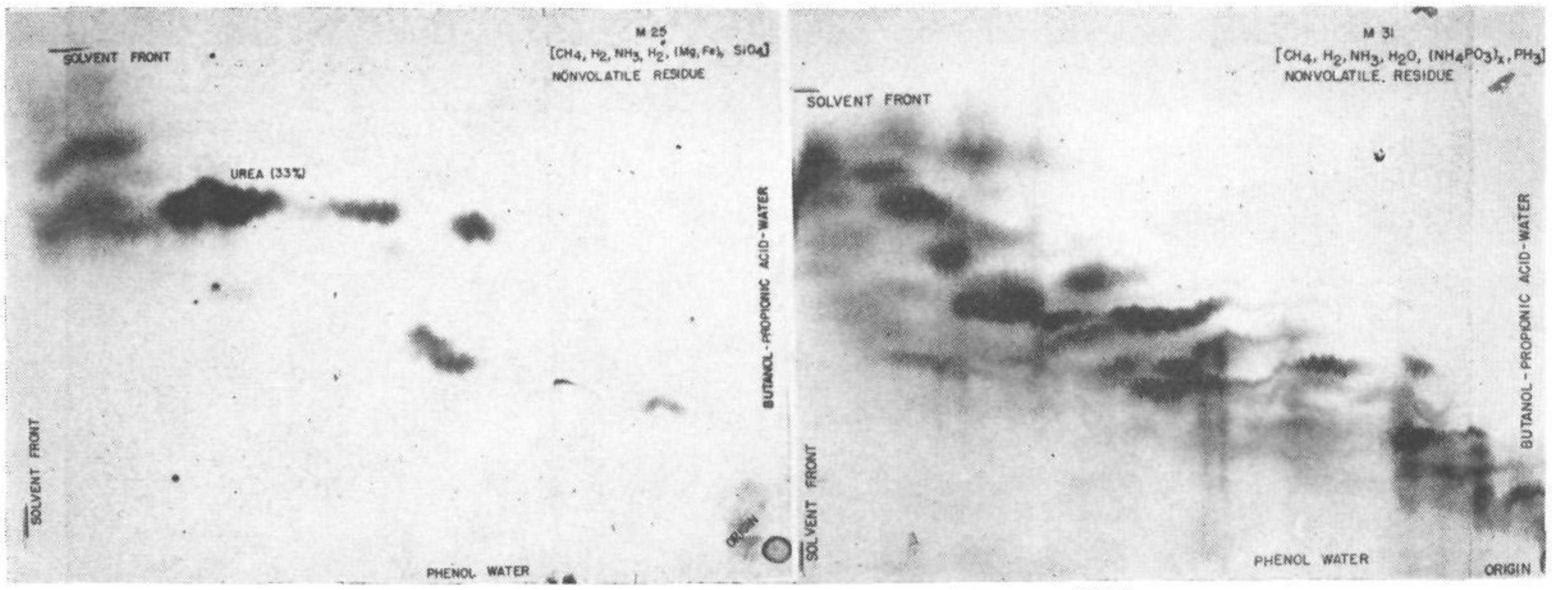
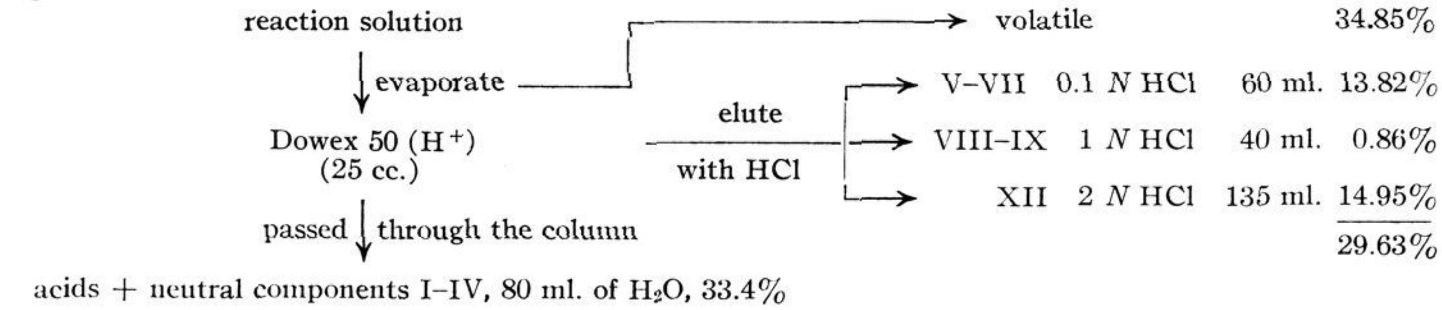


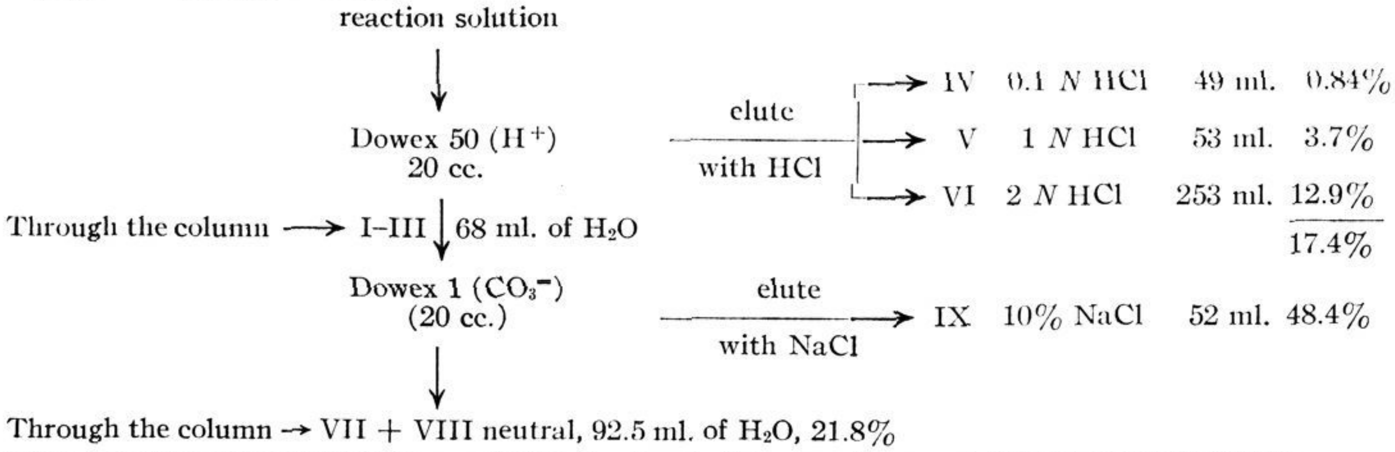
Fig. 2.[a]—Chromatograms of experiments M25 and M31.

[a] The vertical line which appears in the left radioautograph of Fig. 2 and in a number of others here shown is a seam formed by the union of two separate pieces of film required to cover the entire paper.

1. Separation Scheme for M16[a]



2. Separation Scheme for M22



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

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° as the tube, and especially the window, were cooled by an air stream. In experiments M22 and later ones, however, the bottom well was heated to ~80° 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., at 80° to 355 mm.

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 d.p.m. 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 completely that no ignition occurred upon exposure to air. 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 camphor-like 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.

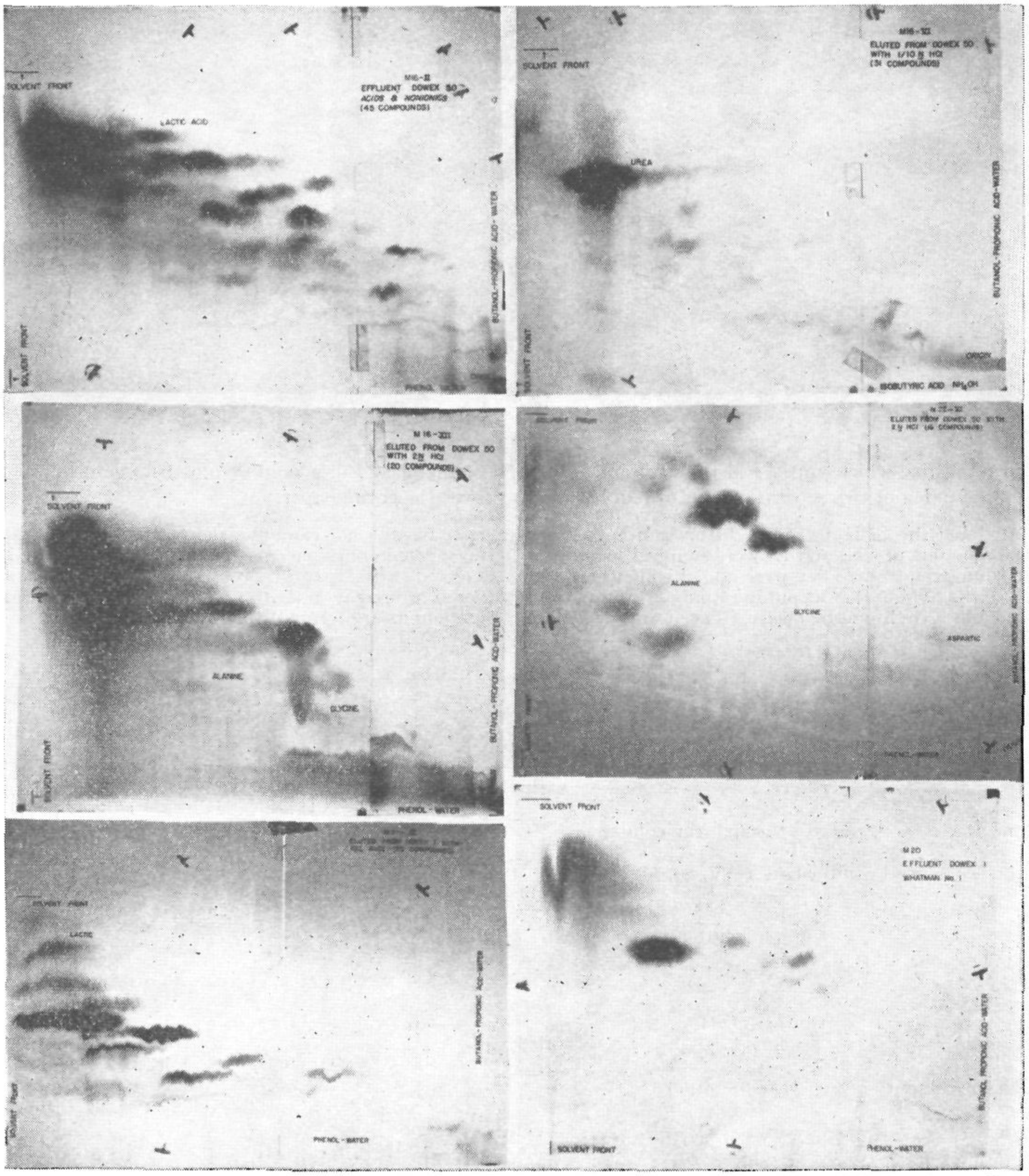


Fig. 3.—Paper chromatograms of experiments M16, fractions II, VI and XII; experiment M22, fractions VI and IX; and experiment M20 (basic and neutral fraction). Fractions defined as in separation schemes 1 and 2.

The C^{14} content of the original solution and the condensate was determined.[24] The total activity in both was assumed to represent conversion of $C^{14}H_4$ 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)[25] and 1-propanol-ammonia-water (PA, 6:3:1)[25] descending in the first direction and, generally, 1-butanol-propionic acid-water (BP, 375:180:245)[25] descending in the second dimension. Examples of radioautographs for each type of reaction mixture are given in Fig. 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

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

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

done in an exploratory way as indicated in schemes 1 and 2 for experiments M16 and M22.

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 non-ionic 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 (lacking phosphine) and phosphine-containing experiments becomes obvious here. The dominating compound in the olivine experiments (M16) (Fig. 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 produced in M16 and separated on chromatography in propanol–ammonia (PA) since they are volatile under these conditions. The main compound of M20 is identical with that of the olivine experiments (M16) and not volatile from PA.

The principal radioactivity in M16 and M20 (phosphine absence in both) could be shown to be due to urea by (a) nitrous acid reaction, (b) cochromatography with unlabeled urea, (c) digestion with ureas 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 experiments lacking phosphine (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 (Fig. 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 sports are indicated in Fig. 3.

Dilution analysis was used to evaluate the HCN content in experiment M22 as HCN can be considered a very important intermediate.[26] A known amount of 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 at 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]

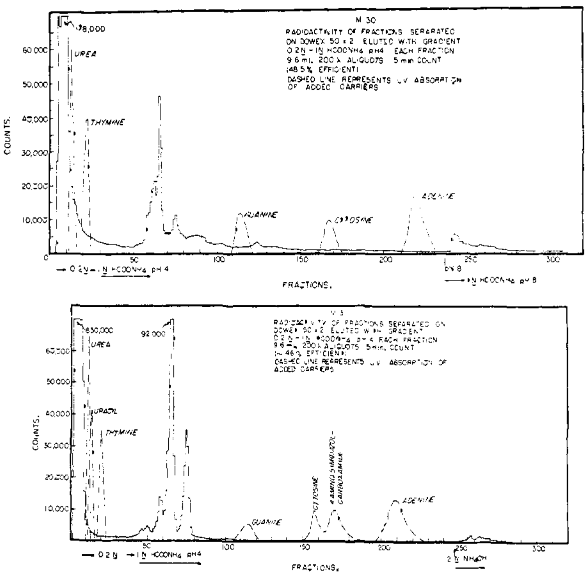

Fig. 4.—Diagrams of ion exchange chromatography elution from Dowex 50 with 0.2 *N*–1 *N* $HCOONH_4$ at *p*H 4; runs M30 and M31.

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 non-ionic 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).

TABLE II

DISTRIBUTION OF VOLATILES, BASES, ACIDS AND NONIONICS[a]

Without PH_3	Volatile	Basic	Acid	Neutral
M16	34.8	29.6	33.4	
M28	37.4	31.9	18.3	6.7
M30	23.5	45.4	20.6	10.6
With PH_3				
M22[b]	17.3	17.4[b]	48.4[b]	21.8[b]
M27	17.0	6.64	63.1	3.5
M31	27.7	18.4	53.3	2.64

[a] In per cent. of C^{14} in the aqueous reaction solution. [b] The volatile fraction was not evaporated prior to fractionation, but determined separately.

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.*,[27] has the advantage of separating, in one run, the bases 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. of Dowex 50-X2, 200–400 mesh, arranged in a column 60 cm. high and 1.5 cm. diameter. Elution was achieved at 25° with a gradient of 0.2

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(26) See, for example, S. Miller, *Biochim. Biophys. Acta*, **23**, 480 (1957); J. Oró, *Nature*, **190**, 389 (1961).

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

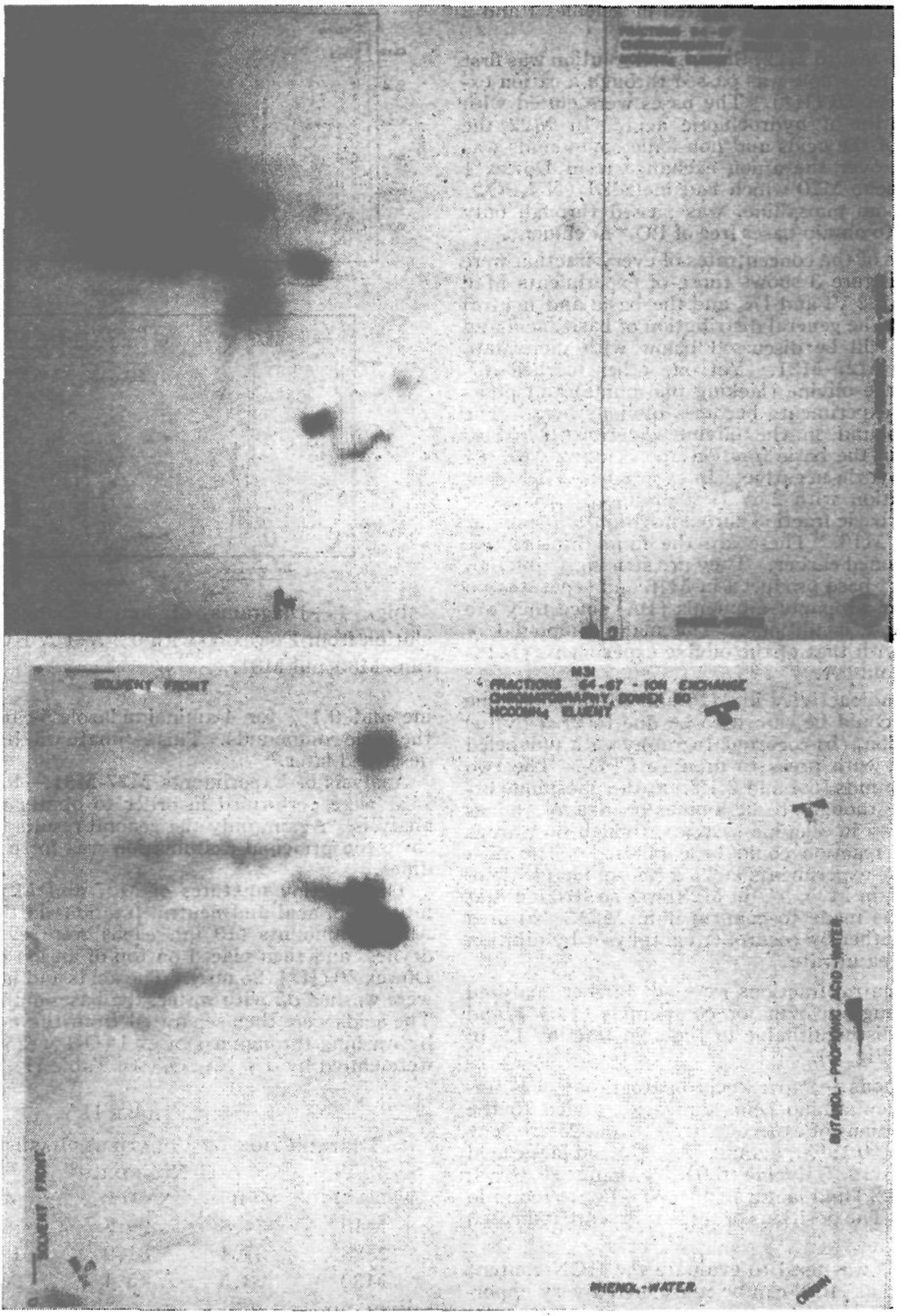

Fig. 5.—Chromatograms of fraction 64 from ammonium formate elution of M30 and M31.

N to 1.0 *N* ammonium formate buffer, *p*H 4, from a 500-ml. mixing chamber.

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

At first sight, the ion exchange elution diagrams appear to present a convenient method of comparison of the products of varied experiments in primordial chemistry; for example, one might suppose that the peaks at fraction 64 in both M30 M31 (Fig. 4) represent very similar products.

Figure 5 shows the chromatogram of fraction 64 in each of the above runs. Although some 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. As yet 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 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 non-ionic compounds. Table II includes all of the bata on the distribution of basic, acid and non-ionic 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 ranging from 3 to 9%. 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. From experiment M22 it appears that the volatiles are mainly neutral 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 non-volatile neutral fractions of M30 and M31, a one-dimensional chromatogram was run together with the products of a $Ca(OH)_2$ condensation of formaldehyde.[28,29] This condensation yields mixtures of aldoses and ketoses.[29] In Fig. 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.[3-20,30,31] The formation of urea in large amounts in one of the irradiated 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.[32]

We suggest the synthesis of urea through oxidation by the reactions[32]

$$2HCN + 2OH(H_2O_2) \longrightarrow 2HOCN + H_2O$$

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

the latter being the well known Wöhler synthesis. 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.[2b]

Perhaps the most astonishing result which appeared in this initial examination is the fact that very nearly all, that is over 90%, 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 as a major product 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.

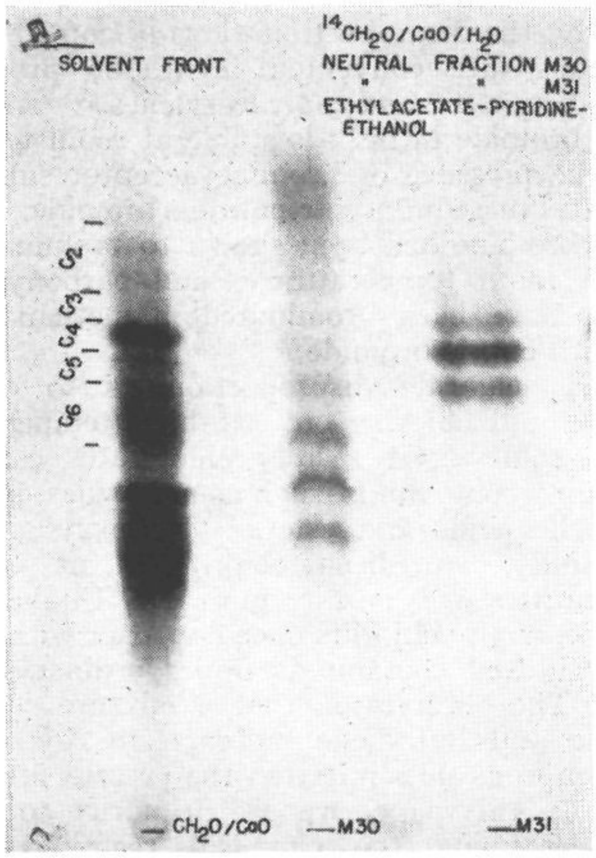

Fig. 6.—Neutral fraction of M30 and M31 in comparison to "formose" from formaldehyde and CaO; solvent: ethyl acetate–pyridine–water 10:3:3.

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. This will apply to electron beam irradiation and should be extendible to other energy sources such as electric discharge and ultraviolet light as well. These latter two processes have heretofore been considered as the principal energy sources in primordial syntheses.

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Photolyses of Metal Compounds: Cupric Chloride in Organic Media

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RECEIVED NOVEMBER 13, 1961

The reactions resulting from the photolysis of cupric chloride in organic solvents have been examined. They can be described as the addition and abstraction reactions of chlorine. Alcohols are converted to carbonyl compounds, olefins to dichlorides and allylic chlorides, and alkanes or aralkanes to the corresponding chlorides. It is tentatively postulated on the basis of the reactivities of substrates and the stoichiometries of the reactions that the photolysis occurs by initial fission to form cuprous chloride and chlorine atoms. Chain termination involves the reaction of cupric chloride with carbon radical intermediates.

Introduction

The relatively accessible oxidation–reduction ranges of copper compounds make them useful agents for electron transfer processes. Thus, cupric ions oxidize iodide, cyanide, sulfite and thiocyanate ions under extremely mild conditions,[2]

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(2) (a) N. Sidgwick, "Chemical Elements and Their Compounds," Oxford Press, New York, N. Y., 1950, p. 148 ff.; J. Baxendale, D.