Chemical Forms Assumed by C14 Produced by Neutron Irradiation of Beryllium Nitride

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The nature of the radioactive compounds formed in the production of C^{14} by neutron irradiation of beryllium nitride has been investigated. Solution of the irradiated powder gave activities corresponding to methane, carbon monoxide, carbon dioxide, hydrogen cyanide, methanol, and formic acid. Formaldehyde was not found. The distribution of activities is not affected by the acidity of the solvent. The results are considered in the light of earlier work.

AS an extension of earlier work,[1] we have made chemical fractionations of the carbon fourteen activity induced in powdered beryllium nitride by neutron bombardment. The nuclear reaction $N^{14}(n,p)C^{14}$ gives the product atom an energy of at least 40,000 ev. Though the velocity associated with such a recoil carbon fourteen atom is approximately that of an electron of 1.6-ev energy, one can expect definite chemical effects.

EXPERIMENTAL

The beryllium nitride was prepared from finely powdered beryllium metal by exposure to nitrogen at high temperature.[2,3] The powder was pressed into aluminum cans for irradiation at Hanford.

The first experiment was an analysis for total carbon radioactivity. Approximately 25 mg of the irradiated powder was placed in a small three-necked flask connected to a copper oxide-filled combustion tube. The tube was held at 650°C and was fitted with an absorption bubbler filled with $1N$ sodium hydroxide. The sample was dissolved by warming in 10 ml of $6N$ sodium hydroxide. When solution was complete a drop of methanol was added (to serve as carrier for any non-gaseous activities) along with 25 ml of saturated potassium permanganate solution. A stream of oxygen was started to sweep gases

evolved into the combustion tube. The solution was brought to a boil and excess $6N$ sulfuric acid added to liberate carbon dioxide. All carbon fourteen activity was recovered by this procedure.

In the second and third experiments about 50 mg of the irradiated powder was dissolved in sodium hydroxide. The gases were swept out with a stream of oxygen and passed through an analytical train consisting of two combustion tubes, each fitted with an absorber, one at 325°, the other at 650°. Activity caused by carbon monoxide was collected in the first absorber, that from methane in the second. After these fractions were collected a small amount of inactive sodium cyanide was dissolved in the contents of the flask and the solution carefully acidified. The gases were swept first through $0.1M$ acetic acid saturated with silver acetate, and then through sodium hydroxide. Hydrogen cyanide was removed as silver cyanide in the first bubbler, and carbon dioxide was absorbed in the second.

Different procedures were used past this point in the second and third experiments. In the second, a small amount of inactive methanol was added and the total non-gaseous (oxidizable) activity collected as in the first analysis. In the third experiment, small amounts of inactive methanol, formaldehyde and formic acid were added. These compounds were then separated from the bulk of the original solution by distilling it to dryness. Formaldehyde was separated from the distillate as the 2,4-dinitrophenylhydrazone. The filtrate from this operation was made alkaline and distilled to about one-tenth its original volume. The distillate contained the methanol

[1] Yankwich, Rollefson, and Norris, J. Chem. Phys. **14**, 131 (1946).
[2] Fichter and Brunner, Zeits. f. anorg. allgem. Chemie **93**, 86 (1915).
[3] The preparation was carried out by Dr. Leo Brewer and Mr. Paul Gillies. An analysis by Dr. B. M. Tolbert showed BeO 2 percent, Be 7 percent, and Be_3N_2 91 percent.

and the residue the formate. These solutions were made alkaline and the carbon compounds oxidized to carbonate with excess potassium permanganate. After acidification the carbon dioxide was swept out with oxygen and converted to barium carbonate for counting.

The radioactivities of the several samples were determined with a thin mica-window counter-tube. This tube and the method of correction for self-absorption of the beta-particles are described elsewhere.[1,4-6] The results of the fractionations are shown in Tables I and II.

A satisfactory material balance has not been obtained yet on the oxidizable fraction, through the formaldehyde is known to be inactive. In this fractionation and in subsequent experiments in which only these oxidizable activities were isolated, about 20 c/m/mg Be$_3$N$_2$ was carried by the original formaldehyde-2,4-dinitrophenyl-hydrazone precipitate. When twice recrystallized from hot 50 percent-ethanol this hydrazone was found to be inactive. Several other experiments gave values for the formic acid and methanol activities which were in approximately the same ratio. In an experiment in which the beryllium nitride was dissolved in 6N sulfuric acid, no significant departure from the activity distribution in Table I was detected.[7]

DISCUSSION

Beryllium nitride powder of this composition has the following atomic constitution: Be, 62.8 percent, N, 36.3 percent, and O, 0.9 percent. In such an environment the first combinations of energetic carbon atoms must be with beryllium, nitrogen, or oxygen, in that order of probability. The eventual distribution of combined radio-carbon with these atomic species is not wholly predictable. No previous analysis has been carried out on substances capable of forming a metallic carbide during irradiation. However, methane is known to be the hydrolysis product of beryllium carbide, Be$_2$C, and it is reasonable to conclude that the active methane is derived from the radio-carbide, Be$_2$C^{14}, formed during

TABLE I. Distribution of activity in irradiated Be$_3$N$_2$.

	c/m/mg Be$_3$N$_2$	Percent
Total activity	31,000±700	100.0
CO	272±7	0.87
CH$_4$	19,700±400	62.7
CO$_2$	1,050±100	3.34
CN$^-$	1,100±100	3.50
Oxidizable	8,530±200	27.2
Not recovered	750±850	2.39

TABLE II. Activities in the "oxidizable" fraction.

	c/m/mg Be$_3$N$_2$
HCHO	0±2
CH$_3$OH	>200
HCOOH	>5000
Known total oxidizable	8530±200

the irradiation.[8] The sources of the radioactive cyanide, and at least part of the active oxides are apparent. Since they both contain hydrogen, methanol and formic acid must be produced during the hydrolysis. It is conceivable that cyanide is the source of the acid, but ordinary cyanide ion is ruled out because it hydrolyzes slowly to formic acid. Some non-ionic C−N combination trapped in the crystal lattice is probably the precursor of this activity. Similarly, radio-carbon monoxide could hydrolyze to formic acid in irradiated aqueous solutions; however, as with cyanide ion, the rate of hydrolysis of the normal compound is known to be slow at room temperature. In view of the large amount of formic acid and the 40:1 nitrogen-oxygen ratio, nitrogen-carbon combinations constitute the more probable source.

In the earlier work methanol was not found in solid hydrazine hydrochloride, and its appearance in this research was therefore not expected. Because of the highly reduced carbon atom, it is probable that the precursor of the methanol is similar to that of methane, not so much a "carbide" carbon as an isolated carbon atom trapped in the crystal. A simple path for its formation is that proposed earlier for its appearance in irradiated aqueous solutions:
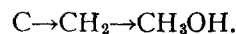
$$C \rightarrow CH_2 \rightarrow CH_3OH.$$

[4] Yankwich, Norris, and Huston, Ind. Eng. Chem., Anal. Ed. 19, (in press).
[5] Dauben, Reid, and Yankwich (to be published).
[6] Libby, Ind. Eng. Chem., Anal. Ed. 19, 2 (1947).
[7] Dr. B. A. Fries performed this analysis.
[8] Professor W. F. Libby first reported the production of a relatively large amount of active methane.