

may be considered as the strength of the bond to be broken, measured from the zero-point energy level; thus,  $k$  decreases with increasing  $E_0$ . The substitution by  $D$  reduces both  $k_b$  and  $k_c$  because the zero-point energies of both C-H and H-Hg bonds in the open structure are reduced. In the present case, the difference in the zero-point energies is governed by the force constant of the bond to be broken; hence, if we make a reasonable assumption that at the transition point the C-H bond is stronger than H-Hg, then the  $D$  substitution affects  $k_b$  more strongly than  $k_c$ . This leads to the decrease in  $\xi$  in agreement with the observed trend in  $\sigma^2$ . The same argument applies also in

the quenching by  $H_2$ ; but in this case, because of the stability of the cyclic complex,  $k_c$  is still quite small and  $\xi$  is close to unity. The isotope effect in  $\sigma^2$  should be thus negligible.

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## Reactions of Energetic Carbon Atoms with Ammonia. II<sup>1,2</sup>

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*Carbon atoms react with gaseous ammonia to give methane, methylamine, and methylenimine. Methylenimine and part of the methylamine are formed in reactions between carbon atoms with excess kinetic energy ("energetic") and ammonia. Most of the methane is formed in thermal reactions. Evidence for the formation of formaldoxime from the reaction between carbon atoms and ammonia-oxygen mixtures is presented. Facile radiolytic reduction of methylenimine and methylamine has been demonstrated. The formation of hydrogen cyanide or any derivative thereof was not demonstrable under the reaction conditions.*

### Introduction

Until the ammonia system was first studied,<sup>2</sup> no system in which energetic carbon atoms were produced and allowed to react to give organic compounds had lent itself to a study of product distribution encompassing a complete determination of the chemical fate of all the carbon atoms produced in the system. The carbon atoms<sup>2</sup> were made *in situ* by using the nuclear reaction  $N^{14}(n,p)C^{14}$ , and the products were determined by identifying the carbon-14 containing compounds. The most significant feature of this study was the fact that all the activity was accounted for as gaseous products. It had not been until the demonstration by Hornig, Levey, and Willard<sup>4</sup> that "hot" iodine-128 atoms could react with gaseous methane to give methyl iodide-I<sup>128</sup> that it was deemed possible for an atom with a large excess of kinetic energy to react in the gas phase. It had been assumed until that time that the amount of energy contained in the intermediate or complex would

be too great to allow stabilization in any other than the liquid or solid states.

Methane- $C^{14}$  accounted for nearly all of the carbon-14 produced under the conditions used in the experiments of Yang and Wolf.<sup>2</sup> Traces of methylamine- $C^{14}$  were also found. It was explicitly stated that the effect of the high extraneous radiation field accompanying hot carbon atom production in the nuclear reactor was difficult to evaluate. Further investigation was clearly needed to determine the effects of radiation chemistry on the distribution of carbon-14 in the products observed. The absorbed dose in the carbon-14 work was between 0.4 and 1.2 e.v./molecule.

Suryanarayana and Wolf<sup>5</sup> pointed out that energetic carbon-11 atoms could be made with considerably lower accompanying radiation dose. The nuclear reactions available for producing carbon-11 are numerous, and one in particular, the  $N^{14}(p,\alpha)C^{11}$  reaction, is ideally suited for studies involving nitrogen-containing systems. Radiation doses accompanying the production of the hot atom could be varied from about  $10^{-4}$  to 10 e.v./molecule. In addition the use of the carbon-11 technique<sup>5</sup> allows greater flexibility in experimental conditions so that gas, liquid, and solid phases and a wider variety of mixtures involving ammonia as the substrate could be studied.

The study of the reactions of energetic carbon atoms<sup>6-8</sup> is of primary interest. Nevertheless the mechanisms of these reactions cannot be studied until the role of the accompanying radiation damage is understood. A quantitative determination of the effect of the concomitant radiation on the spectrum of reaction products obtained by allowing energetic carbon atoms to react with ammonia was delineated in a

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper I: J. Y. Yang and A. P. Wolf, *J. Am. Chem. Soc.*, **82**, 4488 (1960).

(3) Visiting Scientist at B.N.L., 1961-1962, from Centro Chimica Nucleare, University of Rome, Italy.

(4) J. F. Hornig, G. Levey, and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

(5) B. Suryanarayana and A. P. Wolf, *J. Phys. Chem.*, **62**, 1369 (1958).

(6) A. P. Wolf, *Ann. Rev. Nucl. Sci.*, **10**, 259 (1960). This review details primarily the synthetic aspects of carbon atom reactions.

(7) See A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964), for a discussion of mechanism in carbon atom chemistry.

(8) See R. Wolfgang, *Progr. Reaction Kinetics*, in press.

communication by Cacace and Wolf.<sup>9</sup> This paper deals with the experimental results relative to the communication and contains an extended study of the reactions of energetic carbon atoms in the ammonia system.

### Experimental Section

**Materials.** The anhydrous ammonia (Matheson, C.P. grade) used in all experiments was further purified by drying over metallic sodium, followed by distillation *in vacuo*. The liquid was then rigorously outgassed under high vacuum just prior to use. Fresh reagent was prepared for each run.

The methylamine used (Matheson, C.P. grade, stated purity 96.5% minimum) was further purified by bulb-to-bulb distillation and outgassing *in vacuo*. G.l.c. analysis indicated less than 0.5% NH<sub>3</sub> in the purified compound. Other impurities were di- and trimethylamine.

The nitrogen used in irradiations was a mass spectrometrically assayed reagent, O<sub>2</sub> < 5 p.p.m., obtained from the Air Reduction Co.

Matheson research grade oxygen was used for those runs involving oxygen.

All other compounds used were research grade or C.P. reagents.

**Irradiations.** The irradiations were carried out using the 10-Mev. proton beam from the Brookhaven 60-in. cyclotron. Protons were allowed to impinge on the target for periods ranging from 10 sec. to 5 min. Proton currents ranging from 0.1 to 10  $\mu$ a. were employed. The integrating electrometer was used to determine the total irradiation received. The irradiation tank had a volume of 50 ml. A 3-mil Al window was used on the face being bombarded. All irradiations of gases were carried out at atmospheric pressure and the ambient temperature of the cyclotron cave ( $\sim 25^\circ$ ). Liquid and solid samples were irradiated in similar tanks with volumes between 1 and 2 cc. The proton beam entered the reaction vessel through a 10-mil Al window welded to the face of the vessel. A stream of dry helium was directed at the window during irradiation to prevent the condensation of atmospheric moisture (the moisture causes an unwanted increase of effective window thickness). The liquid ammonia was run at  $-47^\circ$  (m-xylene-Dry Ice slurry) and  $-72^\circ$  (ethanol-Dry Ice slurry). Solid ammonia was run at liquid nitrogen temperature. At the end of an irradiation the vessel was attached to the vacuum line and the sample brought to room temperature by rapid heating of the reaction chamber.

**Dose Measurements.** The absorbed dose was determined by using acetylene<sup>10,11</sup> as a dosimeter. Corrections for the different electron density of ammonia were applied and the results compared with the calculated dose. The calculated dose was obtained by using appropriate tables in Hine and Brownell<sup>12</sup> to calculate the energy deposited by the proton in traversing the substrate at 1 atm. Excellent agreement between experimental and calculated values was obtained. The absorbed dose was found to be proportional, over the

range studied, to the values obtained from the integrating electrometer. Thus the values reported as absorbed dose in the tables were obtained by multiplying the "integrated current" (in  $\mu$ a. min.) by the experimentally determined dose for an irradiation of 1  $\mu$ a. min. Below beam currents of about 0.2  $\mu$ a. the c.p.m./ml. of gas was not proportional to the integrated beam current but rather showed an erratic distribution of values. It was found that the total gaseous activity produced provided a more reliable proportionality factor for absorbed dose determinations. At these low intensities then, the absorbed dose was calculated by using a factor in units of absorbed dose/c.p.m./cc.  $\times$  c.p.m./cc. observed.

**Analysis of Products.** After irradiation the ammonia sample was transferred to a vacuum line where it was mixed with suitable carriers, and the mixture was pumped into five glass traps. The gas from each trap was passed through a gas-liquid chromatograph with an effluent stream counting system<sup>13</sup> allowing the simultaneous determination of mass and activity peaks in the sample. Product identification on carrier-free samples was done on the basis of elution time on at least two different columns. Total gas phase activity was determined by injecting the contents of one trap directly into the flow counter under standard flow conditions.

The columns used were: (for amines) 20% cetyl alcohol (by weight) on base-washed firebrick<sup>2</sup> in a glass column 2.43 m.  $\times$  6-mm. i.d. run at  $55^\circ$ ; (for methane and CO) activated charcoal (Columbia Carbon Corp., 20-48 mesh) in a glass column 2.43 mm.  $\times$  6 mm. i.d. run at  $25^\circ$ ; (for hydrocarbons) 0.5% D.C. 550 silicone oil (by weight) on activated alumina (Burrell Corp., Pittsburgh, Pa.) in a glass column 3.04 m.  $\times$  6 mm. i.d. run at  $25^\circ$ ; (for hydrogen cyanide) 20% diethylhexyl sebacate (by weight) on Celite in a glass column, 3.04 m.  $\times$  6 mm. i.d. run at  $25^\circ$ . Helium was used as the carrier gas. Runs on ammonia, ammonia-methylamine mixtures, and methylamine are listed in Table I. Radiation doses and radiochemical yields are given.

**Identification of the "Unknown Activity as Methylenimine.** At low radiation doses the total gaseous activity produced, as determined by "bypass" assay, was always greater than the sum of the activities as methane and methylamine. This activity would not elute from any column used. Its existence was verified by finding it adsorbed on a cetyl alcohol-Celite stripping column, 8.5 mm. long  $\times$  4 mm. i.d. held at  $60^\circ$  and inserted at the head of a standard cetyl alcohol-Celite separation column. Well-type scintillation counting of 2-mm. cuts of the stripping column showed 100% of the missing activity (total activity from bypass determination -  $\Sigma$  activity as CH<sub>4</sub> and CH<sub>3</sub>NH<sub>2</sub>) to be absorbed on the first 2-3 mm. of the stripping column.

Identity of this absorbed activity as methylenimine is based on the following experiments.

1. **Hydrogenation.** The analysis of the irradiated sample was performed in the usual way using hydrogen in the place of helium as carrier gas. The yields of methane, methylamine, and the unknown were determined. Another aliquot of the same sample was passed through a Pyrex tube heated to  $120^\circ$ , containing

(9) F. Cacace and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3202 (1962).

(10) L. M. Dorfman and F. J. Shipko, *ibid.*, **77**, 4723 (1955).

(11) F. W. Lampe, *ibid.*, **79**, 1055 (1957).

(12) G. J. Hine and G. L. Brownell, "Radiation Dosimetry," Academic Press Inc., New York, N. Y., 1956.

(13) G. Stöcklin, F. Cacace, and A. P. Wolf, *Z. anal. Chem.*, **194**, 406 (1963).

**Table I.** Yields of Radioactive Products as a Result of the  $N^{14}(p,\alpha)C^{11}$  Reaction in Ammonia, Methylamine, and Methylamine-Ammonia Mixtures

Run no.	Target	Dose, e.v./molecule	Radiochemical yields, <sup>a</sup> %			Activity on strip. col.	Recovery
			CH <sub>4</sub>	CH <sub>3</sub> NH <sub>2</sub>	CO		
5	NH <sub>3</sub> (g)	6.7 × 10 <sup>-1</sup>	94	3.7	...		97.7
6	NH <sub>3</sub> (g)	1.4 × 10 <sup>-1</sup>	85	9.8	...		94.8
2	NH <sub>3</sub> (g)	3.7 × 10 <sup>-2</sup>	87	14	...		101
1	NH <sub>3</sub> (g)	3 × 10 <sup>-2</sup>	80	19	0.2		99.2
24	NH <sub>3</sub> (g)	3 × 10 <sup>-2</sup>	96 <sup>c</sup>	1.2			97.2
8	NH <sub>3</sub> (g)	1.3 × 10 <sup>-2</sup>	59	29	0.5		88.5 <sup>b</sup>
25	NH <sub>3</sub> (g)	1 × 10 <sup>-2</sup>	98 <sup>c</sup>	0.3			98.3
3	NH <sub>3</sub> (g)	6.6 × 10 <sup>-3</sup>	49	29			78 <sup>b</sup>
4	NH <sub>3</sub> (g)	1.6 × 10 <sup>-3</sup>	42	33	1.1		76.1 <sup>b</sup>
15	NH <sub>3</sub> (g)	5.1 × 10 <sup>-4</sup>	35	31			
16	NH <sub>3</sub> (g)	4.8 × 10 <sup>-4</sup>	44	38		14	98.9
21	NH <sub>3</sub> (g)	3 × 10 <sup>-4</sup>	50	43		13	106
61	NH <sub>3</sub> (g)	3 × 10 <sup>-4d</sup>	44	56		0	100
20a	NH <sub>3</sub> (g)	10 <sup>-4e</sup>	40	36		19	95
20b	NH <sub>3</sub> (g)	10 <sup>-4e</sup>	38	56		0	94
57, 58	NH <sub>3</sub> (l), -47°	3 × 10 <sup>-3</sup>	8.2	71.9			79.6 <sup>b</sup>
52, 53	NH <sub>3</sub> (l), -72°	3 × 10 <sup>-3</sup>	7.6	74.4			82 <sup>b</sup>
49, 50	NH <sub>3</sub> (s), -196°	3 × 10 <sup>-3</sup>	9.1	74.8			83.9 <sup>b</sup>
43, 48	NH <sub>3</sub> (s), -196°	7.5 × 10 <sup>-1</sup>	50.4	32.2			82.6 <sup>b</sup>
10	NH <sub>3</sub> (g) + 0.13% CH <sub>3</sub> NH <sub>2</sub>	7.4 × 10 <sup>-1</sup>	87	6			95.1 <sup>f</sup>
9	NH <sub>3</sub> (g) + 0.13% CH <sub>3</sub> NH <sub>2</sub>	1.5 × 10 <sup>-1</sup>	87	17			107.1 <sup>f</sup>
11	NH <sub>3</sub> (g) + 2.1% CH <sub>3</sub> NH <sub>2</sub>	7.0 × 10 <sup>-1</sup>	73	12			88.9 <sup>f</sup>
12	NH <sub>3</sub> (g) + 4.0% CH <sub>3</sub> NH <sub>2</sub>	6.3 × 10 <sup>-1</sup>	71	17			93.1 <sup>f</sup>
18, 19	CH <sub>3</sub> NH <sub>2</sub> (g)	1	14.5	2 <sup>g</sup>	...	1.4	95.7 <sup>h</sup>
27	CH <sub>3</sub> NH <sub>2</sub> (g)	10 <sup>-3</sup>	3.4	1 <sup>g</sup>	...	0.4	78.2 <sup>h</sup>

<sup>a</sup> Activity in compound/total activity in gas phase (bypass determination). <sup>b</sup> Low recovery probably due to irreversible absorption of unknown activity at head of g.l.c. column. The stripping column was not used in these runs. <sup>c</sup> The NH<sub>3</sub> was irradiated at the dose listed. Aluminum absorbers (144 mg./cm.<sup>2</sup>, run 24; 155 mg./cm.<sup>2</sup>, run 25) were then placed in front of the tank window slowing the protons to an energy below the threshold for carbon-11 production. Irradiation was continued with low-energy protons until a total dose of 3.9 e.v./molecule had been absorbed. <sup>d</sup> The whole sample was passed through the reduction furnace before assay. <sup>e</sup> The first assay, 20a, was taken on the irradiated material. The second assay was carried out on an aliquot, 20b, which had gone through the reduction catalyst; cf. Experimental Section. <sup>f</sup> Ethane and propane were also determined: run 10, 1.8% C<sub>2</sub>H<sub>6</sub>, 0.3% C<sub>3</sub>H<sub>8</sub>; run 9, 2.7% C<sub>2</sub>H<sub>6</sub>, 0.4% C<sub>3</sub>H<sub>8</sub>; run 11, 3.3% C<sub>2</sub>H<sub>6</sub>, 0.6% C<sub>3</sub>H<sub>8</sub>; run 12, 4.1% C<sub>2</sub>H<sub>6</sub>, 1.0% C<sub>3</sub>H<sub>8</sub>. <sup>g</sup> CH<sub>3</sub>NH<sub>2</sub> was not separated from CH<sub>3</sub>CN in these runs. The values given are maximum values based upon CH<sub>3</sub>CN yields from runs not included in this table (cf. footnote h). <sup>h</sup> The product spectrum from CH<sub>3</sub>NH<sub>2</sub> under varying conditions of irradiation is the subject of another paper (F. Cacace, G. Stöcklin, and A. P. Wolf, *Radiochim. Acta*, in press). The rest of the activity is accounted for by some ten other products.

Raney nickel on Celite,<sup>14</sup> before entering the stripping column and analytical column. The activity normally appearing on the stripping column dropped to zero in each case and reappeared as a concomitant increase in methylamine activity. The data are given in Table II.

**Table II.** Reduction of Methylenimine-C<sup>11</sup>

Run no. <sup>a</sup>	Assay	Dose, e.v./molecule	Analysis, %		
			Methane-C <sup>11</sup>	Methylamine-C <sup>11</sup>	Methylenimine-C <sup>11</sup>
20	Assay before reduction	10 <sup>-4</sup>	40	36	19
20	Assay after reduction	...	38	56	0
61	Assay after reduction only	3 × 10 <sup>-4</sup>	44	56	0

<sup>a</sup> The target in each case was NH<sub>3</sub> (1 atm.).

(14) F. Drawert, R. Felgenhauer, and G. Kupper, *Angew. Chem.*, **72**, 555 (1960).

2. *Hydrolysis.* A sample was irradiated and the activity absorbed on the stripping column was then determined. Another aliquot of the sample was condensed into an ampoule containing 5 ml. of 7 N H<sub>2</sub>SO<sub>4</sub>, 39 mg. of carrier formaldehyde, and 50 mg. of carrier methylamine. The ampoule was sealed and heated for 20 min. at 100°. The contents of the ampoule were added to a saturated solution of dimedon and the derivative was collected. The precipitate was purified by alternately dissolving with dilute NaOH and precipitating it from each fresh solution with H<sub>2</sub>SO<sub>4</sub>. This was done three times. The derivative was recrystallized several times from ethanol-water and counted in a well-type counter; the wet crystals were then dried and weighed. In this way the yield of carbon-11 labeled formaldehyde could be determined. In two runs 88.2 and 87.9% of the activity absorbed on the stripping column was now assayed as formaldehyde-C<sup>11</sup>. Neither methane nor methylamine can yield formaldehyde under these conditions. In order to eliminate the possibility that HCN or its hydrolysis and reaction products might be contaminating the derivative, 20 ml. (STP) of HCN, 200 mg. of HCOOH, 200 mg. of HCONH<sub>2</sub>, and 100 mg. of methylamine were added as

**Table III.** Yields of Radioactive Products as a Result of the  $N^{14}(p,\alpha)C^{11}$  Reaction  $N_2-NH_3$  Mixtures<sup>a</sup>

Target $N_2 + NH_3$ % $NH_3$	Radiochemical yields, %				Un-identified peaks	Recov-ery, %
	$CH_4$	$CH_3NH_2$	$CO^b$			
0.5	89.2	$3.5 \pm 0.7$	$\sim 3.2$			95
0.65	75.8	$3.8 \pm 0.8$	8.0	7.5		95.1
0.92	72.4	10.8	2.9	...		86.1
1.98	67.0	14.3	2.1	4.9		88.3
2.90	58.5	15.0	3.9	...		77.4
3.95	52.2	16.6	3.8	...		72.6
5.80	52.7	22.0	3.8	...		78.5
9.50	48.8	26.2	3.5	...		78.5

<sup>a</sup> The dose in each case was  $1.5 \pm 0.5 \times 10^{-3}$  e.v./molecule.

<sup>b</sup> The "spectroscopically" pure  $N_2$  contained traces of  $O_2$ .

methylamine and methylamine- $C^{11}$  using the method described under hydrogenation of methylenimine.

Nitromethane, formamide, O-methylhydroxylamine, formaldehyde, and formic acid were ruled out on the basis of retention time. N-Methylhydroxylamine and others were ruled out on the basis of boiling point. It is, of course, also evident that a number of these compounds will not give methylamine on catalytic reduction with hydrogen.

*Ammonia-Nitrogen and Ammonia-Oxygen Mixtures.* Tables III and IV give all pertinent data relating to runs on mixtures of these gases.

*Photolysis of Diazomethane-Ammonia Mixtures.* Diazomethane was prepared by adding nitrosomethyl-urea to concentrated KOH solution in a 50-ml. flask.

**Table IV.** Yields of Radioactive Products as a Result of the  $N^{14}(p,\alpha)C^{11}$  Reaction of  $NH_3-O_2$  Mixtures

Target $NH_3 + O_2$ % $O_2$	Dose, e.v./molecule	Radiochemical yields, %					Recovery, %
		$CH_4$	$CH_3NH_2$	$CO$	$CH_2NOH$	$CH_3OH$	
0.007	$3 \times 10^{-3}$	24.2	30.8	6.5	23.2	3.6	88.3
0.05	$3 \times 10^{-3}$	14.8	24.0	17.3	31.6	9.6	97.3
0.11	$3 \times 10^{-3}$	...	6.8	41.2	47.2	4.9	99.1
0.33 <sup>a</sup>	$3 \times 10^{-3}$	...	4.9	40.6	40.9	3.9	90.3
1.0 <sup>a</sup>	$3 \times 10^{-3}$	...	5.1	65.0	27.5	3.4	101
1.45	$3 \times 10^{-3}$	...	4.5	66.8	28.0	3.6	102.9
1.98	$3 \times 10^{-3}$	...	5.0	65.8	22.3	3.8	96.9
1.98 <sup>a</sup>	0.69	94.3	1.8	1.2	...	$\sim 1.2$	98.5
1.98	$2 \times 10^{-3b}$	87.5	1.5	1.7	...	0.9	91.6

<sup>a</sup> Average values for two runs; precision  $\pm 5\%$  average deviation. <sup>b</sup> The sample was irradiated to the listed dose. An Al foil (155 mg./cm.<sup>2</sup>) was then placed in front of the window, slowing the protons to an energy below the threshold ( $\sim 3$  Mev.) for carbon-11 production. The sample was then irradiated with these low energy protons up to a dose of 3.0 e.v./molecule.

carriers in addition to the formaldehyde added. Using the same procedure as first outlined, 92% of the activity was found as formaldehyde- $C^{11}$ .

3. *Irradiation in the Presence of Oxygen.* Irradiations of  $NH_3-O_2$  systems involving 0.4 to 1.7% oxygen by volume at low doses resulted in samples which were devoid of activity that could be absorbed by the stripping column. Total recovery in all cases studied was between 90 and 100%. Depending on oxygen concentration this activity was distributed between methane- $C^{11}$ , methylamine- $C^{11}$ , methyl alcohol- $C^{11}$ , carbon monoxide, and a compound with a relative retention of  $2.43 \pm 0.05$  (methylamine = 1.00) on the cetyl alcohol column previously described.

The evidence that this oxygenated compound can be reasonably assumed to be formaldoxime follows. Formaldoxime, prepared according to the method of Dunstan and Bossi<sup>15</sup> (b.p.  $84.5^\circ$ , hydrochloride m.p.  $135^\circ$ ), had a relative retention of  $2.42 \pm 0.1$ . Since the oxime trimerizes rapidly, droplets of distillate had to be injected into the column immediately as they came from the condenser. The trimer (an amorphous solid) was also depolymerized at  $137^\circ$  in a gas injection trap and the gas then swept into the column. Both of these methods yield the same broad and unsymmetrical peak having the same relative retention. In addition, both the gaseous synthetic formaldoxime and the oxygenated carbon-11 compound are quantitatively reduced to

(15) W. R. Dunstan and A. L. Bossi, *J. Chem. Soc.*, 353 (1898).

**Table V.** Photolysis of Diazomethane in Ammonia

Irradiation time, hr. <sup>a</sup>	Pressure, mm.		$CH_3NH_2$ yield, %
	$CH_2N_2$	$NH_3$	
19 <sup>a</sup>	103	637	12.8 <sup>c</sup>
1.25 <sup>b</sup>	119	465	8.5 <sup>c</sup>
1 <sup>b</sup>	88	450	9.5

<sup>a</sup> Pyrex vessel. <sup>b</sup> Quartz vessel. <sup>c</sup> Yield based on diazomethane (average of two runs).

The solution was cooled with liquid  $N_2$ ; the flask was evacuated and then allowed to warm to room temperature. The diazomethane produced was pumped off and dried by multiple distillations through Dry Ice-acetone cooled traps. The diazomethane was finally condensed with liquid nitrogen and outgassed in the conventional manner. It should, of course, be stressed that this is a dangerous procedure. All ground surfaces in the vacuum line need to be well covered with Kel-F grease. A safety shield should be used in front of the line at all times during such experiments. The purity of the diazomethane and the ammonia were checked by g.l.c. Quantitative determination of the composition of the reaction mixture and products was done using an 8-ft. cetyl alcohol column (*cf.* Analysis). Irradiations were done using a Model SL-2537 ultraviolet lamp from Ultra Violet Products, Inc. The samples were contained in a 100-ml. quartz vessel. The results of these experiments are given in Table V.

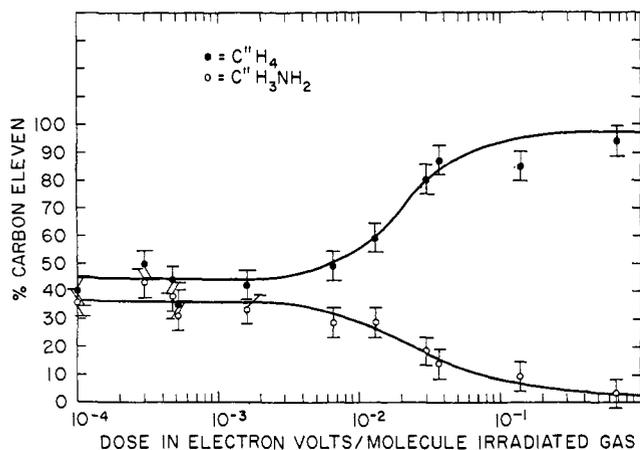


Figure 1. Carbon-11 product spectrum in  $\text{NH}_3$  as a function of dose.

### Radiation Effects

Perhaps the most convincing evidence for a radiation effect is the dramatic change in the carbon-11 product spectrum seen in Figure 1.<sup>16</sup> As the dose is reduced, the yield of methane- $\text{C}^{11}$  decreases and the yield of methylamine- $\text{C}^{11}$  increases. Above doses of 0.1 e.v./molecule the yields of methane- $\text{C}^{11}$  and methylamine- $\text{C}^{11}$  are seen to level off. This incidentally explains the results obtained by Yang and Wolf in reactor work with carbon-14 atoms where the absorbed doses in the gas phase irradiations were always greater than 0.1 e.v./molecule. The product composition was that characteristic of the saturation region<sup>6</sup> and thus did not allow a clear separation of the reactions of energetic carbon atoms from those reactions brought about by the concomitant radiation chemistry.<sup>17</sup>

In order to demonstrate unequivocally that methylamine could be radiolytically reduced, mixtures of methylamine- $\text{C}^{11}$  and methane- $\text{C}^{11}$  were produced at intermediate doses (run 24 at  $3 \times 10^{-2}$  e.v./molecule; run 25 at  $1 \times 10^{-2}$  e.v./molecule). Under these conditions of irradiation, about 0.05% of the total methylamine- $\text{C}^{11}$  being produced in the runs would be destroyed (assuming a  $G_{-\text{CH}_3\text{NH}_2} = 5$ ) by direct radiolysis. Aluminum absorbers (*cf.* footnote *c*, Table I) were then placed in front of the tanks being irradiated so that the protons entering the tank were of such an energy as to be unable to produce carbon-11 but still able to cause radiation damage. The radiation dose finally delivered was 3.9 e.v./molecule in each case. In each instance methane- $\text{C}^{11}$  was essentially the sole product, thus demonstrating that all the compounds produced by

(16) It should be noted here that C. MacKay, M. Pandow, P. Polak, and R. Wolfgang in "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Agency, Vienna, 1961, pp. 17-26, were unable to detect any carbon-11 containing product except CO at "low" (undetermined) doses, but they did find some methane- $\text{C}^{11}$  at "high" (undetermined) doses. In addition, "No methylamine was observed even under the conditions of high radiation intensity." From this experiment they concluded that the "primary product" can be reduced to methane. The absence of experimental detail and quantitative data does not allow speculation about the reasons for the presence of carbon monoxide and methane only and the absence of methylamine under their conditions.

(17) Some recent work (B. G. Dzantiev, R. A. Stukan, A. P. Shredchikov, and A. V. Shiskov, "The Formation of Polymeric Products in Reactions of Polyvalent Recoil Atoms," Symposium on the Chemical Effects Associated with Nuclear Reactions, Vienna, Dec. 1964), notes also that the sole product of reactor irradiation of gaseous anhydrous ammonia is carbon-14 labeled methane.

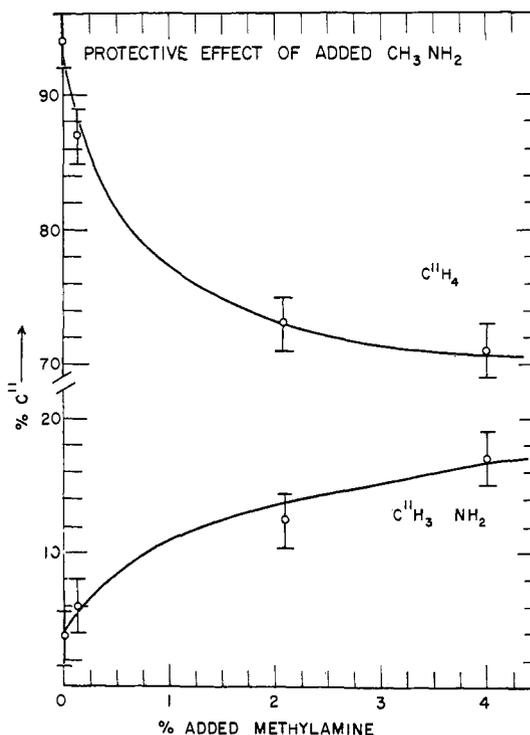


Figure 2. Protective effect of added methylamine.

carbon atom interaction with the substrate, methylamine- $\text{C}^{11}$  included, are readily reduced by radiolysis.<sup>18</sup> The dose of 3.9 e.v./molecule should have destroyed some 19% of the methylamine- $\text{C}^{11}$  produced prior to reduction of the energy of the protons entering the tanks. The almost complete elimination of methylamine- $\text{C}^{11}$  suggests extensive reaction with some of the unlabeled radiolytically produced species leading to reduction. Direct reduction by some product of the radiolysis of ammonia (*e.g.*,  $\text{H}\cdot$ ) can also occur. These views are supported by the striking protective effect observed when bulk methylamine is present during irradiation. If a few per cent of methylamine is added to the ammonia before irradiation, then the total methylamine concentration is about  $5 \times 10^{17}$  molecules/cc. (between  $10^7$  and  $10^8$  molecules/cc. of this gas mixture will contain carbon-11 atoms when the dose level is 0.7 e.v./molecule) during irradiation. Indirect radiolytic destruction of the methylamine- $\text{C}^{11}$  produced is now suppressed because the overwhelming concentration disadvantage of the methylamine- $\text{C}^{11}$  when it is produced carrier free has been overcome. This is illustrated in Figure 2 which plots some of the results given in Table I. It should be noted, of course, that methylamine- $\text{C}^{11}$  is produced in very small yield when neat methylamine is irradiated (Table I, runs 18, 19, and 27). The methylamine- $\text{C}^{11}$  formed in neat ammonia and ammonia-methylamine mixtures can be only ascribed to reaction between the energetic carbon atom and ammonia.

While it is clear from these experiments that the radiation field present during carbon atom production is

(18) F. Cacace and G. Di Marco, private communication, have studied the radiolysis of neat  $\text{C}^{14}\text{H}_3\text{NH}_2$  and also  $\text{C}^{14}\text{H}_3\text{NH}_2$  in  $\text{NH}_3$  at high dilution. Doses of 0.4 e.v./molecule produced some  $\text{C}^{14}\text{H}_4$  in all cases. As the mole per cent of  $\text{C}^{14}\text{H}_3\text{NH}_2$  in the mixtures was decreased, the per cent conversion to  $\text{C}^{14}\text{H}_4$  was increased markedly. This is clearly in support of the suggested radiolytic reduction of  $\text{C}^{11}\text{H}_3\text{NH}_2$  under our conditions.

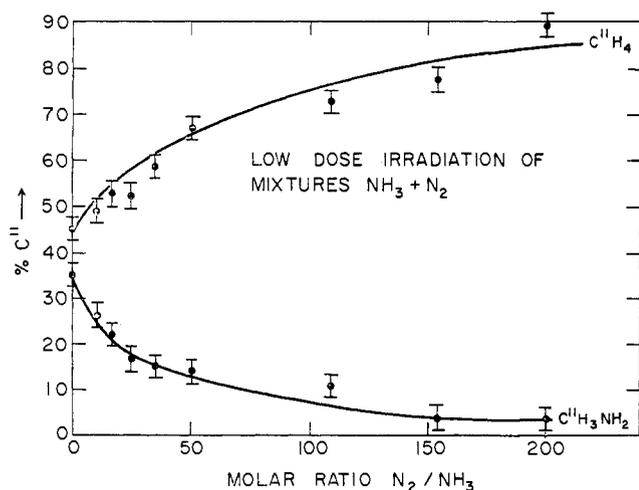
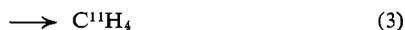
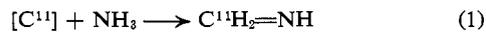


Figure 3. Low dose irradiation of  $N_2$ - $NH_3$  mixtures (moderation by nitrogen).

responsible for the reduction of various intermediates to methane- $C^{11}$ , the data does not allow us to postulate a unique mechanism of reduction in the ammonia system.

**Methylenimine.** The reactions of energetic carbon atoms with ammonia in the gas phase can be summarized by eq. 1-3, several steps being involved in each case. A discussion of the modes of formation



of the three products follows. The identification of methylamine- $C^{11}$  (or  $-C^{14}$ ) and methane- $C^{11}$  (or  $-C^{14}$ ) is on firm ground. The fact that nearly all the carbon atoms produced yield these products when their production is carried out in the presence of a high-radiation field is supported by the work of Yang and Wolf,<sup>2</sup> Dzantiev, *et al.*,<sup>17</sup> and the present work. The presence of another compound at low concomitant radiation intensities has been established and it has been identified as probably being methylenimine- $C^{11}$ . The evidence for its presence and for this assignment, details in support of which are given in the Experimental Section, is based on several facts.<sup>19</sup> It can be quantitatively trapped on a g.l.c. column and its presence quantitatively noted (because of its radioactivity) by direct assay of the section of column involved. Its activity when added to the activity found as methane- $C^{11}$  and as methylamine- $C^{11}$  accounts for 100% of the activity produced. The compound can be quantitatively reduced to methylamine- $C^{11}$ . It can be quantitatively hydrolyzed to formaldehyde- $C^{11}$ . Other combinations of one carbon atom plus hydrogen and nitrogen atoms can be ruled out because of a lack of the

(19) A search of the literature did not provide us with a synthetic route for preparing methylenimine. It would of course be expected to be a highly reactive compound. For example, the possible rapid polymerization of this compound was alluded to in the paper of F. O. Rice and G. J. Grelecki, *J. Phys. Chem.*, **61**, 830 (1957). These authors attempted to prepare it from the  $CH_3N\cdot$  radical. Under the conditions described in our experiments, the methylenimine is in very high dilution ( $\sim 10^6$ - $10^7$  molecules of imine per  $10^{20}$  molecules of ammonia) and would therefore maintain its integrity until mixed with another reactive substance. Polymerization under the time scale of these experiments is unlikely because of the low probability of collision between methylenimine molecules.

observed chemical properties or because they can be eluted from g.l.c. columns which will not pass the compound produced in the reaction of a carbon atom with ammonia. The possible presence of methylenimine- $C^{14}$  in a system involving energetic carbon atoms was first noted by Yankwich and Vaughan.<sup>20</sup> They studied the reaction of carbon-14 atoms in crystalline ammonium bromide and noted that dissolution of the crystals in water always led to a 6% yield of formaldehyde. They suggested that methylenimine- $C^{14}$  was trapped in the crystalline matrix and that dissolving the crystals in water led to the formation of formaldehyde- $C^{14}$ . This evidence is consistent with the postulate that the compound is methylenimine.<sup>21</sup> The intermediacy of methylenimine- $C^{11}$  is further bolstered by the results obtained for the reactions of carbon atoms with oxygen-ammonia mixtures (*vide infra*).

**Moderation of Carbon Atoms in Ammonia.** Another factor involved in the mechanisms of formation of the observed products pertains to whether they are formed by hot or thermal (*cf.* ref. 7 and 8) reactions. The nature of the nuclear reactions involved<sup>22</sup> and other considerations did not allow the use of inert gas moderators in the ammonia system; however, nitrogen was used as a moderator<sup>23</sup> in their place. The results are given in Figure 3. Increasing moderation causes the methylamine- $C^{11}$  to fall off with a concomitant increase in methane- $C^{11}$  production.

**Carbon Atoms in Ammonia-Oxygen Systems.** Support for the hypothesis that some, if not all, of the methylamine- $C^{11}$  is formed in hot reactions and all of the methane- $C^{11}$  is formed in thermal reactions is obtained from the experiments in which varying amounts of oxygen were present in the ammonia during irradiation (*cf.* Figures 4 and 5). The methane yield falls off by a factor of 4.5 over a very small range of oxygen concentrations (Figure 4) and falls to 0 before 0.075%  $O_2$  is reached. This evidence suggests that most if not all the methane- $C^{11}$  observed at low doses is formed in thermal reactions between carbon atoms and ammonia.<sup>24</sup> The methane- $C^{11}$  observed at high doses is formed by both the thermal reaction and by radiolytic reduction of methylamine- $C^{11}$  (*vide supra*).

The curves in Figures 4 and 5 also allow us to focus attention on the source of the methylamine. When

(20) P. E. Yankwich and J. D. Vaughan, *J. Am. Chem. Soc.*, **76**, 5851 (1954).

(21) These experimental results do not rigorously exclude methylenediamine. This compound has not been prepared in its free state but seems to be known as its salt. However, the free diamine should be passed through a cetyl alcohol column. Mechanistic reasons would also militate against the diamine. The formation of gem compounds has been observed in hot atom processes (R. Schuler, private communication) but only in very low (1-3%) yield, whereas the yield of the compound we note is as high as 20% at low doses.

(22) Proton bombardments with inert gas moderators, *e.g.*, He, at concentration levels of the moderator where definite effects are observed are so large as to disallow adequate carbon-11 production. Greater radiation intensities than are attainable at BNL would be required to make high-dilution studies in the ammonia system tenable. In addition, proton bombardments of a moderator such as argon used in admixture results in the production of other activities in sufficient amount to make quantitative assay of carbon-11 activity extremely difficult.

(23) Nitrogen is a reactant which can give rise to  $HC^{11}N$ . Nevertheless it can be considered a moderator in this system since we are looking at the change in relative yields of two products which can only arise from interaction with  $NH_3$ . Further, there is essentially no radiolytic reduction of  $HC^{11}N$  to  $C^{11}H_4$  even at high doses.

(24) Unfortunately this work does not allow us to extrapolate to zero dose. It is possible that there may still be radiolytic reduction going on at doses of  $10^{-4}$  e.v./molecule, the lowest dose attainable in our experiments.

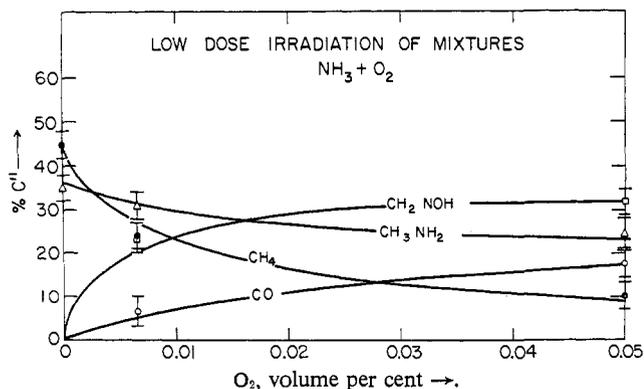


Figure 4. Low dose irradiation of  $O_2$ - $NH_3$  mixture.

oxygen is used in admixture with ammonia during a run at low doses, the methylenimine- $C^{11}$  disappears and a new carbon-11 containing compound is produced, the evidence for which indicates it to be formaldoxime- $C^{11}$ . The carbon-11 compound can be quantitatively reduced to methylamine- $C^{11}$  and the compound has the same emergence time as formaldoxime. In addition to the disappearance of methylenimine- $C^{11}$ , the methylamine- $C^{11}$  yield is seen to fall sharply to a constant yield of 5%, over the oxygen concentration range studied (Figure 5). The oxygen is therefore not only reacting with methylenimine- $C^{11}$  but with a precursor of methylamine- $C^{11}$  which could be methylenimine- $C^{11}$  or some other compound. Another interesting feature of the curves in Figure 5 is that there is a rapid rise to a maximum 48% yield of the oxime followed by a gradual decline in yield of the oxime compensated for by a gradual increase in  $C^{11}O$  yield. This type of behavior has also been noted in the reaction of carbon atoms with pure methane<sup>25</sup> and is characteristic of the action of oxygen first as a scavenger of thermal carbon atoms and reactive intermediates, and then as a competitor for reaction with hot carbon atoms. Oxygen is seen here to react with what is probably an excited precursor. This is possible in this system because of the low reactivity of ammonia.

**Carbon Atoms in a Propane-Ammonia Mixture.** Further evidence for the low efficiency of the reaction of carbon atoms in ammonia is garnered from the low dose irradiations of equimolar mixtures of ammonia and propane. The carbon atoms show a marked preference for reaction with propane (*cf.* Table VI). This

Table VI. Irradiation<sup>a</sup> of an Equimolar Mixture of  $NH_3$  and  $C_3H_8$

C <sup>11</sup> -containing product	Radiochemical yield, %		
	Neat $NH_3$	Neat $C_3H_8$	Mixture $NH_3 + C_3H_8$
$CH_4$	45.0	2.9	7.3
$CH_3NH_2$	35.0	...	5.0
$C_2H_2$	...	25.0	21.3
$C_2H_4 + C_2H_6$	...	19.6	17.4
$C_3H_6$	...	12.2	8.7
Butanes	...	10.1	10.8
Total recovery <sup>b</sup>	80	77	75

<sup>a</sup> Dose  $\cong 3 \times 10^{-8}$  e.v./molecule. <sup>b</sup> Recovery of all assayed products.

(25) G. Stöcklin, H. Stangl, D. R. Christman, J. B. Cumming, and A. P. Wolf, *J. Phys. Chem.*, **67**, 1735 (1963).

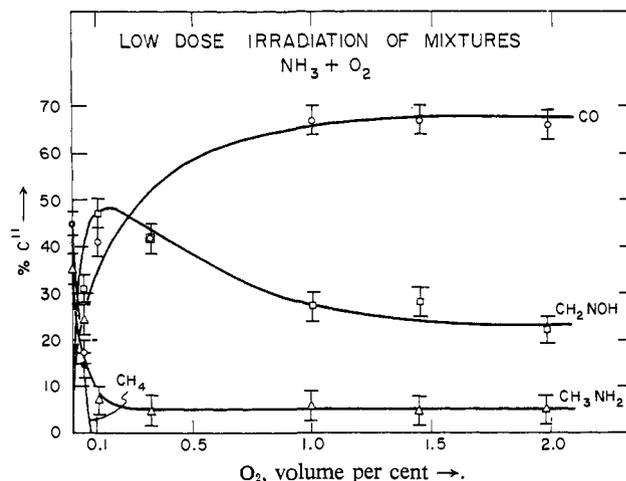


Figure 5. Low dose irradiation of  $O_2$ - $NH_3$  mixture.

lack of reactivity is also reflected in the  $C^{11}O$  yield being 60% when 0.58%  $O_2$  is present in the  $NH_3$  as opposed to a 15.6%  $C^{11}O$  yield when 0.58%  $O_2$  is present in propane.<sup>26</sup> The oxygen is considerably more effective in competing for the carbon atom when ammonia is the substrate than when propane is the substrate.

**Carbon Atoms in Liquid and Solid Ammonia.** The yields of methylamine- $C^{11}$  and methane- $C^{11}$  undergo a marked change in the liquid and solid phase at low dose (*cf.* Table I) with  $\sim 74\%$  of the activity now appearing as methylamine- $C^{11}$  and  $\sim 8\%$  of the activity now appearing as methane- $C^{11}$ . The remaining 18% again was found to be absorbed at the head of the g.l.c. columns, but no attempt was made to prove it to be a compound identical with the compound found in the gas phase work. As the dose was raised, methane- $C^{11}$  again became the dominant product, incidentally demonstrating that radiolytic reduction may be possible in the solid phase. Rapid reduction in the transitory liquid phase (*cf.* Experimental Section) is not ruled out in these experiments. The liquid and solid phase results also suggest that an excited intermediate containing both carbon and nitrogen gets reduced by direct interaction with its surroundings to give a considerable fraction of the methylamine- $C^{11}$  observed. It is interesting to note that in the work of Yankwich and Vaughan,<sup>20</sup> the yield of methylamine- $C^{14}$  in irradiated ammonium bromide crystals was 79%. Unfortunately a precise dose calculation for the reactor<sup>20</sup> irradiation cannot be made and the irradiation conditions were not varied. There is no necessary correspondence between mechanisms in the two systems (a low-melting solid in which there is covalent bonding and a high-melting ionic crystal), but it would be of considerable interest to see if radiolytic conversion of methylamine- $C^{14}$  to methane- $C^{14}$  were also possible in crystalline ammonium bromide in order to gain further insight into the mechanism.

## Discussion

A scheme for the reactions of discrete carbon atoms in ammonia is given in Figure 6. Carbon-11 atom insertion (*cf.* ref. 7 and 8) is seen to give a highly excited in-

(26) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).

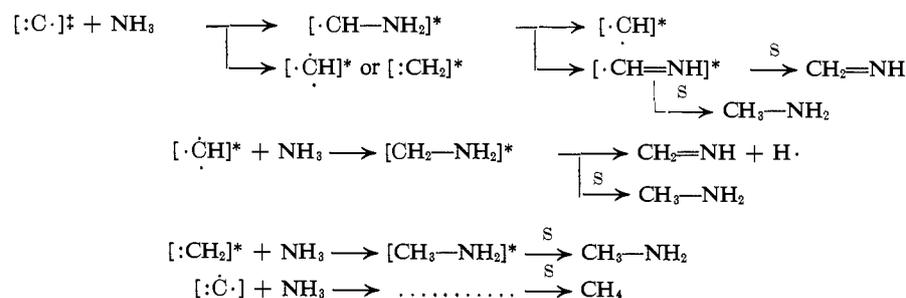


Figure 6. Reactions of carbon atoms in ammonia. This work does not give any information as to the spin state of the carbon atom or of the spin state of any of the intermediates depicted here. The radiolytic behavior of the system is not included in this depiction:  $\ddagger$  denotes excess kinetic energy;  $*$  denotes the fragment or molecule being in an excited state but not necessarily having excess kinetic energy. S denotes reaction with the substrate, *i.e.*,  $\text{NH}_3$ , or with other fragments present in the ammonia during the lifetime of the highly reactive species. While the "simple" abstraction of a hydrogen or successive abstractions could give  $2\text{NH}_2\cdot$  or  $\text{NH}\cdot$ , etc., as products, no direct evidence of such products is at hand. We have therefore chosen not to write balanced equations. Deexcitation of any of the excited intermediates may come in the reaction step or by a nonreactive collision with the substrate. The number of steps involved in the last reaction are not implied.

intermediate which by hydrogen migration<sup>27</sup> can lead to methylenimine- $\text{C}^{11}$  which in turn can become collisionally stabilized. The oxygenated compound would most probably be derived from interaction with excited methylenimine- $\text{C}^{11}$  or its immediate precursor. The reduction of methylenimine- $\text{C}^{11}$  to methylamine- $\text{C}^{11}$  can occur by direct interaction of the excited methylenimine- $\text{C}^{11}$  with its surroundings. Radiolytic reduction of methylenimine- $\text{C}^{11}$  to methylamine- $\text{C}^{11}$  can occur by a number of mechanisms which the work of Cacace and Di Marco<sup>18</sup> hopefully will serve to elucidate.

The low but constant yield of methylamine- $\text{C}^{11}$  observed, which increasing amounts of oxygen present in the reactive system do not serve to reduce, is probably due to another mechanism, *e.g.*, methylene- $\text{C}^{11}$  insertion into an NH bond in ammonia. That methylene can indeed form methylamine by reaction with ammonia certainly seems reasonable on mechanistic grounds and is supported by the experiments on the photolysis of diazomethane in ammonia reported in the Experimental Section. The evidence for methylene- $\text{C}^{11}$  produced by hot atom reactions in hydrocarbon systems is amply documented<sup>7,8</sup> and further the gas phase yields of products due to the reactions of excited methylene- $\text{C}^{11}$  and a particular hydrocarbon are in the same region in all systems studied to date and comparable to what is found in ammonia. Although there is no direct evidence for the presence of methyne<sup>28</sup> in the ammonia system, another mechanism for methylenimine- $\text{C}^{11}$  and methylamine- $\text{C}^{11}$  formation could involve methyne- $\text{C}^{11}$  insertion. It should again be em-

(27) Proof of extensive hydrogen migration in a reactive intermediate was reported by H. Ache and A. P. Wolf, International Atomic Energy Agency Symposium, Vienna, Dec. 1964; acetylene- $\text{C}^{11}$  obtained from carbon atom reaction with 1,1-dideuteriocyclopropane contained not only the expected  $\text{HC}^{11}\equiv\text{CH}$  and  $\text{DC}^{11}\equiv\text{CD}$  but also considerable  $\text{HC}^{11}\equiv\text{CD}$ . An uncomplicated insertion decomposition mechanism would only have allowed the formation of the diprotio or dideuterio compound.

(28) Evidence for the formation of methyne- $\text{C}^{11}$  in hydrocarbon systems was presented by G. Stöcklin and A. P. Wolf at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

phasized at this point that in these hot reactions multiple pathways for product formation are possible since the intermediates that can be formed have in all cases an amount of energy in excess of any activation energy necessary for further reaction. The energy of the intermediate derives not only from the exothermic nature of most of these reactions but also from the initial kinetic energy brought into the complex by the carbon-11 atom. Apropos of this an important series of papers by Marshall, MacKay, and Wolfgang<sup>29</sup> and Dubrin, MacKay, and Wolfgang<sup>30</sup> indicate that both hot and thermal (*cf.* footnote 40 of ref. 29) carbon atoms produce a qualitatively similar but quantitatively different product spectrum when carbon-11 atoms are allowed to react with ethylene. It is shown from this work in ammonia that most, if not all, of the methylamine- $\text{C}^{11}$  derives from the reaction of hot carbon atoms and that methane- $\text{C}^{11}$  is produced by thermal reactions.

## Conclusion

Energetic carbon atoms react with ammonia to give methylenimine, methylamine, and methane. The methylenimine and methylamine are produced in hot reactions. Most, if not all, of the methane is produced in thermal reactions. Facile radiolytic reduction of methylamine to methane occurs in our system. A consistent picture of the mechanism involves the postulate of excited intermediates or complexes<sup>31</sup> and insertion reactions. The formation of  $\text{HC}^{11}\text{N}$  or a derivative thereof under our reaction conditions was not demonstrable.

*Acknowledgment.* The authors wish to acknowledge the generous help of Dr. C. Baker and the cyclotron operators at the B.N.L. 60-in. cyclotron.

(29) M. Marshall, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

(30) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(31) This distinction is made since there is still no direct proof of the discrete structure one ascribes to an intermediate *vs.* the geometrically less well-defined structure one ascribes to a collision complex (*cf.* ref. 2 and 26).