probed these energetic relationships calculationally. Nevertheless, experiments aimed at the preparation of IIa–Va in solution, in matrix isolation, or in the bulk solid phase would seem to hold considerable promise.

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Reaction of Atomic Carbon with Ammonia. The Mechanism of Formation of Amino Acid Precursors[†]

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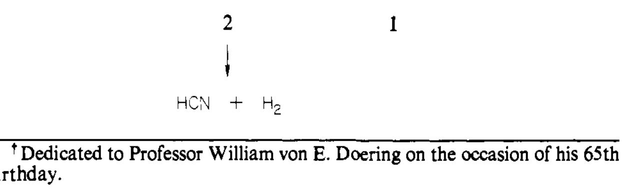
Abstract: The reactions of arc-generated carbon atoms with ammonia have been investigated. Primary reactions of C_1 are NH inserton and hydrogen abstraction. The NH insertion leads to methyleneamine (**1**) and HCN. The hydrogen abstraction proceeds in a stepwise manner to generate CH_2, which reacts with NH_3 to produce CH_3NH_2. Hydrolysis of the nonvolatile residue from this reaction produces the amino acids glycine, alanine, *N*-methylglycine, *β*-alanine, and aspartic acid. Serine is also formed when H_2O is included with the reactants. The mechanism of formation of the amino acid precursors is discussed. Labeling experiments (^2H and ^{13}C) rule out a hydrogen cyanide polymer as a major precursor to the amino acids.

In a recent preliminary communication,[1] we reported that amino acids were produced when arc-generated carbon vapor is cocondensed at −196 °C with aqueous ammonia or by the hydrolysis of the products of the reaction between carbon vapor and anhydrous ammonia.[2] In this paper, we shall discuss the primary products of the reaction of carbon with ammonia and present evidence concerning the mechanism of formation of amino acid precursors. Since carbon,[3,4] ammonia,[4] and water[5] have all been detected as extraterrestrial species, these studies may provide information concerning the mechanism of formation of extraterrestrial amino acids such as those which have been detected in meteorites[6] and lunar samples.[7]

Results and Discussion

Reactions are typically carried out by condensing gaseous reactants with carbon vapor on the walls of a reactor at −196 °C. At the conclusion of the reaction, volatile products are removed at room temperature and the residue is hydrolyzed with 6 N HCl. Treatment of the hydrolysate with acidic 1-butanol followed by trifluoroacetic anhydride forms the *N*-trifluoroacetyl *n*-butyl esters of the amino acids,[8] which are analyzed by gas chromatography–mass spectrometry (GC–MS).[9] Yields of volatile products are shown in Table I and those of the amino acids under various sets of reaction conditions are listed in table II. Total yields are on the order of 4.7% based on carbon vaporized. Amino acids that have been detected are glycine, alanine, *β*-alanine, *N*-methylglycine, and aspartic acid. When aqueous ammonia is used as a reactant, serine is also observed. While most of the products can be rationalized from the reaction of atomic carbon, acetylene has been shown to be a product of C_2 reactions.[10]

Mechanism of Formation of Glycine. Cacace and Wolf[11] have investigated the reaction of nucleogenic carbon atoms with NH_3 and have demonstrated that methyleneamine, **1**, is a primary product. The methyleneamine is undoubtedly formed by insertion of carbon into an NH bond of ammonia to generate aminomethylene, **2**, which rearranges to **1**. We find that a number of products observed in the present study may also be rationalized in terms of the intermediacy of **1**. Hydrogen cyanide, a major product, most probably arises via the decomposition of either energetic **1** or **2**. The reaction of C(^{1}D) with NH_3 to form **1** is exothermic by 164 kcal/mol,[12] and this excess energy could be directed into the production of HCN.



$$C + NH_3 \longrightarrow \underset{2}{H-\ddot{C}-NH_2} \longrightarrow \underset{1}{H_2C{=}NH} \longrightarrow HCN + H_2$$

$$\mathbf{2} \longrightarrow HCN + H_2$$

Table I. Volatile Products and Their Yields in the Reaction of Carbon (88 mmol) with NH_3 (104 mmol)

product	yield, mmol
HCN	8.7×10^{-1}
C_2H_2	1.1×10^{-1}
CH_3NH_2	2.5
$CH_3C{\equiv}N$	4.6×10^{-1}

In the preliminary account of this work, we proposed that the precursor to glycine was aminoacetonitrile, **3**, which could be

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[†] Dedicated to Professor William von E. Doering on the occasion of his 65th birthday.

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(12) DeFrees and Hehre (DeFrees, D. J.; Herhe, W. J. *J. Phys. Chem.* **1978**, *82*, 391–393) have determined the ΔH_f of **1** to be 26.4 ± 3.2 kcal/mol.

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formed by the addition of HCN to **1** (eq 1). For further confirmation of this mechanism, a mixture of $H^{13}CN$ and NH_3 was reacted with carbon vapor. Hydrolysis of the product mixture resulted in glycine, which has derivatized and analyzed by GC–MS. The mass of the various fragments gave the ^{13}C distribution shown in eq 2. These results demonstrate that the ^{13}C is incorporated almost exclusively into the carboxyl group of glycine as demanded by the mechanism in eq 1 and constitute further proof for the intermediacy of **1**.

$$\underset{\mathbf{1}}{CH_2{=}NH} + HCN \rightarrow NH_2\text{-}CH_2\text{-}CN \xrightarrow{H_2O} \text{glycine} \qquad (1)$$

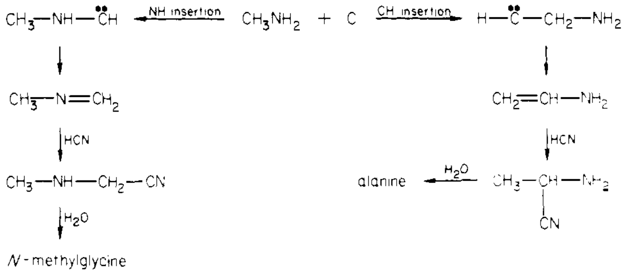
$$\begin{gathered} CF_3CONHCH_2CO_2C_4H_9 \xrightarrow{ei} \underset{2.0\%\ ^{13}C}{CF_3CONHCH_2^+} + \\ \underset{75.3\%\ ^{13}C}{C_4H_9OCO^+} + \underset{75.0\%\ ^{13}C}{CF_3CONHCH_2CO^+} + \underset{74.2\%\ ^{13}C}{CF_3CONHCH_2CO_2^+} \end{gathered} \qquad (2)$$

Polymeric HCN as Possible Amino Acid Precursor. The ^{13}C labeling studies also serve to rule out a mechanism for glycine formation involving the hydrolysis of an HCN polymer formed under the reaction conditions. The hydrolysis of HCN polymers and oligomers has been shown to produce amino acids.[13] However, if HCN were to polymerize under the conditions of the present reaction, hydrolysis of the polymer would generate glycine in which both carbons had incorporated ^{13}C. Equation 2 shows that this is clearly not the case and that no more than 2.6% of the glycine could have arisen from an HCN polymer. When carbon vapor was reacted with HCN alone, only a very small amount of glycine was generated.

In another attempt to evaluate the importance of an HCN polymerization mechanism for the formation of the amino acids, we have reacted ND_3 with carbon vapor. It has been shown that glycine, generated by D_2O hydrolysis of an HCN polymer, incorporates two deuteriums in the methylene group.[14] Hence, amino acids generated by the reaction of carbon with ND_3 and subsequent hydrolysis of the DCN polymer should contain no deuterium. In fact, GC–MS analysis reveals that all the amino acids generated in this experiment were deuterated. Thus we conclude that these amino acids do not have polymeric HCN as their sole precursor.

Formation of Alanine and *N*-Methylglycine. Since amino acid yields are rather variable and appear to depend upon factors that are difficult to control, such as the rate of carbon vaporization, we have normalized the yield of each amino acid to that of glycine in Table II. In this manner, we are able to carry out a number of experiments and obtain a reasonable estimate of experimental errors. Since the mechanism of glycine formation is established, a measure of the change in the ratio of a particular amino acid to glycine in the presence of various additives should provide evidence concerning the mechanism of formation of that amino acid. Absolute yields of amino acids from typical runs are listed in the Experimental Section.

Alanine and *N*-methylglycine contain an additional carbon and are postulated to result from the reaction of carbon with methylamine followed by HCN addition as shown in eq 3.



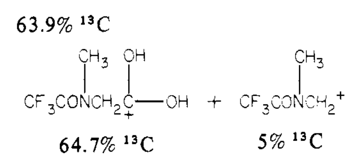
(3)

Table I shows that methylamine is formed in substantial yield in our system; it is also reported in the reaction of nucleogenic carbon with ammonia.[11] This product is most probably the result of the reaction of CH_2 with NH_3. The CH_2, in turn, is formed by a series of hydrogen abstractions by C_1 (eq 4), of ammonia to generate methylamine has been reported.[16] An alternate mechanism involving a series of hydrogen abstractions by aminomethylene, **2**, appears unlikely for thermodynamic reasons.

$$C + NH_3 \rightarrow NH_2 \xrightarrow{NH_3} NH_2 + CH_2 \xrightarrow{NH_3} CH_3NH_2 \qquad (4)$$

Carbon vapor was reacted with a mixture of NH_3 and CH_3NH_2 to further establish the role of methylamine in the formation of *N*-methylglycine and alanine. This reaction resulted in a substantial increase in the ratio of both alanine and *N*-methylglycine to that of glycine (Table II).

When carbon vapor was reacted with a mixture CH_3NH_2 and $H^{13}CN$, the mass spectrum of *N*-methylglycine derivative showed the majority of the ^{13}C in the carboxy group (eq 5). Although the mass spectrum of the alanine derivative did not show fragments containing the carboxyl group, the $CF_3CONHCHCH_3^+$ fragment of $m/e = 140$ showed only 7.7% ^{13}C incorporation. These labeling studies support the mechanisms for the formation of alanine and *N*-methylglycine in eq 3.



$$\begin{gathered} CF_3CO\overset{CH_3}{\overset{|}{N}}CH_2CO_2C_4H_9 \xrightarrow{ei} \underset{63.9\%\ ^{13}C}{CF_3CO\overset{CH_3}{\overset{|}{N}}CH_2CO^+} + \\ \underset{64.7\%\ ^{13}C}{CF_3CO\overset{CH_3}{\overset{|}{N}}CH_2\underset{+}{\overset{OH}{\overset{|}{C}}}\text{—}OH} + \underset{5\%\ ^{13}C}{CF_3CO\overset{CH_3}{\overset{|}{N}}CH_2^+} \end{gathered} \qquad (5)$$

Since CH_3NH_2 is formed by a series of hydrogen abstractions, the addition of a better hydrogen atom donor than NH_3 (D_{N-H} = 109 kcal/mol) should increase the yield of alanine and *N*-methylglycine relative to that of glycine. For simplicity, we have chosen H_2 (D_{H-H} = 104 kcal/mol) as a hydrogen donor. Table II demonstrates that inclusion of H_2 among the reactants increases the ratio of both alanine and *N*-methylglycine to that of glycine by a factor of 2.

The substitution of D_2 for H_2 results in substantial deuterium incorporation in the alanine and *N*-methylglycine as shown in Table III. The fact that d_1 as well as d_2 amino acids are produced indicates that hydrogen abstraction by carbon proceeds in a stepwise manner through the intermediacy of CH·. We have observed a similar effect in the products of the reaction between carbon and a mixture of benzene and benzene-d_6.[15]

It is interesting that the inclusion of D_2 as a reactant results in the formation of glycine and β-alanine with the incorporatin of small amounts of d_1. This deuterium incorporation may result from a competing reaction of CD with NH_3 to generate **1** and a hydrogen atom (eq 6) in a reaction analogous to that of CH with CH_4 that produces ethylene and a hydrogen atom.[17]

$$:\dot{C}D + NH_3 \rightarrow CHD{=}NH + H\cdot \qquad (6)$$

Precursors to the Remaining Amino Acids. Although mechanistic sequences leading to the precursors of β-alanine, aspartic acid, and serine have not been elucidated, several observations may be relevant. Since the above amino acid precursors are secondary products, it may be that they arise from reactions

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Table II. Amino Acid Yields (mmol) in the Reaction of Carbon with Ammonia in the Presence of Various Additives

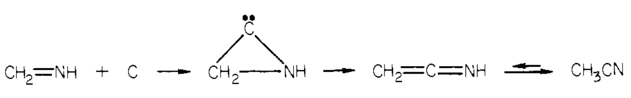
products	$C + NH_3$	$C + NH_3 + HCN$	$C + NH_3 + H_2$	$C + CH_3NH_2 + NH_3$
glycine	1	1	1	1
alanine	$5.3 \pm 2.1 \times 10^{-2}$	$5.9 \pm 1.3 \times 10^{-2}$	$10.5 \pm 1.1 \times 10^{-2}$	23.4×10^{-2}
N-methylglycine	$12.3 \pm 4.6 \times 10^{-2}$	$12.6 \pm 3.2 \times 10^{-2}$	$23.8 \pm 0.7 \times 10^{-2}$	3.45
β-alanine	$7.9 \pm 2.8 \times 10^{-2}$	$3.8 \pm 1.3 \times 10^{-2}$	$5.7 \pm 0.3 \times 10^{-2}$	5.03×10^{-2}
aspartic acid	$9.6 \pm 6.5 \times 10^{-3}$	$2.5 \pm 7 \times 10^{-2}$	$3.2 \pm 0.8 \times 10^{-2}$	3.6×10^{-2}
N-methylalanine	trace	trace	trace	5.07×10^{-2}

Table III. Deuterium Labeling in Amino Acids Produced from the Reaction of Carbon with $NH_3 + D_2$

amino acid	$\% d_0$	$\% d_1$	$\% d_2$	$\% d_3$
glycine	85.5 ± 2.2	14.6 ± 2.2		
alanine	46.6 ± 5.1	30.4 ± 1.8	21.3 ± 1.0	
N-methylglycine	36.1 ± 2.0	41.2 ± 1.0	18.6 ± 2.0	4.1 ± 4.0
β-alanine	83.2 ± 4.5	16.9 ± 4.5		

between carbon and one or more of the stable reaction products. To test this possibility, we have carried out reactions in which acetylene, acetonitrile, and aminoacetonitrile are mixed with NH_3 prior to reaction with carbon. However, none of these additives resulted in an increase in the yield of either β-alanine or aspartic acid.

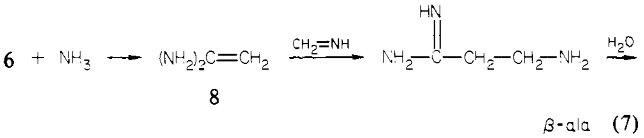
An additional possibility is the reaction between C_1 and **1**



1 **6** **7**

leading to keteneimine, **6**, which may serve as a amino acid precursor. The reaction of carbon with **1** to generate **6** is analogous to the reaction between C_1 and ethylene, which yields allene.[2] Although **6** has never been isolated, calculations indicate that it should tautomerize to acetonitrile, **7**.[18] The fact that **7** is detected in the volatile reaction products (Table I) argues for the intermediacy of **6**. Although the probability of reaction of C_1 with a rather reactive product molecule such as **1** may seem low, it should be noted that large amounts of carbon are vaporized in this system with the molar quantities of carbon approaching or exceeding those of NH_3. The low-temperature matrix may also increase the lifetime of **1**, thereby increasing the probability of reaction with an additional carbon atom.

If **6** is an intermediate, the sequence of reactions in eq 7 could



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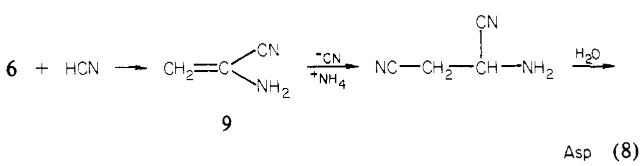
(7)

lead to β-alanine.[19] In analogy with the reactions of substituted keteneimnes,[21] **6** should add NH_3 to generate the enediamine **8**. Nucleophilic addition of **8** to **1** generates a precursor to β-alanine.

A possible mechanism leading to an aspartic acid precursor involves two successive additions of HCN to **6** as shown in eq 8.



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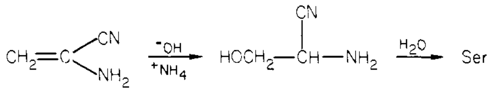
(8)

Although 2-aminoacrylonitrile, **9**, is unknown, nucleophilic addition to 3,3-dichloro-2-aminoacrylonitrile occurs in the manner postulated in eq 8.[22] Nucleophilic addition of ^-OH to **9** would generate a precursor to serine (eq 9), an amino acid which we detect only when water is added to the reactants.



(9)

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It is interesting that the route to β-alanine in eq 7 requires no HCN while two molecules of HCN are needed to generate aspartic acid by the mechanism in eq 8. The effect of HCN on amino acid yields (Table II) qualitatively supports this mechanism. Addition of HCN decreases the β-Ala:Gly ratio by a factor of 2 while the Asp:Gly ratio is increased by a factor of 2.5.

It should be emphasized that the pathways in eq 7–9 are speculative. If these reactions do occur, they may represent only one of several routes on the amino acid precursors. In particular, hydrolysis of an HCN polymer may be partially responsible for the formation of β-alanine. Small amounts of this amino acid and glycine are generated when carbon is reacted with HCN itself.

Conclusions

These investigations demonstrate that arc-generated carbon atoms, like those produced by nuclear recoil,[11] undergo primary reaction with NH_3 by NH insertion and hydrogen abstraction. The NH insertion leads ultimately to methyleneamine and HCN while the hydrogen abstraction proceeds in a stepwise manner to generate methylene which reacts with NH_3 to produce methylamine. Since the reactions are carried out in the condensed phase at −196 °C and large amounts of carbon are vaporized, secondary reactions of atomic carbon with stable as well as kinetically unstable products occur. These reactions lead to the formation of the amino acid precursors. The CH and NH insertion reactions of carbon atoms with methylamine are analogous to those observed for the reaction of carbon with methanol.[2a] As we have pointed out, the low-temperature reaction conditions employed here may simulate those that lead to the formation of extraterrestrial amino acids. It is not difficult to imagine that condensation of carbon vapor on a surface containing ammonia, under the low-temperature, high-vacuum conditions of outer space, could lead to amino acid precursors similar to those reported here. These extraterrestrial reaction conditions would be similar to those used in our investigations in that species which are kinetically labile at higher temperatures would be stabilized at the low temperatures and remain available for further reaction.

Experimental Section

Materials. The AGSKP high-purity carbon electrodes were purchased from National Spectrographic Laboratories. The 90% ^{13}C-enriched sodium cyanide and 99.96% D_2O were obtained from Stohler Isotope Chemicals. Ammonia, methylamine, and deuterium were purchased from Matheson Co. and used without further purification. Magnesium nitride was purchased from Alfa Products.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 580 spectrometer. The GC/MS data were obtained with a Varian 2700 chromatograph interfaced to a Du Pont 21-491-B mass spectrometer and a Finnigan Incos data system. Amino acid derivatives were analyzed with a 3% OV101 on Chromasorb W-HP (60/80 mesh) 2-m glass column. Volatile amines were determined on a 20% cetyl

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(19) An alternate sequence leading to β-alanine involves addition of NH_3 to acrylonitrile followed by hydrolysis.[20] However, we can detect no acrylonitrile among the products. Control experiments indicate that acrylonitrile would be detectable under the reaction conditions.

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alcohol on methanolic NaOH washed firebrick (60/80 mesh) glass column.[23]

Reactor. The reactor is modeled after that described by Skell et al.[24] Carbon is vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and cocondensed on the walls of the reactor at −196 °C ($\sim 10^{-4}$ torr) with a reactant. The power source is a Sears Dual Range 295 amp arc welder set at 110 amps. The inlet and outlet tubes of the reactor are attached to a vacuum line.

Reaction of Carbon Vapor with Ammonia. In a typical reaction, ammonia (103.6 mmol) is introduced into the reactor through a vacuum line at a flow rate of ~0.19 mmol/s and cocondensed on the walls of the reactor at −196 °C with carbon vapor (88.0 mmol). If more than one reactant gas is used, for example, ammonia and methylamine, the two gases are allowed to mix for 1 h in the vacuum line before the reaction is run. After all the ammonia is condensed onto the walls of the reactor, the carbon vapor is deposited for an additional 3 min. The reactor is allowed to warm to room temperature for 0.5 h and the volatile products are pumped out through traps at −78 and −196 °C. These volatile products are then analyzed by GC–MS for methylamine (2.5 mmol), by ^{1}H NMR for acetonitrile (4.6×10^{-1} mmol), and by IR for HCN (0.87 mmol) and HC≡CH (1.1×10^{-1} mmol).

The residue in the reactor is taken up in 6 N HCl and hydrolyzed at 100 °C for 24 h. The hydrolysate is filtered, evaporated, and derivatized to the *N*-trifluoroacetyl *n*-butyl esters of the amino acids, by the method of Roach and Gehrke,[8] and analyzed by GC–MS.[9] The amino acids detected are alanine (2.7×10^{-2} mmol), glycine (1.5×10^{-1} mmol), *N*-methylglycine (3.2×10^{-2} mmol), β-alanine (1.9×10^{-2} mmol), *N*-methylalanine (trace), and aspartic acid (2.2×10^{-3} mmol). Table II shows the average yields of these amino acids from nine runs, normalized to that of glycine, along with their standard deviations.

Reaction of Carbon Vapor with Aqueous Ammonia. The reaction was carried out as described above with the cocondensation of NH_3 (100.7 mmol), H_2O (55.6 mmol), and carbon vapor (64.2 mmol). Analysis of the residue for amino acids revealed the presence of alanine (8.6×10^{-3} mmol), glycine (1.1×10^{-1} mmol), *N*-methylglycine (1.1×10^{-2} mmol), β-alanine (7.5×10^{-3} mmol), *N*-methylalanine (trace), aspartic acid (2.6×10^{-3} mmol), and serine (1.1×10^{-2} mmol).

Reaction of Carbon Vapor with Preformed Ammonia and Hydrogen Cyanide Surfaces. Ammonia (93.2 mmol) was first condensed on the walls of the reactor at −196 °C in increments of ~20.0 mmol. In between the deposition of ammonia, carbon vapor was condensed on the walls for ~3 min. After the final aliquot of ammonia had been condensed, the carbon vapor was deposited for an additional 5 min. Total amount of carbon vapor condensed was 64.1 mmol. The reactor was then allowed to warm to room temperature for ~0.5 h, and the following amino acids were analyzed as above: alanine (9.1×10^{-3} mmol), glycine (1.2×10^{-1} mmol), *N*-methylglycine (1.3×10^{-2} mmol), β-alanine (1.0×10^{-2} mmol), *N*-methylalanine (trace), and aspartic acid (2.4×10^{-3} mmol).

The same procedure was followed for the reaction of carbon vapor (53.2 mmol) with a preformed hydrogen cyanide (60.0 mmol) surface. The only amino acids detected were glycine (7.66×10^{-3} mmol) and β-alanine (2.58×10^{-3} mmol).

Reaction of Carbon Vapor with Ammonia and Hydrogen (or Deuterium). Ammonia (79.9 mmol) and hydrogen (20.6 mmol) were allowed to mix for 1 h in a vacuum line. The gas mixture was then cocondensed with carbon vapor (133.0 mmol) at −196 °C at a flow rate of ~0.19 mmol/s to keep the pressure low. After the reactor had warmed to room temperature for ~0.5 h the volatile products were analyzed for HCN (3.5 mmol) and acetylene (3.5 mmol). The nonvolatile products were hydrolyzed and analyzed as above. The following amino acids were detected: alanine (3.55×10^{-2} mmol), glycine (3.63×10^{-1} mmol), β-alanine (1.99×10^{-2}), and *N*-methylglycine (8.43×10^{-2} mmol). Average normalized amino acid yields from two runs are listed Table II. When the hydrogen was replaced by deuterium, the amount of deuterium incorporation (Table III) was evaluated from the following mass spectral fragments: glycine ($CF_3CONHCH_2^+$), alanine ($CF_3CONHCHCH_3^+$), *N*-methylglycine ($CF_3CONCH_3CH_2^+$), and β-alanine ($CF_3CONHCH_2CH_2^+$).

Reaction of Carbon Vapor with Ammonia and HCN (or H^{13}CN). Hydrogen cyanide was prepared by the reaction between sodium or potassium cyanide and concentrated sulfuric acid and checked for purity by IR spectroscopy. Ammonia (15.8 mmol) and the hydrogen cyanide (6.1 mmol) were allowed to mix for 1 h. The gas mixture was then cocondensed with carbon vapor (67.9 mmol) as above. Analysis of the residue for amino acids revealed the presence of glycine (4.02×10^{-1} mmol), alanine (7.85×10^{-2} mmol), *N*-methylglycine (7.36×10^{-2} mmol), β-alanine (8.9×10^{-2} mmol), and aspartic acid (1.18×10^{-2} mmol). Average normalized amino acid yields from four runs are listed in Table II. When H^{13}CN was used, the ^{13}C content of the glycine was determined from the mass spectral fragments in eq 5.

Reaction of Carbon Vapor with Deuterated Ammonia. The ND_3 was prepared by reacting D_2O with Mg_3N_2 on a vacuum line.[25] Infrared analysis of the ammonia showed mainly ND_3 with a small amount of ND_2H and no detectable NH_2D or NH_3.[26] The ND_3 (51.6 mmol) was reacted with carbon vapor (89.7 mmol) as above. GC–MS analysis revealed the following amino acids: glycine (1.04×10^{-1} mmol, 59.4% d_2), alanine (1.51×10^{-2} mmol, 38.0% d_4), *N*-methylglycine (3.08×10^{-2} mmol, 30.8% d_5), β-alanine (7.66×10^{-3} mmol, 31.0% d_4), and aspartic acid (6.68×10^{-3} mmol, 5.2% d_2, 20.1% d_1, 74.7% d_0).

Reaction of Carbon Vapor with Methylamine and Ammonia. The reaction was carried out in the usual manner by cocondensing carbon (116.7 mmol) with a mixture of NH_3 (81.1 mmol) and CH_3NH_2 (22.4 mmol). The following amino acids were detected: glycine (1.55×10^{-1} mmol), alanine (3.63×10^{-2} mmol), *N*-methylglycine (5.34×10^{-2} mmol), β-alanine (7.86×10^{-3} mmol), aspartic acid (5.62×10^{-3} mmol), and *N*-methylalanine (7.76×10^{-2} mmol).

Reaction of Carbon Vapor with CH_3NH_2 and H^{13}CN. Carbon vapor (132.8 mmol) was cocondensed with CH_3NH_2 (77.9 mmol) and H^{13}CN (16.7 mmol) in the usual manner. Analysis of the residue revealed glycine (6.6×10^{-2} mmol), alanine (3.5×10^{-2} mmol), *N*-methylglycine (1.55×10^{-1} mmol), and *N*-methylalanine (6.7×10^{-2} mmol). Mass spectral analysis indicated that the glycine contained 43.9% ^{13}C on the carboxyl group and 7.8% on the methylene group. The *N*-methylglycine showed 64.3% ^{13}C on the carboxyl group and 5% in the remainder of the molecule. The mass spectrum of the alanine and the *N*-methylalanine did not show fragments containing the carboxyl group. The ^{13}C content in the decarboxylated fragments was 7.7% in the case of alanine and 1.4% in the case of *N*-methylalanine.

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Registry No. 1, 2053-29-4; **2**, 35430-17-2; **3**, 540-61-4; **6**, 17619-22-6; **7**, 75-05-8; **8**, 4363-36-4; **9**, 69245-10-9; methylamine, 74-89-5; carbon, 7440-44-0; ammonia, 7664-41-7; glycine, 56-40-6; DL-alanine, 302-72-7; *N*-methylglycine, 107-97-1; β-alanine, 107-95-9; DL-aspartic acid, 617-45-8; *N*-methyl-DL-alanine, 600-21-5; DL-serine, 302-84-1; hydrogen cyanide, 74-90-8; hydrogen, 1333-74-0; deuterium, 7782-39-0; glycine-d_2, 84009-43-8; alanine-d_4, 83998-91-8; *N*-methylglycine-d_5, 83998-92-9; β-alanine-d_4, 83998-93-0; aspartic acid-*d*, 83998-94-1; H^{13}CN, 56162-23-3; ND_3, 13550-49-7.

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