The Fate of Nitrogen-13 Formed by the $^{12}C(d,n)^{13}N$ Reaction in Inorganic Carbides[1]

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Abstract: The behavior of nitrogen atoms in the inorganic matrices Al_4C_3, CaC_2, Li_2C_2, and Na_2C_2 was studied by inducing 10-min half-lived nitrogen-13 in the carbides by the $^{12}C(d,n)^{13}N$ nuclear reaction. Upon dissolution in acid solution the methanide (Al_4C_3) gave $^{13}NH_3$ and $CH_3{}^{13}NH_2$ as the major products while the acetylides gave $^{13}NH_3$, $C^{13}N^-$, and $CH_3C^{13}N$. The variation in product yield with varying cyclotron beam current, total irradiation dose, and postirradiation thermal annealing was studied. The products formed and their yields are correlated with the structures of the various carbides in the solid phase.

Many studies have been carried out on the fate of atoms in inorganic matrices, especially on the fate of carbon atoms induced by nuclear recoil in ammonium salts, nitrides, and cyanides.[2-9] In contrast, few investigations have dealt with nitrogen atoms in inorganic matrices. The fate of 10-min half-lived nitrogen-13 has been studied in sodium and potassium cyanide,[10] sodium and lithium nitrate, and sodium nitrate[11] and sodium azide.[12] In all these studies the nitrogen-13 was induced by the $^{14}N(n,2n)^{13}N$ nuclear reaction. Kuhry[10] has discussed the problems of using this reaction to study the fate of ^{13}N in KCN. By using 14-MeV neutrons he induced a mixture of ^{38}K, ^{13}N, ^{11}C, ^{38}Cl, and an unknown 4-hr half-lived isotope, all of which were positron emitters in potassium cyanide; thus, it was necessary to separate out the ^{13}N contribution.

In the present study, nitrogen-13 was induced in a series of inorganic carbides by the $^{12}C(d,n)^{13}N$ nuclear reaction, and the irradiation times were such that nitrogen-13 was the only positron emitter present in large yield. The fate of the nitrogen species was studied by the dissolution of the irradiated carbides in aqueous solvents.

Experimental Section

Samples of the carbides Al_4C_3, CaC_2, Na_2C_2 (all from Alfa Inorganics), and Li_2C_2 (Lithium Corporation of America) were irradiated by mounting 500 mg of the powder in an aluminum pouch perpendicular to the 7-MeV deuteron beam of the Washington University Medical School cyclotron. The sample was irradiated in a helium atmosphere. After removal of the sample from the pouch, dissolution in a solvent was also performed under a helium atmosphere. The sample was counted in fixed geometry over a scintillation crystal with the discriminator set to count the positron annihilation radiation before and after dissolution to check for loss of activity during this process. After dissolution the samples were analyzed for volatile components by radiogas-liquid partition chromatography (rglpc) and for $C^{13}N^-$ by conventional chemistry. In all the cases studied, over 99% of the activity was released as $^{13}NH_3$, $CH_3{}^{13}NH_2$, $CH_3C^{13}N$, or $C^{13}N^-$. The amounts of the first three compounds were measured by rglpc using an 8-ft glass column packed with Poropak-Q treated with tetraethylenepentamine in a Perkin-Elmer 820 chromatograph, temperature programmed between 40 and 100°. The sample injected into the chromatograph was made slightly basic before injection to release gaseous ammonia and methylamine. The chromatograph was used in conjunction with a gas-flow proportional counter.[13]

To determine the amount of labeled cyanide present, an aliquot of the solution was added to a solution of potassium cyanide. A 0.5 *M* solution of silver nitrate was used to precipitate the silver cyanide which was filtered, and both the precipitate and a measured aliquot of the filtrate were counted. After the silver cyanide had been counted it was recrystallized from concentrated ammonia solution[9] to confirm that only $C^{13}N^-$ had precipitated. The precipitate and aliquots of the filtrates were counted in a Picker well counter by counting the 511-keV annihilation radiation. The relative efficiencies of the three counters used in this study were determined using separated $^{13}NH_3$, and it was confirmed that in all the experiments 96 ± 4% of the activity initially in the carbides was recovered in the observed products.

In a series of experiments the carbides were thermally annealed after irradiation for 10 min in an oven at 700° in an inert atmosphere.

Results

Aluminum Carbide. In all the studies with aluminum carbide 97% of the ^{13}N activity induced in the solid was recovered as $^{13}NH_3$ and $CH_3{}^{13}NH_2$. The remaining activity was in the form of $C^{13}N^-$. The aluminum carbide was always dissolved in hydrochloric acid solution and the relative yields of $^{13}NH_3$ and $CH_3{}^{13}NH_2$ did not alter when the acid strength was varied from 0.1 to 6 *N*. Altering the total radiation dose to the sample did affect the yields, as shown in Figure 1. This figure includes studies performed at deuteron beam currents from 5 to 15 μA. It was found that the beam current did not affect the product distribution. In the studies where the sample was thermally annealed, the 10-min thermal annealing period had no observable effect upon the product distribution.

Calcium Carbide. When calcium carbide was dissolved in acid solution the product spectrum consisted of three major products plus two present in trace quantities. The major products were $^{13}NH_3$, $C^{13}N^-$, and $CH_3C^{13}N$ and the trace products were $CH_3{}^{13}NH_2$

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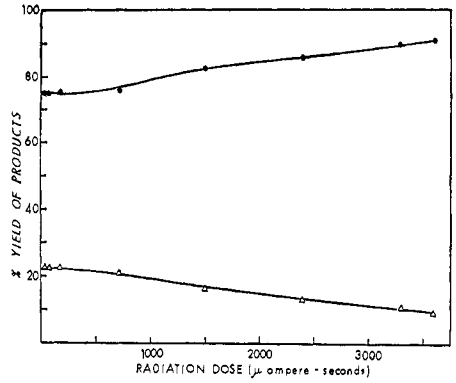

Figure 1. Variation in the yields of ammonia (●) and $CH_3{}^{13}NH_2$ (Δ) obtained upon dissolution of Al_4C_3, with radiation dose.

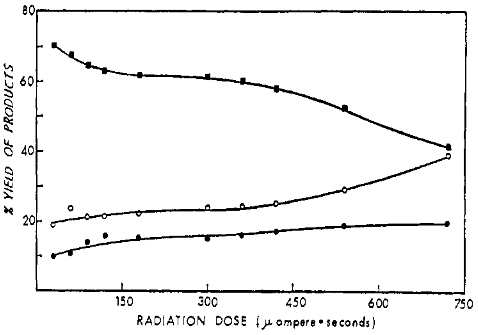

Figure 2. Variation in the yields of ammonia (●), cyanide (○), and acetonitrile (■) obtained upon dissolution of CaC_2, with radiation dose at a 6-μA beam current.

and $C_2H_5{}^{13}NH_2$ (tentatively identified). The latter products were present in yields of less than 0.2%. The dissolution was carried out in 0.1 *N* HCl at 0°, under which conditions the reaction was relatively slow (the dissolving taking approximately 5 sec) and all the activity remained in the solution. With this carbide the product spectrum was dependent upon both the deuteron beam current and the total radiation dose. Figure 2 shows the variation in product spectrum with radiation dose at a 6-μA beam current, while Figure 3 shows this variation at a 12-μA beam current. Post-irradiation thermal annealing also altered the product spectrum as shown in Table I.

Table I. Effect of Thermal Annealing[a] on the Products Formed from Calcium Carbide

	Beam current, μA			
	6	6	12	12
	Irradiation time, sec			
	60	60	120	120
	No annealing	Annealing	No annealing	Annealing
$C^{13}N^-$	24	49	48	48
$^{13}NH_3$	16	28	24	34
$CH_3C^{13}N$	60	22	28	18

[a] 10 min at 700°.

Sodium and Lithium Carbides. Sodium and lithium carbides were less stable to deuteron radiation than the other carbides studied; at high radiation doses the burned carbide did not dissolve completely and the recoverable activity was mainly $C^{13}N^-$. Tables II and III show the product spectrum at low radiation dose, each value being the mean of three separate determinations. Owing to the unstable nature of these carbides, annealing studies were not attempted.

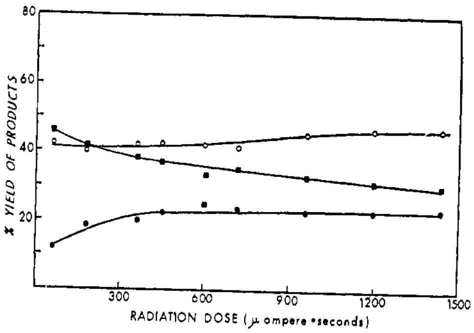

Figure 3. Variation in the yields of ammonia (●), cyanide (○), and acetonitrile (■) obtained upon dissolution of CaC_2, with radiation at a 12-μA beam current.

Table II. Products Formed upon Dissolution of Na_2C_2 in 0.1 *N* Acid Solution

	Beam current, μA	
	6	6
	Irradiation time, sec	
	10	30
$^{13}NH_3$	12	7
$CH_3C^{13}N$	3	1
$C^{13}N^-$	85	92

Table III. Products Formed upon Dissolution of Li_2C_2 in 0.1 *N* Acid Solution

	Beam current, μA			
	6	6	6	6
	Irradiation time, sec			
	10	15	30	60
$^{13}NH_3$	26	28	28	27
$CH_3C^{13}N$	10	9	4	3
$C^{13}N^-$	64	63	68	70

Discussion

In all the carbides studied it has been observed that upon dissolution nitrogen atoms induced into the crystal lattice by nuclear recoil form small molecules containing none, one, or two carbon atoms. This behavior can be compared with the behavior of carbon atoms induced in nitrides, where small molecules are also formed[5,6,8,9] and with that of macroscopic quantities of nitrogen reacting with carbides or carbon.[14–19] In the latter case it has been observed that compounds containing more than one nitrogen atom have been formed. This is very unlikely at the low nitrogen concentration produced by the nuclear recoil process, as species containing more than one nitrogen atom will only be formed if the reactivity of the ^{13}N atom with nitrogen is many orders of magnitude greater than that of any possible competing reaction.

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The chemical structures of the four carbides studied are well known and so it is also possible to correlate qualitatively the behavior of the nitrogen atoms in the various carbides with the chemical structure of the carbide.

In aluminum carbide[20] each carbon atom is surrounded by four aluminum atoms at the corners of a tetrahedron with each carbon atom's nearest neighbor 3.14 Å away. When a carbon atom is converted into nitrogen-13, the nitrogen can either insert into the lattice as a free nitrogen atom or react with a carbon atom to form a CN group in the lattice. It is known that when nitrogen atoms are induced in metals by nuclear recoil[21,22] dissolution in acid releases the activity quantitatively as $^{13}NH_3$; also, macroscopic amounts of nitrogen when induced into uranium carbide[14] and silicon carbide[15] have been shown to replace the carbon in the crystal structure. It has also been reported that a chemisorbed CN species was formed as an intermediate when active nitrogen containing hydrogen was passed over carbon rods.[16,17]

At low radiation doses it is seen that the CN species/N atom ratio is about 1/4 and the CN species in the lattice upon dissolution is mainly reduced to $CH_3{}^{13}NH_2$, with only a small amount of $C^{13}N^-$ being observed. Excess radiation appears to break down the $C^{13}N$ species in the lattice and as the radiation dose is increased so the ammonia yield increases. The small amount of thermal annealing that was possible using the 10-min half-lived isotope had no observable effect on the product spectrum. This is to be expected, as radiation annealing had a minor effect on the product spectrum. In similar studies on carbon-14 in magnesium nitride[9] annealing effects were observed for up to several days, annealing at 500°; such time studies were of course not possible in this work.

In the other three carbides studied the carbon is present as C_2.[23-25] The interstitial spaces are largest in the calcium carbide structure. In these cases the nitrogen atom can remain as nitrogen in the lattice, substitute for a carbon atom in a C_2 group to form a CN species, or add to the C_2 to form a C_2N species. It must be emphasized that a species such as C_2N_2, which has been observed from the reaction of active nitrogen with graphite,[18,19] is very unlikely to be formed owing to the low nitrogen concentration.

It is seen from the product spectrum that at low radiation dose a C_2N species ($CH_3C^{13}N$) prodominates in the calcium carbide case, while in the other two acetylides studied $C^{13}N$ predominates. From the crystal structures of the carbides it can be estimated that in the CaC_2 lattice there is a space of diameter about 2.5 Å along the $C{\equiv}C$ bond axis for the nitrogen atom in a CCN species to be placed, while in the Li_2C_2 lattice the space is less than 1 Å in diameter. It appears that the CCN species predominates in the lattice where there is room for the nitrogen group to fit without disturbing the lattice structure.

In these three carbides the carbon group in solution forms an unsaturated molecule, acetylene. Correspondingly, the nitrogen-containing molecules are also unsaturated as opposed to the aluminum carbide case, where they are saturated. The acetylide systems do show greater radiation sensitivity than the aluminum carbide; the aluminum carbide has been reported to be much harder than the acetylides,[26] and in this study did appear to be able to stand higher radiation doses without decomposition than the other carbides. The average dose rate given to the samples is about 0.08 eV/(molecule μA sec), so at a beam current of 6 μA about 0.5 eV/(molecule sec) is deposited in the compound, and at 12 μA about 1.0 eV/(molecule sec) is deposited. The different curves shown in Figures 2 and 3 can be qualitatively explained by assuming higher localized heating at the higher currents and, therefore, greater decomposition of the intermediates. The greater decomposition of the more complex compound at high radiation doses parallels the effect observed in other hot-atom studies involving both recoil nitrogen[27] and carbon.[28,29] The large difference in product spectrum with radiation dose is less than that observed in gas-phase studies of recoil carbon with nitrogen–oxygen mixtures, where an alteration of dose rate by a factor of 2.5 altered the ^{11}CO yield by a factor of 3 at the same total dose.[30] Large differences in product spectrum have also been observed in the fate of radiocarbon atoms in magnesium nitride annealed at 300 and 500°, the yields of major products varying by as much as a factor of 5 after the different treatments.[9] It is possible that in this study the localized heating at the higher beam current may break down the C_2N species and this would resemble the decomposition of the similar CN_2 species in sodium cyanamide, where breakdown occurs at approximately 350° in the carrier-free state[10] and at 940° in the bulk compound.[31] Comparison of Table I and Figure 3 shows that high-temperature annealing and a high radiation dose give a very similar $C^{13}N^-$ yield, and both radiation and thermal effects tend to break down the C_2N species into $C_2 + N$ and $CN + C$ fragments.

In all compounds studied, radiation or heating tends to give products containing fewer carbon atoms than the untreated cases. This is in contrast with the effect reported for behavior of carbon atoms in magnesium nitride, where annealing altered the products formed but retained the number of nitrogen atoms. It is, however, a similar effect to that reported[10] for ^{13}N formed in sodium cyanide, where thermal annealing altered the products from a 4:3 ratio of cyanide:cyanamide ($CN^{13}N$ fragment) to a 10:1 ratio. Here, as in the carbide studies, annealing simply reduced a three-atom fragment to a two-atom species.

This work has demonstrated that when recoil nitrogen is induced into the carbide lattice, carbon–nitrogen bonds are formed; such bond formation has not been observed with the reaction of molecular nitrogen with carbides,[14,15] and the product spectra are more

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complex than those observed from the reaction of nitrogen atoms with carbon, where CN and C_2N_2 are observed products.[16-19] Gas-phase recoil-nitrogen studies[32] with both C_1 (methane) and C_2 hydrocarbons (ethylene) have led to $HC^{13}N$ as the only identified major product, while other gas-phase work has suggested that the reaction

$$^{13}N + N_2 \longrightarrow {}^{13}NN + N$$

has a very large cross section.[27,33]

The observance of a large amount of $^{13}NH_3$ and the difference between the behavior of a C_1 carbide, a C_2 carbide with large interstitial spaces, and a C_2 carbide with small interstitial spaces are in great contrast to published gas-phase results.[27,32,33] It appears, therefore, that the products obtained in this work are determined mainly by the crystal structure of the irradiated carbides, not as in the gas-phase case by the spin conservation in the reaction of $N(^2D)$ with methane and ethylene to form HCN. As studies using nitrogen atoms formed by chemical means, which are produced at lower energies than the recoil species, have been carried out only on graphite, it is impossible at this time to estimate the excitation of the nitrogen species at the time of reaction.

Conclusions

It has been shown that different product spectra are observed when a methanide (Al_4C_3) or an acetylide (CaC_2, Li_2C_2, Na_2C_2) has ^{13}N induced into the lattice and is dissolved in acid solution. These differences can be explained by considering the possible ^{13}N-containing fragments in the crystal lattices and by the fact that with acetylides, dissolution leads to an unsaturated species. By varying the carbide and irradiation conditions, it is possible to prepare $^{13}NH_3$ (from Al_4C_3 at high radiation dose), $CH_3C^{13}N$ (from CaC_2 at low radiation dose), and $C^{13}N^-$ (from any acetylide at high radiation dose) in very high yields. Recently, interest has been revived in the use of short-lived isotopes of carbon, nitrogen, and oxygen as biomedical tracers.[34] Irradiation of carbides leads to useful nitrogen-13-containing synthetic intermediates as well as large amounts of $^{13}NH_3$, which, prepared from aluminum carbide, has been used to study ammonia metabolism in animals, using nitrogen-13 as the radioactive tracer.[35]

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