

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

To be published in Science

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

RL

Sumner

11771

NOV 1958

FORMATION OF CYANAMIDE 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 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 μ c/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-28) 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 $^{14}\text{CH}_4\text{-NH}_3\text{-H}_2\text{O}$ 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

<u>Reactants</u>	<u>Energy Source</u>	<u>Total Activity Irradiated, μc</u>	<u>% Activity Fixed as Non-Volatile Comp.</u>	<u>% C^{14} Substrate Converted to Dicyandiamide*</u>
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_3 , ^{14}CN and 1.9×10^{-3} molar NH_3	UV	10	3.2	3.5
$^{14}\text{CH}_4$, NH_3 , H_2O	e^- beam	500	2.4	0.02
$^{14}\text{CH}_4$, 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.

Anneliese Schimpl (7)

Richard M. Lemmon

Malvin Calvin

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

References

1. G. Steinman, R. M. Lemmon, and M. Calvin, Proc. Nat. Acad. Sci. 52, 27 (1954).
2. S. L. Miller, J. Am. Chem. Soc. 77, 2351 (1955).
3. C. Ponnamparuna, Nature 201, 337 (1964).
4. C. Ponnamparuna, R. M. Lemmon, and M. Calvin, Proc. Nat. Acad. Sci. 49, 737 (1963).
5. J. Oró and A. P. Kimball, Arch. Biochem. Biophys. 94, 217 (1961).
6. H. E. Williams, Cyanogen 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.