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The question of the conditions under which living matter originated on the surface of the earth is still a subject limited largely to speculation. The speculation has a greater chance of approaching the truth insofar as it includes and is based upon the ever wider variety of established scientific fact. One of the purposes of the herein reported observation was to add another fact to the ever increasing information which might have any bearing upon this most interesting question. It is not our purpose in the present communication to discuss the various proposals or the arguments which have been adduced for and against them.

One of the most popular current conceptions is that life originated in an organic milieu on the surface of the earth. (1,2,3,4,5) The problem to which

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(1) A. I. Oparin, "Origin of Life", Translated by S. Morgulis. Macmillan Co., New York, N. Y. (1938). pp 271.

(2) N. H. Horowitz, Proc. Nat. Acad. Sci., 31, 153 (1945)

(3) George G. Simpson, "Meaning of Evolution", Yale University Press, New Haven, Connecticut (1950)

(4) C. B. van Niel, "Photosynthesis in Plants", Chapter 22, Iowa State College Press, Ames, Iowa (1949), pp 437-495.

(5) J. B. S. Haldane, Pelican Books (1932).

we are addressed is the origin of that organic milieu in the absence of any life. It appeared to us that one source, if not the only source, of reduced carbon compounds in complex arrangements might be the interaction of various high energy radiations with aqueous solutions of inorganic materials, particularly carbon dioxide, and nitrogenous compounds such as ammonia and nitrogen, since it appears that these compounds were the commoner forms in which the essential elements found themselves on the primordial earth (6,7).

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(6) W. M. Latimer, Science, 112, 101 (1950).

(7) H. Wartenburg, Naturwiss., 18, 400 (1950).

While it has long been known that high energy radiations can cause organic decomposition and oxidation, it seemed useful to us to demonstrate that conditions could be found in which high energy radiations could induce the reduction with water of carbon dioxide and the ultimate creation of polyatomic molecules (other than simple polymerization of monomers) of carbon, oxygen, hydrogen and nitrogen.

Experimental

The general technique employed in this investigation was to bombard air-free aqueous solutions of C^{14} labelled CO_2 in a closed system with and without the addition of ferrous sulfate. The bombardments were made using the 40 Mev helium ion beam of the 60-inch cyclotron at Crocker Laboratory. To detect the amount and nature of the reduction products, chemical separations were made on the bombarded solution after the addition of carrier amounts of formic acid, formaldehyde, and methyl alcohol. These were separated as solid derivatives and assayed for C^{14} activity. In most of the bombardments one millicurie of from 5 to 9 percent C^{14} labelled CO_2 was used. This made it possible to detect the reduction of approximately one part in 10^6.

Target Assembly

A diagram of the target assembly is shown in Figure 1. The aqueous solutions were bombarded in an all-glass target cell (A) which consisted essentially of a 50 ml pyrex flask one side of which was drawn in to give a window (B) having an average thickness of approximately 5 mil over the bombarded area. The cell had a volume of 12 ml. It was connected to a glass manifold (C) which in turn was connected through stopcocks to a 100 ml product gas storage bulb (D) to a 25 ml CO_2 reservoir (E) to a mercury manometer (F) and to an outlet (G) through which the entire system could be evacuated. The assembly was supported on a bracket (H) which was fastened to the bell-jar type target (I). The helium ion beam was brought out of the cyclotron vacuum through a 1.5 mil aluminum foil (J) and was delimited in cross section by the aperture (K) in plate (L). The target window was cooled by means of an air stream which entered at (M) and emerged through the aperture (K). The beam current was monitored through the electrode (N). With the all-glass target cell, it was necessary, because of the non-uniform thickness of the window, to calculate the number of ion-pairs produced from the amount of Fe^{+2} oxidation, assuming the same ion-pair yield for this reaction in the glass cell as was obtained in the cell having the platinum window. With the latter target cell, it was possible to estimate within a few percent the energy loss of the helium ions in penetrating the 1.5 mm aluminum foil, 10 cm of air path, and the one mil platinum window.

Bombardment Procedure

The target cell was first flushed with nitrogen, then filled with triple-distilled deaerated water, or deaerated one molar ferrous sulfate solution at a pH of approximately 3.5. The water was deaerated by boiling and then allowed to cool in a glass-stoppered vessel which had been filled with nitrogen gas. The one molar ferrous sulfate solutions were prepared by adding a known weight of ferrous sulfate. After the target cell was filled, it was immediately

connected to the manifold which was then evacuated until roughly 5 percent of the target solution had been evaporated. Stopcock (1) was then closed and the manifold was evacuated including the product gas storage bulb and that portion of the manifold to stopcock (2) which was connected to the CO_2 reservoir containing approximately one millicurie of from 5 to 9 percent C^{14} labelled CO_2. After the evacuation was complete, the manifold was isolated by closing stopcock (3). Stopcocks (1)(2) were then opened and the CO_2 was allowed to equilibrate with the target solution. The target cell was then bombarded with a 0.5 μa beam of 40 Mev helium ions. Bombardment data for each of the experiments are summarized in Table I.

Chemical Procedures

After bombardment, the target cell was allowed to stand for from 1 to 2 hours to permit the induced radioactivity to decay out. Stopcocks (1)(2) were closed and the target cell was removed from the manifold. The solution was then treated with sulfuric acid to dissolve the ferric hydroxide and adjusted to pH 1. The unreacted $C^{14}O_2$ was stripped with nitrogen and recovered in NaOH solution. After most of the high specific activity $C^{14}O_2$ had been removed, the solution was then flushed with tank CO_2 which was discarded. A sample of the solution was withdrawn at this point for ferric ion analysis.

To the remainder of the solution was added formic acid, formaldehyde and methyl alcohol carriers in amounts to give 100 milligrams of the isolated product, i.e., barium formate, methone derivative of formaldehyde, and barium carbonate prepared from the CO_2 formed on oxidation of the methyl alcohol fraction.

The pH of the solution was then adjusted to 7 and the formaldehyde and methyl alcohol were distilled "in vacuo". The distillate was treated with methone solution in 50 percent excess and acidified. This precipitated the methone-formaldehyde derivative and the methyl alcohol was separated from this mixture by a second vacuum distillation. The methyl alcohol distillate was

wet oxidized with a chromium trioxide-sulfuric acid mixture containing potassium iodate and the evolved CO_2 was recovered as barium carbonate. In none of the bombardments was this barium carbonate fraction active.

The methone-formaldehyde precipitate was filtered off, washed and dissolved in sodium hydroxide. The solution was acidified and the precipitate centrifuged, washed, redissolved in NaOH, and reprecipitated. This procedure was repeated and then the methone-formaldehyde reaction product was recrystallized twice from acetone-water. A sample of the purified methone-formaldehyde product was counted.

The residue from the first distillation containing the formic acid was acidified to pH 1 and distilled "in vacuo". The distillate was titrated to phenolphthalein endpoint with a saturated barium hydroxide solution after flushing with CO_2 followed by nitrogen. The precipitate of barium carbonate which formed was centrifuged off. The supernatant containing the barium formate was evaporated to approximately 0.5 ml and while warm, was treated with absolute ethyl alcohol which precipitated crystalline barium formate. This was redissolved in water and recrystallized in this manner four times.

A fraction of original solution which had been removed for iron determination was acidified with 6 N H_2SO_4 and titrated with standard solution of potassium permanganate. A second fraction of this solution was reduced with SO_2 and titrated with $KMnO_4$ after the excess SO_2 was removed by boiling. The Fe^{+3} concentration in the target solution was calculated from the difference in titre. In Table I, bombardments 1, 2, and 3 were made using the all-glass cell. Bombardment 4 was made using the cell having a one mil platinum window. With this cell, the helium ion beam incident on the solution had an energy of 35.8 Mev. The number of ion-pairs produced in bombardments 1, 2, and 3 were calculated assuming that the ion-pair yield for ferric ion oxidation obtained in bombardment 4 was also obtained using the all-glass target cells. This assumption is considered

reasonable since the energy loss in the glass and platinum windows were of the same order of magnitude.

To insure that $HC^{14}OOH$ and $HC^{14}HO$ were actually produced by helium ion bombardment, the following additional control experiments were made: (1) A sample of the original unbombarded target solution containing $C^{14}O_2$ and $FeSO_4$ was retained at approximately 30°C. for one week and then processed in a manner identical to that used in separating the HCOOH, HCHO and CH_3OH fractions in the bombarded samples. No C^{14} activity could be detected in these fractions from the unbombarded solution indicating that reduced C^{14} compounds were not present in the original solution or formed by a metabolic process involving mold or other organisms. (2) A blank bombardment (#5) was made without added $C^{14}O_2$ and the isolated HCOOH and HCHO carriers were inactive. (3) Mass absorption curves run on active barium formate produced in the radiation reduction of $C^{14}O_2$ were identical with those obtained using known samples of active barium formate prepared chemically and having the same specific activity and counting geometry. (4) No decay could be detected in the activity of the radiation produced $HC^{14}OOH$ and $HC^{14}HO$.

Discussion

An examination of Table I demonstrates unequivocally that it is quite possible to reduce appreciable quantities of carbon dioxide to formic acid by means of water through the agency of radiation. In fact, it appears that approximately one-fourth of the dissolved carbon dioxide was reduced in experiment #4. Whether or not the formic acid is further reduced to formaldehyde or whether the formaldehyde has its origin in a direct reduction of carbon dioxide still remains to be demonstrated, but formaldehyde can also be produced from carbon dioxide and water under the influence of radiation.

The actual ion-pair yield is certainly not optimal even in the experiment #2 in view of the large excess of the number of ion pairs produced over the number of molecules of carbon dioxide in the solution. Presumably, this reduction is achieved by means of the secondary hydrogen atoms resulting from the ionization. The actual amount of reduction observed is clearly still only the resultant of the reduction and oxidation reactions. The oxidation reaction is presumably minimized by the destruction of the hydroxyl radicals by their reaction with ferrous ion. (8,9,10)

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(8) J. Weiss, et al, J. Chem. Soc., 1949 - 3241, 3245, 3254, 3256; 1950 - 2704, 2709; 1951, 25.

(9) M. Burton, J. Phys. Colloid Chem. 51, 611 (1947)

(10) A. O. Allen, J. Phys. Colloid Chem. 52, 479 (1948)

Whether or not carbon-carbon bonds and carbon-nitrogen bonds can be formed and more highly organized structures created under the influence of high energy radiations is at present under investigation.

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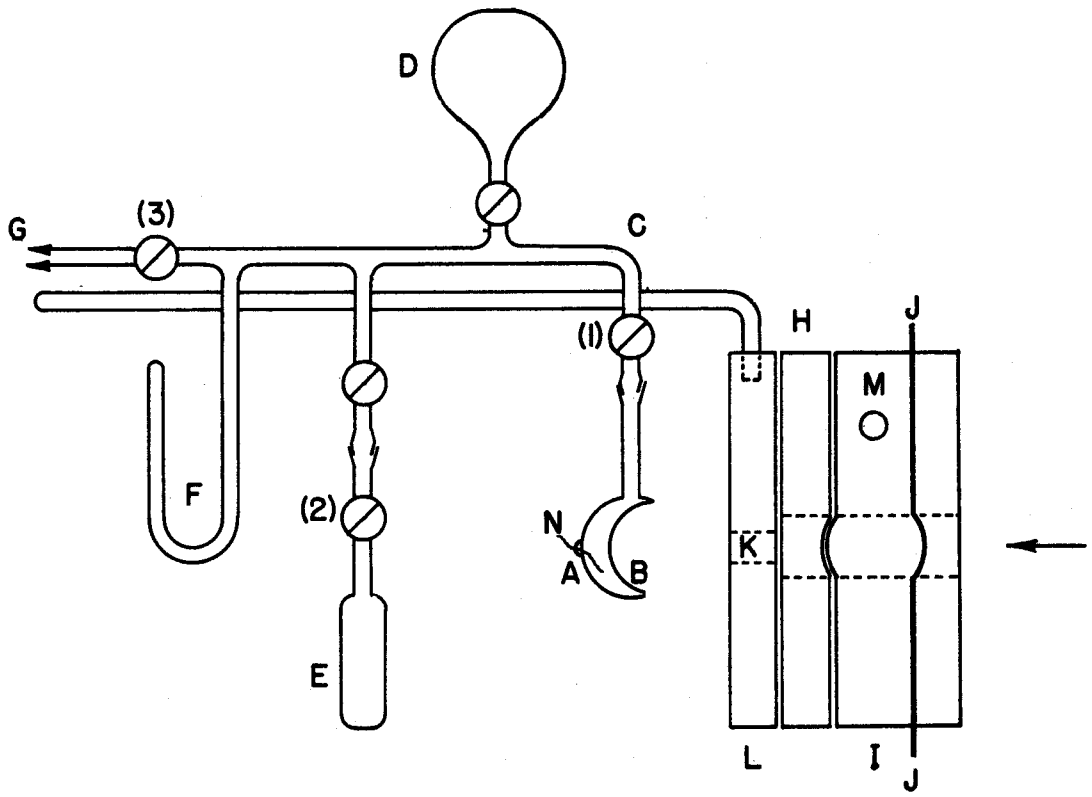
TABLE I

Bombardment	(1)	(2)	(3)	(4)	(5)
Cell Window	glass	glass	glass	platinum	glass
Solute	$C^{14}O_2$+$FeSO_4$	$C^{14}O_2$+$FeSO_4$	$C^{14}O_2$	CO_2+$FeSO_4$	CO_2+$FeSO_4$
Volume of solution (cc)	12.0	12.0	12.0	13.0	12.0
Gas volume, manifold + product gas bulb (cc)	145.	145.	145.	145.	145.
Initial concentration of $C^{14}O_2$ in solution (M)	6.8×10^{-5}	8.2×10^{-5}	1.0×10^{-5}	8.2×10^{-5}	$\sim 8\times10^{-5}$
Number of CO_2 Molecules dissolved in H_2O phase	5.5×10^{17}	6.7×10^{17}	8.3×10^{17}	6.2×10^{17}	$\sim 7\times10^{17}$
Partial pressure of $C^{14}O_2$ in gas space (mm Hg)	2.4	2.9	3.6	2.7	
C^{14} activity (mc)	1	1	1	none	—
C^{14} in CO_2 (%)	9.0	6.0	4.8	—	—
Energy of emerging helium ions (Mev)	40.	40.	40.	40.	40.
Bombardment current (μa)	0.5	0.5	0.5	0.5	0.5
Total bombardment (μa-hr)	0.75	0.042	0.042	0.13	0.13
Number of ion-pairs produced in solution(assuming 32.5e.u./i.p.)	7.8×10^{21}	4.4×10^{20}	4.4×10^{20}	3.1×10^{21}	1.3×10^{21}
Hydrogen pressure after bombardment (mm Hg)	208.	8.	(*)	(*)	(*)
Number of hydrogen molecules produced	1.1×10^{21}	$.43\times10^{20}$	—	—	—
Initial concentration of Fe^{+2} (M)	0.80	(*)	none	0.77	—
Concentration of Fe^{+3} after bombardment	0.23	—	—	0.10	—
Number of Fe^{+3} atoms formed	1.5×10^{21}	—	—	6.2×10^{20}	—
Ion-pair yield for Fe^{+3} formation	0.20	—	—	0.20	—
Total C^{14} activity in the HCOOH fraction (μc)	0.21	1.32	8.7×10^{-3}	inactive	inactive
Number of CO_2 molecules reduced to HCOOH	2.2×10^{16}	1.5×10^{17}	1.2×10^{15}	—	—
Fraction of dissolved CO_2 reduced to HCOOH	0.04	0.22	1.4×10^{-3}	—	—
Ion-pair yield for HCOOH formation	2.9×10^{-6}	3.4×10^{-4}	2.8×10^{-6}	—	—
Total C^{14} activity in the HCHO fraction (μc)	5.7×10^{-3}	8×10^{-3}	inactive	inactive	inactive
Number of CO_2 molecules reduced to HCHO	6.4×10^{14}	9×10^{14}	—	—	—
Ion-pair yield for HCHO formation	0.82×10^{-7}	2.1×10^{-6}	—	—	—

(*) not determined



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