Title

Formation of Cyanamide Under "Primitive Earth" Conditions

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Abstract. The dimer of cyanamide, dicyandiamide, is formed on the ultraviolet irradiation of dilute cyanide solutions, and by the electron irradiation of a methane-ammonia-water mixture. These results further indicate that cyanamide may have played an important role in chemical evolution.

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A recent paper by Steinman, et al. has pointed to cyanamide and its dimer, dicyandiamide, as possible key compounds in chemical evolution (1). These compounds cause the formation of pyrophosphate from orthophosphate, glucose-6-phosphate from glucose and H_3PO_4, and adenosine-5'-phosphate from adenosine and H_3PO_4. In all these reactions appreciable yields (1-3%) of products were obtained in a few hours from dilute (about one millimolar) aqueous solutions at room temperature.

If cyanamide played a major role in chemical evolution, it must have been formed steadily on the primitive Earth. Consequently, we undertook to look for cyanamide formation under the kinds of "primitive Earth conditions" (e.g., ultraviolet irradiation of HCN solutions, ionizing irradiations of CH_4-NH_3-H_2O mixtures) that are known to form such biologically-important compounds as the amino acids (2), sugars (3), and adenine (4,5).

Experimental

The labeled cyanide, $K^{14}CN$ (15.4 uc/mg) used in these experiments was obtained from the Cal Rad Corp., Burbank, Calif. The $H^{14}CN$ was prepared by reacting the $K^{14}CN$ with concentrated sulfuric acid on a vacuum line and trapping the evolved $H^{14}CN$ at 77°K. Ammonium cyanide solutions were prepared by adding NH_4OH solutions directly to the $H^{14}CN$. Control experiments (chromatography of the unirradiated solutions) showed the absence of any detectable cyanamide or dicyandiamide.

For the ultraviolet irradiations the solutions (Table I) were placed in quartz tubes and irradiated for 20 hours with a high-pressure mercury arc (General Electric type A-H6) at a distance of 7.5 cm. During the irradiations the samples were kept at 25-35° by an air stream. After irradiation, the reaction mixtures were evaporated to dryness *in vacuo* at room temperature, and the total (non-volatile) radioactivity determined. Aliquot portions were paper chromatographed on oxalic acid-washed Whatman No. 4 paper or on "Ederol" chromatography paper (J. C. Binzer Co., Hatzfeld am Eder, West Germany). The initial solvent systems used were n-butanol-propionic acid-water (75:36:49 by vol.) and propanol-16 *N* NH_4OH-water (6:3:1). Radioactive spots (shown by autoradiographs) that had the same Rf values as those for cyanamide and dicyandiamide were cut out, eluted, and co-chromatographed with the authentic compounds in (1) n-butanol-ethanol-water (4:1:1) and (2) isopropanol-methanol-water (18:1:1). The cyanamide and dicyandiamide were made visible by spraying the paper with a solution of 5% potassium nitroprusside-10% NaOH-3% H_2O_2-water (2:1:5:15).

The electron irradiations of the $^{14}CH_4$-NH_3-H_2O mixture were carried out as previously described (4), except that no H_2 was used in the present experiment. After the irradiation, the chromatographic search for cyanamide and dicyandiamide was done in the same way as in the cyanide solution-UV irradiations.

Table I lists the conditions employed and the results obtained in the search for cyanamide and dicyandiamide.

Table I

Formation of Dicyandiamide in "Primitive Earth" Experiments

Reactants	Energy Source	Total Activity Irradiated, μc	% Activity Fixed as Non-Volatile Cpds.	% C^{14} Substrate Converted to Dicyandiamide*
1 ml of 7.5×10^{-5} molar $H^{14}CN$	UV	10	7.3	1.9
1 ml of 7.5×10^{-5} molar $NH_4{}^{14}CN$ and 1.8×10^{-3} molar NH_3	UV	10	3.2	3.5
$^{14}CH_4$, NH_3, H_2O	e^- beam	500	2.4	0.02
$^{14}CH_4$, NH_3, H_2O	"	500	1.2	0.002

*There was no detectable cyanamide monomer produced in these experiments. However, the monomer is known to dimerize readily in both acidic and basic solutions (6).

The above experiments reinforce the idea that the cyanamide dimer (dicyandiamide) was formed on the pre-biotic Earth and that this compound could have played a key role in chemical evolution.

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