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Gas Phase Reactions of Recoil Carbon-14 in Anhydrous Ammonia[1a]

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RECEIVED OCTOBER 19, 1959

Radiative neutron capture reactions of nitrogen in anhydrous ammonia have been studied in the gas phase. An uniquely high and specific yield of methane-C^{14} has been observed. This high yield of methane-C^{14} as essentially the sole significant product from operations of the recoil carbon in gaseous ammonia was not affected by the addition of inert moderating gases. The presence of oxygen as radical scavenger did not produce any significant effects. Reactions of the recoil carbon in the presence of methane and methylamine, however, gave a complex mixture of radioactive products. All carbon-14 systems reported to date show the latter behavior. A process of hydrogen abstraction is proposed to account for the apparently unique result from the operations of the recoil carbon in the presence of ammonia in the gas phase. The nature of the recoil fragments is discussed and the possibility of a *collision complex* mechanism being operative is explored.

Introduction

Yankwich and co-workers[2] have shown that carrying out the nuclear transformation $N^{14}(n,p)C^{14}$ in nitrogen-containing inorganic crystals can lead to a large number of labeled species. Their investigations involved the dissolution of the irradiated target materials in water. This, of course, may allow secondary reactions of the recoil products with water to take place. The actions of a recoiling carbon-14 in an organic medium also results in the formation of a large number of labeled compounds. A medium, in which complicating factors could be minimized, was desired so as to simplify the task of studying the nature and reactions of the recoil fragment. Ammonia appeared to be the logical compound with which to undertake such a study.

Investigations on the chemical effects of the nuclear transformation $N^{14}(n,p)C^{14}$ have all been carried out in the liquid or solid phase. Gas phase reactions involving recoiling tritium and recoiling halogens have been reported by Willard,[3,4] Wolfgang[5] and others. The relatively low thermal neutron collision cross section for the target nitrogen-14, together with the rather long half life of the product activity, renders similar studies on recoiling carbon-14 less convenient to carry out. With recent advances in radiochemical assay and by the use of gas chromatographic flow counting,[6] however, the difficulty of handling small amounts of sample with relatively low activities has been largely overcome. An investigation of the ammonia system in the gas phase (in order to avoid the unnecessary complication due to effects of liquid cages) was therefore made feasible.

Experimental

Materials.—Ammonia, methylamine, methane, oxygen, neon and xenon were obtained in lecture bottles as C.P. products from the Matheson Company. The first two gases were further purified before use, by drying over sodium metal and degassing under high vacuum. Cetyl alcohol was Eastman Kodak Company yellow label product. The diethylhexyl sebacate column was purchased from the Burrell Corporation. Molecular sieve 5A was obtained from the Linde Company and silica gel (20-200 mesh) from the Fischer Scientific Company.

Neutron Irradiation.—All samples were sealed under vacuum in quartz ampoules equipped with break-off tips. Irradiations were carried out in the water-cooled facility in the center of the Brookhaven nuclear reactor at the ambient air temperature (30°). Gaseous ammonia samples were exposed to irradiation for five days at a thermal neutron flux of about 1×10^{13} neutrons $cm.^{-2}$ $sec.^{-1}$ and a gamma dosage of about 2×10^6 r./hr. Methylamine was irradiated under the same conditions for three days; liquid ammonia 2-3 days.

Radioassay.—Each macro sample tube was accompanied by a sealed quartz capillary containing a weighed amount of ammonia. Total carbon-14 assay of the material in the capillary allowed calculation of the carbon-14 produced in the macro sample by using the ratio of nitrogen in the two tubes. The small tube was assayed by being opened in a closed quartz tube containing a measured amount of carrier carbon dioxide and excess cupric oxide. Following combustion at 700° for about 8 hr., the carrier carbon dioxide was collected and counted in a Bernstein–Ballentine[7] counter in the proportional region. Radiochemical analyses of methane and methylamine were carried out in a similar fashion by combustion of the corresponding carrier in the presence of cupric oxide. Determination of the specific activity of the resultant carbon dioxide-C^{14} was then made. Calculation of all other carbon-14 activities detected from gas chromatographic analyses was made by comparison of peak areas using methane-C^{14} as the internal standard.

Gas Chromatographic Analysis.—Carbon-14 radioanalysis by gas chromatographic flow counting according to the method of Wolfgang and Rowland[8] was used for qualitative detection and quantitative determination of the activities produced. A window flow counter as described by Wolfgang and Mackay[9] was employed as the detector at the exit of the chromatographic system. Thermal conductivity was used to detect the mass peaks.

An 8 ft. column, $^1/_4$ inch i.d., filled with 60–80 mesh methanolic sodium hydroxide washed[10] fire brick coated with 20% of its own weight of cetyl alcohol was used for separation of the amines, methyl hydrazine and acetonitrile. A 16 ft. column packed with diethylhexyl sebacate as the stationary phase was utilized for the detection of hydrogen cyanide. Two 8 ft. columns with molecular sieve 5A and high activity silica gel (20–200 mesh) as packing, respectively, were employed for the separation and identification of the non-condensable gases as well as ethane and CO_2. The sequence of appearance for the molecular sieve was

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(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) Requests for reprints should be addressed to this author.

(2) (a) P. E. Yankwich and W. R. Cornman, Jr., THIS JOURNAL, **77**, 2096 (1955). (b) P. E. Yankwich and W. R. Cornman, Jr., *ibid.*, **78**, 1560 (1956). (c) P. E. Yankwich and J. D. Vaughan, *ibid.*, **76**, 5851 (1954).

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(8) R. L. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

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TABLE I

YIELDS OF RADIOACTIVE SPECIES AS A RESULT OF THE $N^{14}(n,p)C^{14}$ NUCLEAR TRANSFORMATION IN GASEOUS AMMONIA AND METHYLAMINE

Material irrad.	Ammonia atm.	Mole fract., diluent	Ratio of diluent/ ammonia	Total C^{14} prod., μc	Distrib. C-14,[a] % Methane	Methylamine	Others	
Ammonia	1	...	..	1.6	89.4	0.10	[b]	
	4	...	..	5.6	104	.03	[b]	
	8	...	..	10.9	92.1	.06	[b]	
	12	...	..	14.3	94.4	..	[b]	
Ammonia[b] + Neon	8	0.189	0.23	10.0	96.1	.15	[b]	
	4	.286	.41	5.5	96.0	.14	[b]	
	4	.475	.91	5.0	98.0	.10	[b]	
	1	.773	3.36	1.33	93.2	.13	[b]	
Ammonia[b] + Xenon	8	.442	0.79	10.6	102	.07	[b]	
	4	.628	1.70	5.3	105	.06	[b]	
Ammonia[b] + Oxygen	4	.03	0.03	5.8	90	<1	CO_2	6
							CO	~0
Ammonia[b] + Methane	4	.667	2.00	5.3	60	~0.6	C_2H_6	6
							Polymer	34
Methylamine (4 atm.)	None	...	..	2.79	6.8	1.5	C_2H_6	4.5
							CH_3CN	0.6
							Polymer (1)	10–20%

[a] The standard deviation of the radiochemical analyses as done by the carrier method is about 5%. Somewhat larger errors may be involved in values determined by the gas chromatographic flow counting method. [b] No other species were detectable by the methods used in these experiments. In addition HCN was not detectable in neat ammonia.

H_2, O_2, N_2, CO, CH_4 and C_2H_6. The sequence of appearance from the silica gel was H_2, O_2 + N_2, CH_4, CO, CO_2. Helium was the carrier gas in all cases.

The cetyl alcohol column was operated at 55° with a carrier gas flow rate of 60 ml./min. The diethylhexyl sebacate column was operated at 25° with the same gas flow rate as above. Both the molecular sieve and the silica gel columns were kept at 25° for the separation of the noncondensable gases. The temperature was subsequently raised to 80° for the detection of ethane using the molecular sieve. Carbon dioxide was detected using silica gel at 80°. The helium gas flow rates for the two columns were 100 ml./min. and 60 ml./min., respectively.

Sample Processing.—All irradiated samples were handled on a vacuum line and each was allowed to expand into a large bulb containing the desired carrier gases. Sufficient time, usually two or more days, was allowed for complete mixing of the sample with the added carriers. Small portions of the mixture were then withdrawn and subjected to gas chromatographic radioanalyses. Carrier methane (molecular sieve 5A) and methylamine (cetyl alcohol) were isolated and purified by gas chromatography. Radiochemical yields of these two species were based on the specific activities obtained by combustion analysis of each material.

Results of Runs.—The data obtained by the procedures described are given in Table I.

Irradiation of Liquid Ammonia.—Pressures produced in liquid ammonia during irradiation were high, resulting in rupture of all of the containers but one. In this run, methane-C^{14} was again the most important radioactive product. Methylamine-C^{14} and acetonitrile-C^{14}, though detectable by gas chromatographic flow counting, amounted to a very small percentage of the total activity produced. Another radioactive species yet to be identified may have accounted for at least 20% of the carbon-14 in the mixture. The evidence (based on retention time alone, obtained by running authentic samples) indicated that it could not have been azomethane, methyl azide, hydrogen cyanide, methylhydrazine, ethylamine or dimethylamine.

Discussion and Results

The Ammonia Systems.—The investigation of the systems reported in this paper produced a result which is unique in the study of the recoil chemistry of carbon-14. The high and indeed specific production of methane-C^{14} in gaseous ammonia is without parallel in any other system involving a recoiling carbon-14. This result is to be contrasted with all other organic systems reported to date, in which one always finds a multitude of products and is confronted with the further difficulty of not being able to account for greater than 25–50% (at best) of the total activity isolable as recognizable species.[11,12]

It can be seen from Table I that the variation of the ammonia pressure and the addition of inert diluents did not affect the yield of methane-C^{14}. The presence of nonradioactive methane in ammonia during irradiation decreased the methane yield by a factor of about 1.6 and, finally, irradiation of pure methylamine with no ammonia present gave a methane yield a factor of about 15 less than that found in pure ammonia.

Clearly the moderation of translational energy alone is not the key to understanding product distribution (*cf.* ref. 13). It can be suggested that methane is formed by a reaction between a carbon radical and a steady state concentration of hydrogen atoms. This, however, implies a longer life for a carbon radical (necessitated by the very low steady state concentration of hydrogen atoms in such a system) than seems reasonable. In addition, one would not predict any substantial difference in yield in different systems since the steady state concentration of H atoms will not vary greatly in the systems under study. It can also be suggested that a direct encounter with a hydrogen donor can effect transfer. Clearly displacement on hydrogen would be affected by the nature of the R–H bond if this reaction takes place above thermal energies. Such reactions may be plausible in terms of what is known about systems of this sort undergoing radiolysis, but they do not seem to offer a consistent or unique picture of the action of the recoil fragment.

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(11) A. P. Wolf, *Angew. Chem.*, **71**, 237 (1959).

(12) A. P. Wolf, Radioisotopes in Scientific Research, vol. 2, Pergamon Press, London, 1958, pp. 114–135.

(13) H. M. Frey and G. B. Kistiakowsky, THIS JOURNAL, **79**, 6373 (1957).

A hypothesis which is attractive and not inconsistent with the observed results involves hydrogen transfer during the limited but finite lifetime of an intermediate formed by an inelastic collision between the carbon fragment and the hydrogen source. In this picture attention is focused on the redistribution of energy and the chemistry possible in the intermediate formed after collision (*i.e.* a *collision complex*), rather than basing product distribution on the absolute amount of translational energy of the reactive fragment just prior to collision. Clearly the carbon-14 must first have its translational energy moderated before chemical reaction can even be considered to take place, but implicit and product determining in our picture is the redistribution of energy into vibrational (and to a lesser extent rotational) excitation and possibly conversion into electronic excitation. An additional factor is the probability of deexcitation of intermediates which are formed. Product distribution might well be a function of the efficiencies of further collisional deactivation.

The charge state of carbon is left indeterminate since our results give no explicit information on this point (*cf.* ref. 14). An explicit mechanism for hydrogen transfer is also not stated for the same reason. The collision complex intermediate is a true intermediate (or series of intermediates) with little activation energy involved between sequential formation of different species and should not be considered as a transition state. It may undergo collapse before complete hydrogen transfer is possible.

Moderation of translational energy alone by the addition of neon and xenon (the former being the more efficient of course) did not seem to affect the chemical result, underlining the fact that in these systems mechanisms cannot be realistically described in terms of translational energy alone. What is most difficult to evaluate is the effect of the extraneous radiation (from reactor radiations) on product type and product distribution. Since no information is available on the lifetimes of the recoil fragments we cannot say what the probable effect of the reactive radiation damage fragments (*e.g.*, $H\cdot$, $NH_2\cdot$, $[NH_3]^*$, $[NH_4]^+$, etc.) is on the recoil fragment. Calculations based on the doses given to our samples suggest that the steady state concentration of these reactive fragments is low. A recoil fragment might well be thermalized before the probability of collision with a damage fragment became high. This aspect of the recoil chemistry of carbon-14 in the gas phase *certainly* needs further investigation.

The decrease of the methane yield when methane is present during irradiation is also consistent with the collision complex hypothesis. Collision with methane will produce a collision complex of longer lifetime since the increased number of degrees of freedom allow for better energy distribution into internal modes. Further chemical reaction is now possible, leading to the formation of two, three and possibly four carbon compounds (nitrogen-containing or non-nitrogen-containing), and to the formation of polymer (clearly impossible in pure ammonia).

Finally, the irradiation of methylamine, which has substantially *the same* atom concentrations of C, H and N, produces only a small percentage of methane-C^{14} plus a host of other products. Equation 1, which is implied by our hypothesis, describes the reaction sequence

$$\overbrace{[\mathrm{C}] + \mathrm{CH_3NH_2}}^{\mathrm{A}} \longrightarrow \overbrace{([\mathrm{C}]\ldots\mathrm{CH_3NH_2})}^{\mathrm{B}} \longrightarrow$$

$$\overbrace{\mathrm{C^{14}H_4}}^{\mathrm{C}} + \overbrace{\mathrm{C^{14}H_3NH_2}}^{\mathrm{D}} + \overbrace{\mathrm{C^{14}H_3CN}}^{\mathrm{E}} + \mathrm{F,G\ldots etc.} \quad (1)$$

Not only are hydrogen transfer and polymerization possible but exchange, dehydrogenation and further complexing (by collision with another body prior to collapse) can occur. Since these reactions are all occurring with high internal energies available to the reacting species it is to be expected that differences in activation energy will be small and hence a multitude of pathways will be available. It would be interesting to look at product composition in a methylamine inert-moderator system in order to determine the relative energy ranges in which CH_4 and these other products are produced. If CH_4 is produced at lower energies than other products then removal of sufficient translational energy without the possibility of chemical reaction might allow the carbon-14 recoil-methylamine complex only sufficient energy to form methane.

An interesting contrast is made with the results in liquid ammonia. In spite of the fact that collisional deactivation is considerably more efficient and might therefore be expected to drastically affect product composition, the major product was still found to be methane. The other major product is as yet unidentified. A large number of one carbon nitrogen compounds have been eliminated (*i.e.* on the basis of retention times alone) as possibilities. It is interesting to speculate that we may have formed isodiazomethane or the as yet unreported diazacyclopropane. The energy available and chemical reactivity of the surroundings would at least make such a hypothesis plausible.

The charge state of the fragment prior to and during reaction is difficult to evaluate.[14] Consideration of possible charge transfer by the recoil fragment would tend to favor a negatively charged ionic species. The ionization potential for NH_3 is 10.52 e.v.[15] This value is sufficiently low to permit charge transfer from the possible positively charged ions, C^+, CH^+, CH_2^+ and CH_3^+ whose appearance potentials are 11.26, 11.13, 11.9 and 10.0, respectively.[16,17] This is to be contrasted with the relatively low appearance potential of 6.0 e.v.[17] for NH_2^- from NH_3, which would fit well with the apparent ease of hydrogen abstraction from ammonia by the recoiling species through a reaction of the type given in eq. 2

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(14) P. E. Yankwich, *Can. J. Chem.*, **34**, 301 (1956).

(15) J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952).

(16) "Atomic Energy Levels," Vol. I, Circular 467, National Bureau of Standards, 1949.

(17) F. H. Fields and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

$$CH_3^- + NH_3 \longrightarrow CH_4 + NH_2^- \quad (2)$$

This applies, of course, to recoil fragments at thermal equilibrium. It may be that various carbon fragments are in differently charged states and that a complex combination of charge transfer processes is involved during the lifetime of the intermediate involved. Competition experiments might serve to clarify this point.

Oxygen was added to the ammonia system in an attempt to detect (by observing a possible change in product composition) the presence of radicals. The methane yield was not appreciably affected. This evidence alone cannot be used to eliminate radical intermediates from consideration since it is always possible that oxygen may not be sufficiently efficient as a scavenger in this system. Certainly the formation of methane from radicals through hydrogen abstraction would need to go *via* a methyl radical in the last stage. Steacie and Trotman-Dickenson[18] have shown that the activation energy required for hydrogen abstraction by methyl radicals from ammonia is higher than the activation energy for hydrogen abstraction from many other compounds, methylamine included. If H abstraction by a near thermal radical were responsible for methane production, then there should be little difference between ammonia and methylamine. This, of course, does not take into account the many other reactions that methylamine can undergo at higher energies. Examining product composition from methylamine and moderator and from competition experiments might shed some light on this problem.

The 6% radiochemical yield of $C^{14}O_2$ as compared to the 3% (mole fraction) oxygen present in the original mixture indicates a slight preference of the recoil carbon for reactions with oxygen. The fact that the $C^{14}O$ yield was below the limits of detection (gas chromatographic flow counting) is in agreement with the findings of Sharman and McCallum.[19] They found the ratio of the radiochemical yields between CO_2 and CO from the $C^{12}(\gamma,n)C^{11}$ process in sodium carbonate to be 22:1.

The studies carried out by Yankwich and coworkers[2a,c] on crystalline ammonium salts after thermal neutron irradiation are an interesting contrast to these findings. The fact that an entirely different product distribution is observed may serve as a clue to both the charge state and configuration of the intermediates that may be formed.

Methylamine and Ethane Production.—A rationale for the formation of methylamine, ethane and other one and two carbon fragments may also be described in terms of a collision complex mechanism. There are, however, several other interesting features involved.

The formation of a possible *collision complex* may be

$$[C]^* + NH_3 \longrightarrow [C\ldots NH_3]^* \quad (3a)$$

$$[C\ldots NH_3]^* + NH_3 \longrightarrow [CH_3NH_2] + \text{residue} \quad (3b)$$

In pure ammonia, at least two collisions are necessary to provide a sufficient number of hydrogens to give methylamine.[20] The addition of inert moderators serve only to decrease translational energy and do not necessarily aid in methylamine formation. Since no change was observed in the yield of methylamine from the moderated system, one may conclude that energy distribution of the reactive fragment is not product-determining in the sense that with a greater number of degraded carbon fragments, the probability of CH_3NH_2 formation over CH_4 formation is not increased. It is further noteworthy that as the degrees of freedom available for energy redistribution increase, the yield of methylamine goes up,[21] being 0.6% in CH_4 and 1.5% in CH_3NH_2.

Methylamine formation may also be described in terms of a one-step displacement[22] process involving a hot methyl radical (insensitive to O_2) as in eq. 4

$$[CH_3\cdot]^* + NH_3 \longrightarrow [CH_3NH_2]^* + H\cdot \quad (4)$$

The energy distribution in $[CH_3\cdot]^*$ would have to be relatively narrow and the absolute amount of energy low, in order that the product $[CH_3NH_2]^*$ would not fly apart after formation.

An insertion reaction between a hot methylene and ammonia is a further possibility (*cf.* ref. 13).

If either the displacement reaction or the insertion reaction are operative, however, it is difficult to see why methylamine-C^{14} production should go up in the methane–ammonia mixture or in methylamine (*cf.* footnote 21 on scavenging). In addition, it is again clear that if simple reduction of translational energy is all that is required to reduce the just formed energy-rich methylamine to thermal energies, the addition of inert gas should increase the probability of methylamine product formation. It should be noted, however, that the cooling *efficiency* of methane and methylamine may be the deciding factor and one can not *a priori* rule out displacement or insertion reactions.

Interesting in this respect is the formation of labeled ethane. Three mechanisms can be suggested, the collision complex, a displacement reaction and fragment recombination. The displacement reaction would have to occur at high enough energies so that the reaction would be insensitive to the character of the leaving group, since there seems to be little difference in the ethane yield from the ammonia–methane system (displacement of hydrogen) and the methylamine system (displacement of NH_2). In addition, if insensitivity to the leaving group in terms of displacement were

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[18] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.* **20**, 1041 (1952).

[19] L. J. Sharman and K. J. McCallum, THIS JOURNAL, **77**, 2989 (1955).

[20] Our mechanism does not exclude the possibility that hydrogen atoms may add to the complex or fragment at some point.

[21] It may also be that methylamine-C^{14} is more efficiently scavenged when formed in methylamine and that part or all of the increased yield may be due to the difference of having carrier present during the irradiation *versus* adding the carrier after the irradiation has been completed.

[22] The word displacement is used in the sense that the physical organic chemist uses it. There is a collision between two fragments A + BC to give a product AB + C. Implicit in this definition is the formation of a transition state ABC and collapse of this state to AB in what is essentially a one step process. This clearly delineates it from the *collision complex* in which ABC has a finite lifetime (at least greater than several bond vibrations) allowing for energy redistribution, internal rearrangement and other processes following from further reaction of the collision complex.

important here, then the methylamine yield in pure ammonia and methane–ammonia should be comparable to the ethane yield from methane-ammonia and methylamine. The collision complex, however, concerns itself with the nature of atom transfer and bond scission that can occur in the complex itself. Here there is no *necessary* correlation between yields of ethane and of methylamine in the different systems under comparison.

Although work in another system[23] would indicate that synthesis products (ethane from methane and ammonia) are produced by hot reactions, it would be of interest to test the fragment recombination mechanism (presumably of radicals) by the addition of oxygen to the methylamine and the methane–ammonia system.

The formation of acetonitrile seems best explained by assuming that a collision complex is operative.

The observed 79% yield of methylamine from irradiated crystalline ammonium bromide[2c] is a sharp contrast to these results. Also of interest in the ammonium bromide system is the fact that the methane yield was only 7.5% and the methyl bromide yield 1.8%.

Polymer Formation.—A considerable fraction of the carbon-14 was found in polymer[24] both in the methane–ammonia system and the methylamine system. The specific activity of the polymer in the CH_4–NH_3 system was much higher than that of the methane. Chain initiation by carbon-14 fragments seems to be involved. Two types of chain initiation can be considered. The recoil fragments themselves may be effective chain initiating agents,[25] or an exchange between the recoil fragments and the methane radiation damage products may take place with the resultant radioactive radiation damage fragments subsequently initiating polymerization. In this regard it has been observed that polymer production in an ammonia-containing methane sample is nearly 5–10 times greater than that produced in methane alone when the irradiations were carried out in the pile under identical conditions (polymerization is, of course, impossible in pure ammonia). It would seem that the recoil carbon fragments serve as effective initiators unless we suppose that it is the presence of ammonia that induces the radiation polymerization of methane. This latter hypothesis is certainly less attractive. Elucidation of this point might well result from the irradiation of methane–nitrogen samples.

There is little question that a chain mechanism involving entrapment of carbon-14 is operative in the gas phase. Exchange between (or entrapment of) the carbon-14 in the gas phase and the radiation damage polymer in the liquid phase is not consistent with the large fraction of carbon-14 incorporated or with the high specific activity of the polymer.

Conclusion

Further studies on the systems reported in this paper should provide us with a real understanding of the action and reaction of a recoiling carbon-14, at least in the gas phase and perhaps in condensed media also. The large number of easily controlled variables, the relatively uncomplicated product distribution and the ease of analysis make these gaseous systems most attractive for continued study. A number of experiments suggest themselves. It may be argued that consideration of cooling probabilities demands a much higher inert moderator to reactant ratio in order to achieve efficient cooling of the recoil carbon. Experiments with higher mole fractions of neon would definitely be of value here. Since NH_3 can act as its own moderator, studies at lower ammonia pressures would be useful. Experiments at lower methylamine pressures, neat, in the presence of neon, and with added oxygen would aid in elucidating the mechanisms which are operating. Adding carrier compounds such as ethylamine, etc., to irradiated methylamine would provide additional information. Determination of charge type as in the case of carbon-14 may be possible in these systems. Of great importance would be the comparison of products obtained from methane–ammonia and the methane–nitrogen systems. The latter system would allow an interesting contrast between products from a chemically reactive carbon-14 source and one which is unreactive. This should bring into sharp focus the chemical role of ammonia *and* its efficiency as a moderator. The question of the effect of extraneous radiation also requires a definitive answer.

More than one mechanism may be operative in these systems. Some products may be formed by more than one reaction path. Some mechanisms may be ruled out on statistical grounds or on chemical grounds but the gap between compatible mechanisms and the number of hypothetical mechanisms is still very large. The collision complex mechanism seems to offer a consistent working hypothesis for understanding some of the results.

The question of energy distribution of reacting fragments is an extremely important one. Trying to separate hot from thermal reactions in terms of operational criteria such as radical traps, etc. does not seem to lend itself to understanding the chemistry that is occurring. A disproportionate amount of attention has been centered on the transfer of translational energy alone. While there may be a large spread in the energies at which these various products are formed, it seems to us that this spread has been exaggerated particularly with regard to hot *vs.* epithermal reactions. We believe a more useful approach to be the elucidation of specific mechanisms *in conjunction* with a determination of the energies at which they occur.

Acknowledgments.—The authors are indebted to Dr. David R. Christman and Mrs. Catherine Paul for their assistance in the radiochemical analyses.

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

[24] These polymers were not described in the experimental section because of the paucity of evidence on them. It is in both cases a light brown viscous liquid. The polymer from CH_4–NH_3 contained little nitrogen. The polymer from CH_3NH_2 was only present in sufficient quantity to allow a qualitative activity analysis to be done.

[25] Y. Landler and M. Magat, *Bull. soc. chim. Belges*, **57**, 381 (1948).