[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Chemical Forms Assumed by C^{14} Produced by the Reaction Be_3N_2(n,p)

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Chemical fractionations have been made of the radiocarbon activities produced when pile neutron-irradiated beryllium nitride crystals are dissolved in 2 *N* sulfuric acid. Methane is formed in greatest amount (26% of the total activity); other radio compounds found are guanidine (19%), carbon dioxide (14%), methylhydrazine (11%), formic acid (8%), hydrogen cyanide (7%), urea (6%), cyanamide (5%), methylamine (4%), formaldehyde (2%), and methanol and carbon monoxide (each less than 0.2%). Similar results were obtained upon solution of the target in 12 *N* sulfuric acid. Physical models for the slowing down of the C^{14} recoil fragment in the target matrix suggested by Libby and by the work of Seitz and Koehler are compared; the two result in similar chemical predictions where a simple ionic target substance is involved.

When samples of neutron-irradiated beryllium nitride are dissolved in aqueous alkali, numerous one-carbon compounds containing C^{14} can be identified among the products.[1] In the early work the chemical fractionation procedures applied to the non-gaseous fraction of the products were sufficiently crude that a detailed analysis and activity balance could not be obtained with the limited amount of target material then available. In this paper we report the results of analyses of solutions in dilute aqueous sulfuric acid of pile-irradiated beryllium nitride; the analytical scheme is based on that reported in two recent papers.[2,3]

Experimental

Sample Preparation and Irradiation.—The beryllium nitride was prepared at the Oak Ridge National Laboratory, and was reported to be 48–50% nitrogen. A confirmatory analysis in this Laboratory on a small sample showed 50 ± 1% N, corresponding to about 98% Be_3N_2. At the time of analysis the remainder appeared to be mostly BeO; but, since the sample had been exposed to air after irradiation, the remainder probably consisted largely of unreacted Be metal at the time of packaging for insertion in the pile. The target, 28 g. of beryllium nitride powder, was irradiated for 12 weeks in the Oak Ridge Pile in a thermal neutron flux of 6.6×10^{11} cm.$^{-2}$ sec.$^{-1}$ and a gamma flux of 2.8×10^{11} photons-sec.$^{-1}$ cm.$^{-2}$ with an average energy of 0.9 m.e.v.[4] at a temperature of about 110°. Twenty-four months elapsed between the irradiation and the analysis; the nitride was stored in its original sealed container during this period, then transferred to an ordinary weighing bottle from which small samples were withdrawn for analysis. The irradiated crystals were in contact with air for the 4 months during which experiments were carried out.

Chemical Fractionation Procedures.—The general analytical scheme employed in this study was that described previously[2,3]: carbon dioxide, carbon monoxide and methane were removed from the solution of the target material in 2 *N* sulfuric acid by aeration, then separated by differential absorption and combustion; cyanide was precipitated as the silver salt; the other non-gaseous carriers were isolated from the filtrate from the cyanide precipitation by distillation procedures, by derivative preparation or by specific chemical reaction.

We identify here the method employed for the characterization of each activity, adding detail only for those carriers which were not used in the previous studies.

Carbon dioxide: direct absorption in aqueous sodium hydroxide. **Carbon monoxide**: differential combustion over Hopcalite. **Methane**: combustion over copper oxide wire. **Cyanide**: precipitated from acidic solution upon addition of aqueous silver nitrate. **Methylamine**: preparation of hydrochloride or chloroplatinate (the latter to test for possible contamination of the former with methylhydrazine hydrochloride). **Formic acid**: differential oxidation with mercuric acetate. **Formaldehyde**: formation of Methone derivative. **Methanol**: distillation separation from the above. **Urea**: hydrolysis with buffered jackbean urease. The beryllium ion behaves as a urease poison; accordingly, the results for urea activity are subject to unusually large error because a sizable blank correction was required. **Guanidine**: formation of the picrate. **Methylhydrazine**: methylhydrazine is converted partly to carbon dioxide and partly to methane by treatment with hot alkaline permanganate solution. Since no other species present yields methane under these vigorous conditions, the methylhydrazine activity was calculated from the specific activity of the methane produced. The yield of methane observed in trials was variable between about 35 and 45%, and, since the total activity per unit weight of target was estimated through alkaline permanganate oxidation, the corrected activity base reflects this variability. **Cyanamide**: removed, after cyanide, from an ammoniacal solution as the silver salt. **Formamidine and Methylenediamine**: these possible products hydrolyze in alkaline solution to formate and formaldehyde, respectively. They were estimated by comparing the activities of formate and formaldehyde fractions separated after such an hydrolysis with those of the same fractions obtained from solutions which were maintained acidic. The large imprecision noted in the compilation of results is a consequence of this difference method.

Results

The activities of carbon dioxide, methane, cyanide and an aliquot of the solution remaining (called Total Non-Gaseous in a previous paper[2]) were determined for every sample; other carriers, usually two or three per experiment, were separated as noted above. Where incomplete sample solution was effected, the carbon dioxide, methane, cyanide and TNG activities were observed to stand in the same ratios as when the sample did dissolve completely and their sum could thus be used as a base for computation of the percentage activities in the other carriers. In Table I are collected the average percentage activities due to each species, and the number of results obtained. The estimate of error is the average deviation from the mean value where the number of results is three or more; it is twice the difference of results where only two were obtained. For those activities given as zero, the estimated imprecision is that percentage activity which could have been masked by virtue of the difference technique employed.

In two early experiments, the beryllium nitride was dissolved in 12 *N* aqueous sulfuric acid. This solvent was not used later when other species had been discovered in the solutions, so the results are not of great merit; they do indicate, however, that the spectrum of products produced in the more concentrated acid medium is quite similar to that found in 2 *N* acid solvent. These results are collected in Table II.

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[1] P. E. Yankwich, *J. Chem. Phys.*, **15**, 374 (1947).

[2] P. E. Yankwich and J. D. Vaughan, THIS JOURNAL, **76**, 5851 (1954).

[3] P. E. Yankwich and W. R. Cornman, Jr., *ibid.*, **77**, 2096 (1955).

[4] The dose rate at this sample position was 5.0×10^5 R. per hour.

TABLE I

DISTRIBUTION OF C^{14} AMONG VARIOUS CHEMICAL FORMS; TARGET DISSOLVED IN 2 *N* SULFURIC ACID

Carrier	No. of results	Total of activity, %
CO_2	19	14.4 ± 1.1
CO	2	0.06 ± 0.01
CH_4	19	25.8 ± 1.1
HCN	19	6.5 ± 0.4
CH_3NH_2	6	4.1 ± 1.2
HCOOH	4	8.3 ± 0.4
HCHO	4	2.4 ± .4
CH_3OH	2	0.15 ± .05
$CO(NH_2)_2$	5	6.2 ± 1.4
$CNH(NH_2)_2$	2	18.7 ± 0.4
CH_3NHNH_2	2	11.2 ± .2
$CN(NH_2)$	3	4.6 ± .2
$HCNH(NH_2)$	2	0 ± .8
$CH_2(NH_2)_2 + CH_2NH$	3	0 ± .6
		102.2 ± 2.7

TABLE II

PARTIAL DISTRIBUTION OF C^{14}; TARGET DISSOLVED IN 12 *N* SULFURIC ACID

Carrier	Total activity, %	Carrier	Total activity, %
CO_2	10.9, 9.7	HCOOH	8.0, 11.1
CH_4	27.0, 23.6	HCHO	4.4, 6.5
HCN	6.9, 6.7	$CO(NH_2)_2$	4.5, 8.9
CH_3NH_2	3.5, 5.6		

Discussion

The results displayed in Table I are significantly different from those obtained in the first work on this target material.[1] In that study methane appeared to constitute 63% of the total radiocarbon activity, as opposed to 26% in the present instance; other results obtained then were: carbon dioxide, 3.3%; carbon monoxide, 0.9%; cyanide, 3.5%; TNG, 27%; methanol, 0.6%; formic acid, 16%. Part of the difference between the old and new results is certainly a reflection of incomplete analysis in the former, though it is difficult to explain the methane datum in this fashion. We shall limit our discussion to the results obtained during the exhaustive analysis of the present research.

At the moment of its creation, the C^{14} particle is a quadruply charged negative ion with a kinetic energy near 40 kev. The velocity of this ion is that of an electron of 1.56 e.v. energy; therefore all electrons bound to it by less than that energy will be swept off by the field of lattice ions, and, furthermore, it will be ineffective in causing the excitation of any electron unless the energy required for such a transition is close to 1.56 e.v. The electron affinity of the neutral carbon atom is about 1.2 volts, so an energetic C^{14} particle may exist as a C^- ion when its kinetic energy is less than about 30 kev.; since the electron affinity of $N^=$ is negative, the nitride ion is likely the source of the electrons which increase the negative charge of the radiocarbon recoil fragment. Though the cross-sections for ionization and electron excitation are very small, positive states of carbon could be formed by direct electron transfer to Be^{++} ions of the lattice. Carbon more highly oxidized or reduced than when as C^+ or C^- probably results from *chemical* processes in which binuclear or more complicated aggregates are formed, and their occurrence is unlikely before the energy of the carbon hot-atom has been reduced below 10–25 e.v.

Several models have been proposed which describe the physical events in which the recoil fragment participates while its energy is lowered from the initial 40 kev. to the 25 e.v. level where chemical reactions resulting in stable aggregates can take place. In an early paper dealing with these matters, Libby[5] assumed that the mean free path of an energetic recoil particle in an ionic lattice would be of the order of the mean ionic separation, for hard-sphere collisions. In beryllium nitride about 8 such collisions suffice to reduce the energy of a carbon hot-atom to the chemical reaction level, and this would correspond to the release of 40 kev. of energy in a volume containing about 150 ions: the local temperature of the region would be nearly 10^7°K. and the relaxation time for cooling of the heated zone (*i.e.*, for the temperature to fall to $1/e$ of its initial value) would be of the order of 10^{-9} second. More recently, Seitz and Koehler[6] have considered the problem with the view that at high particle energies the particle-lattice ion collision cross section is much smaller than the mean geometric cross-section. Under these conditions, the recoil fragment cannot be said to be entrapped by the lattice much before its energy has fallen to the order of 20–50 e.v.; this corresponds to a hot-spot temperature of less than 10^5°K., and a relaxation time for cooling of the order of 10^{-12} second, if the energy in this terminal hot spot is, at first, shared by the hot atom and 4 or 5 of its nearest neighbors.

The specifically chemical consequences of the two final environmental situations predicted by these models would be quite different if the target crystal consisted of molecular or complex ionic lattice units, where energy could be expended in disruption of covalent linkages as well as in the production of lattice displacements and deformation, but are similar where a simple ionic target substance is involved, as in the present case.

The appearance of nitrogenous compounds among the final products is evidence that the skeletons of complex chemical species are formed and persist in the irradiated crystals. The present study does not afford evidence that moderate changes in the character of the solvent have any important effects upon the spectrum of radiocarbon compounds observed (compare Tables I and II), provided that carriers are present for all activities when solution of the target takes place,[3,7] and allowance is made for possible alterations in the occurrence of exchange reactions. The presence of methylhydrazine among the products is important because it alone contains nitrogen of oxidation number different from −3 (that of ammonia and nitride ion); this may be an indication that intra-"molecular" oxidation–reduction processes take place upon destruction of the target matrix.

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(5) W. F. Libby, THIS JOURNAL, **69**, 2523 (1947).

(6) F. Seitz and J. S. Koehler, Technical Report No. 6, USAEC Contract AT(11-1)-182, June 1, 1955. See also, *Advances in Solid State Physics*, **2** (1956). This is an extensive treatment of the theory of lattice displacements produced during irradiation.

(7) W. S. Koski, THIS JOURNAL, **71**, 4042 (1949).

In Table III is shown the distribution of radiocarbon activity among various formal oxidation states. Where the individual ion charges in a simple ionic crystal are not very different we would expect the energetic carbon recoils to come to rest in terminal hot-spots which exhibited a more or less symmetrical distribution of oxidizing and reducing characters. Provided that the solvent has a similar character (*e.g.*, it is not capable only of causing reduction, as would be the case with liquid ammonia), we would expect a similar symmetrical distribution of radiocarbon among various final oxidation states. This result is actually observed not only for beryllium nitride, but for ammonium sulfate target[3] where both reducing and oxidizing species are available in the lattice.

TABLE III

PERCENTAGE OF TOTAL RADIOCARBON ACTIVITY IN VARIOUS OXIDATION STATES, Be_3N_2 TARGET

	%
+4	43.9
+2	14.9
0	2.4
−2	15.4
−4	25.8

Effect of Pile Radiations.—In the foregoing discussion we have presumed that there is no sensible integrated effect of the pile flux of γ-- and X-rays. In the absence of more detailed information concerning the specific origins of the several product species, one can only estimate the possible importance of radiation-induced reactions. Following the calculation method employed in a previous publication,[3] we find that the chance for direct influence of radiation on the state of radiocarbon at the end of the irradiation is of the order of 0.02. This is an approximate lower limit for the occurrence of a radiation effect. Any estimate of a reasonable upper limit will depend upon a decision concerning the size of the volume about the entrapped hot-atom in the crystal within which the occurrence of a radiation-induced process will affect the state of the hot-atom.

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Reactions of Carbon(IV) Iodide with Ammonia and Hydrazine[1]

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Carbon(IV) iodide is stable toward solvolysis by liquid ammonia at or near its boiling point, but is reversibly ammoniated to form only $CI_4 \cdot 2NH_3$; the first-order rate constant for this ammoniation at -35.0° and 420 mm. is 1.28×10^{-4} sec.$^{-1}$ and the dissociation pressure of the 2-ammoniate at -35.0° is 95 mm. On the basis of potentiometric titration data, the initial reaction between carbon(IV) iodide and potassium amide in liquid ammonia at -37° is interpreted as involving a base-catalyzed ammonolysis to form iodoform and iodoamide. The primary reaction between carbon(IV) iodide and hydrazine in liquid ammonia yields iodoform and elemental nitrogen.

Earlier studies in these laboratories have shown that the halides of carbon(IV) undergo solvolytic cleavage when treated with anhydrous liquid ammonia at elevated temperatures[2] but suggest that these halides are ammoniated but not ammonolyzed at or near the boiling point of liquid ammonia. The existence of a 2-ammoniate of carbon(IV) iodide was reported, and this has since been confirmed by means of pressure–composition isotherms and the 2-ammoniate has been characterized. Also, the reaction between carbon(IV) iodide and potassium amide in liquid ammonia has been studied by means of potentiometric titrations with a view to detecting the formation of the tetramide of carbon(IV). The interaction of carbon(IV) iodide and hydrazine in liquid ammonia also has been investigated.

Experimental

Materials.—The following materials were prepared and purified by the methods to which reference is made: carbon(IV) iodide,[3] anhydrous hydrazine[4] and potassium amide.[5]

Methods.—Methods used for the detection or determination of guanidine[6] and hydrazine[7] are described elsewhere. For the analysis of solutions containing both hydrazine and iodide ion, the total concentration of these two constituents was determined by iodate titrations[7] and hydrazine was determined separately as benzalazine by adding a slight excess of benzaldehyde to solutions made slightly acidic with acetic acid.

All reactions involving either gaseous or liquid ammonia were carried out under strictly anhydrous conditions. The quartz helix balance and the procedures employed in the establishment of pressure–composition isotherms are described elsewhere.[8] The equipment and methods used in carrying out potentiometric titrations in liquid ammonia also have been described previously.[5]

Results.—The pressure–composition isotherm for the system carbon(IV) iodide–ammonia is

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] G. W. Watt and H. T. Hahn, THIS JOURNAL, **77**, 312 (1955).

[3] R. E. McArthur and J. H. Simons, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 37.

[4] C. F. Hale, THIS JOURNAL, **33**, 1071 (1911).

[5] G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 46 (1955).

[6] G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 2751 (1955).

[7] W. R. McBride, R. A. Henry and S. Skolnik, *Anal. Chem.*, **25**, 1042 (1953).

[8] G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 1317 (1955).