Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

FORMATION OF CYANAMIDS UNDER ""PRIMITIVE EARTH"" CONDITIONS

Permalink

https://escholarship.org/uc/item/35w6c15n

Authors

Schimpl, Anneliese Lemmon, Richard M. Calvin, Melvin

Publication Date

1964-11-01

University of California

Ernest O. Lawrence Radiation Laboratory

FORMATION OF CYANAMIDE UNDER "PRIMITIVE EARTH" CONDITIONS

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

UCRL-11771

UNIVERSITY OF CALIFORNIA Lawrence Radiation Laboratory Berkeley, California

AEC Contract No. W-7405-eng-48

FORMATION OF CYANAMIDE UNDER "PRIMITIVE EARTH" CONDITIONS

Anneliese Schimpl, Richard M. Lemmon, and Melvin Calvin
November 1964

NOV: ----

FORMATION OF CYAHAMIDE UNDER "PRIMITIVE EARTH" CONDITIONS

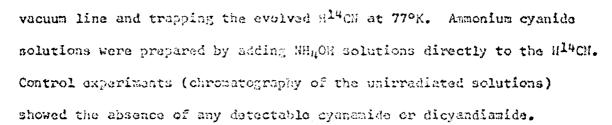
Abstract. The dimer of cyanamide, dicyandiamide, is formed on the ultraviolet irradiation of dilute cyanide solutions, and by the electron irradiation of a methane-ammonia-water mixture. These results further indicate that cyanamide may have played an important role in chemical evolution.

A recent paper by Steinman, et al. has pointed to cyanamide and its dimer, dicyandiamide, as possible key compounds in chamical evolution (1). These compounds cause the formation of pyrophosphate from orthophosphate, glucose-5-phosphate from glucose and HgPOq, and adenosine-5'-phosphate from adenosine and HgPOq. In all these reactions appreciable yields (1-35) 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 CHu-NH3-H2O mixtures) that are known to form such biologically-important compounds as the amino acids (2), sugars (3), and adenino (4,5).

Experimental

The labeled cyanide, Kl4CH (15.4 µc/mg) used in these experiments was obtained from the Cal Rad Corp., Burbank, Calif. The H¹⁴CH was prepared by reacting the K¹⁴CH with concentrated sulfuric acid on a



For the ultraviolet irradiations the solutions (Table I) were placed in quartz tubes and irradisted for 20 hours with a high-pressure mercury arc (General Electric type A-HC) 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 exalic acid-washed Whatman No. 4 paper or on "Ederol" chromatography paper (J. C. Binzer Co., Hatzfold am Eder, West Germany). The initial solvent systems used were n-butenol-propionic acid-water (75:36:49 by vol.) and propanol-16 % NHaOH-water (6:3:1). Radioactive spots (shown by autoradicaraphs) 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-mathanol-water (18:1:1). The cyanamide and dicyandiamide were made visible by spraying the paper with a solution of 5% potaesium nitroprussida-10% NaOH-3% HoOo-water (2:1:5:15).

The electron irradiations of the 14CH4-NH3-H2O mixture were carried out as previously described (4), except that no H2 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 cyanida solution-UV irradiations.

			r
			,
			1

ENT.

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		Total Activity Irradiated, uc		Converted to
1 ml of 7.5 x 10 ⁻⁵ molar H ¹⁴ CH	υv	10	7.3	1,9
1 ml of 7.5 x 10-5 molar NH ₄ 14CH and 1.8 x 10-3 molar NH ₃	î UV	10	3.2	3.5
14сни, лиз, н20	e- beam	500	2.4	0.02
14СНц, инз. н20	n `	500	1.2	0.002

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

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

Anneliese Schimpl (7)
Richard M. Lemmon
Melvin Calvin

Lawrence Radiation Laboratory and Department of Chemistry (8) University of California Berkeley, California

References

- G. Steinman, R. H. Læmmon, and H. Calvin, Proc. Hat. Acad. Sci. <u>52</u>,
 27 (1954).
- 2. S. L. Miller, J. Am. Chem. Soc. 77, 2351 (1355).
- 3. C. Ponnamperuma, Nature 201, 337 (1984).
- 4. C. Ponnamperuma, R. M. Lemmon, and M. Calvin, Proc. Nat. Acad. Sci. 49, 737 (1963).
- 5. J. Oré and A. P. Kimball, Arch. Biochem. Biophys. 34, 217 (1961).
- 6. H. E. Williams, Cyunogen Compounds (Edward Arnold and Co., London, 2nd Ed., 1948), p. 19.
- 7. Present address: Organisch-Chemisches Institut der Universität Wien, Austria.
- 8. This work was sponsored, in part, by the U. S. Atomic Energy Commission.