

A STUDY OF THE REACTIONS OF  
ACTIVE NITROGEN

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of the University of Manitoba

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In Partial Fulfillment  
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Doctor of Philosophy

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by  
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### ABSTRACT

This investigation of active nitrogen reactions was undertaken in order to determine the mechanism for the formation of ammonia and the conditions under which ammonia would become a principal product of the reactions of active nitrogen with hydrocarbons.

The reaction of methane with active nitrogen, produced by passing both nitrogen and nitrogen-argon mixtures through a condensed discharge, was studied in an unheated reaction vessel. The reactions of ethane and acetylene with active nitrogen from the nitrogen-argon system also were investigated. Hydrogen cyanide and ammonia were the principal products.

Methane, ethane, ethylene, acetylene, hydrogen cyanide, nitrous oxide and ammonia were reacted at  $-196^{\circ}$  with active nitrogen, produced from a nitrogen discharge. Methane showed little or no reactivity but large amounts of ammonia and hydrogen cyanide were produced from ethane and ethylene. Some hydrazine was produced from the ammonia reaction. Preliminary experimentation on the reaction of active nitrogen with water, formamide, and phosphine was performed for the elucidation of the overall mechanism.

The discussion of the results contains several proposed mechanisms based on excited species of nitrogen atoms and molecules.

## INTRODUCTION

## INTRODUCTION

When nitrogen is subjected to an electrical discharge at low pressures, a brilliant yellow glow is emitted. In 1900 Lewis (1) discovered that when the discharge is shut off a yellow afterglow persists for several seconds. In 1911 Strutt (2) named the glowing gas "active nitrogen" and suggested that many of its properties could be attributed to the presence of atomic nitrogen. During the past decade the nitrogen afterglow and the chemical reactivity of active nitrogen have been, with seemingly increasing interest, the object of a great deal of study. Several theories have been proposed to explain the mechanism of the afterglow and much spectroscopic and chemical evidence has been accumulated for the purpose of identifying the species present in active nitrogen. In order to provide the background necessary for the discussion of the active nitrogen reactions which provide the subject matter for this thesis, a brief outline of both the physical and chemical aspects of the problem will be given, together with some relatively detailed theoretical discussions.



### Physical Studies of Active Nitrogen

Lewis (1) observed that nitrogen had to be free of oxygen and had to contain traces of water vapour to obtain an intense glow. He found that the banded spectrum of the nitrogen afterglow was quite different from the continuous spectrum of air under similar discharge conditions. Strutt (2) observed that the afterglow was chemically active and he found that the afterglow could be obtained from nitrogen which had been purified from oxygen by bubbling it through molten phosphorus. He was able to produce an afterglow which lasted for as long as six hours and to show that the intensity of the afterglow was greater at lower than at higher temperatures.

To obtain oxygen-free nitrogen, Tiede and Domcke (3) heated barium azide. They were unable to obtain the afterglow until traces of oxygen were introduced by the addition of silver oxide. Baker and Strutt (4) repeated this work in a thoroughly clean and baked out system and were able to obtain the afterglow using fused potassium azide as the nitrogen source. To clarify this contradiction, Tiede and Domcke went to London where the apparatus and techniques of the two groups were compared. When the discharge tube of

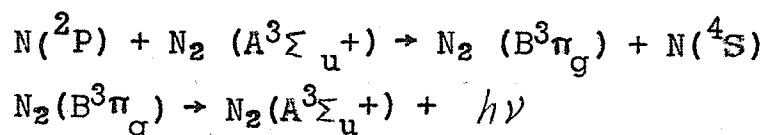
Baker and Strutt was used in conjunction with the nitrogen supply of Tiede and Domcke, the afterglow was obtained. It was thus concluded (5) that the shape of the discharge tube influenced the ease and ability of producing an afterglow.

Throughout his work, Strutt assumed that the chemical reactivity of the afterglow was due to atomic nitrogen. Saha and Sur (6), however, showed from classical quantum concepts that active nitrogen probably consisted of excited molecules having about 8.2 ev. of energy. The most direct evidence to that time for the presence of atoms in the afterglow was obtained by Wrede (7) who made use of the relative rates of diffusion of the atoms and molecules through an orifice. He demonstrated that nitrogen atom concentrations as high as 40% could be obtained in the glowing nitrogen stream.

By the year 1945 there were three totally different theories of active nitrogen gleaned from the masses of information collected up to that time. Rayleigh (2) first suggested that active nitrogen contained nitrogen atoms and Sporer (8) later put forward a two-step mechanism:  $M + N + N \rightarrow M + N_2^{\text{AA}} \rightarrow N_2^{\text{A}} + h\nu$ . The work of Wrede (7) and Herzberg (9) suggested that

active nitrogen contains appreciable quantities of nitrogen atoms thus supporting the atomic theory of active nitrogen. This hypothesis, however, could not explain the selective enhancement of certain vibrational bands in the afterglow spectrum and could not account for the electrical properties of active nitrogen.

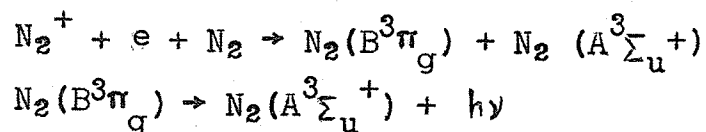
Kaplan and Cario (10) interpreted the long life of active nitrogen to indicate the presence of atoms. They assumed that metastable atoms were produced in addition to metastable molecules. They proposed the following afterglow mechanism (11):



This theory successfully accounted for the selective enhancement of some vibrational bands. The absence, however, from the afterglow of the Vegard-Kaplan bands, due to the transition  $\text{A}^3\Sigma_u^+ \rightarrow \text{X}'^3\Sigma_g^+$ , indicated that no appreciable concentration of molecules in the A state, would be present in the afterglow.

In 1945 Mitra (12) put forward the hypothesis that active nitrogen consisted of a mixture of  $\text{N}_2^+$  ions and electrons. This readily explained the electrical conductivity of the afterglow. This theory was based on analogous processes that were thought to occur in

the emission of the spectrum of the night sky, and on the very large energies transferred to metal foils in some experiments made by Rayleigh (13). The following reactions were postulated to account for the afterglow:



It was demonstrated by Benson (14) that a beam of glowing gas was not affected by a magnetic field and that the intensity of the glow was unaffected by the removal of charged particles. He estimated that the concentration of active particles was about  $10^6$  as great as the concentration of charged particles. It became clear, therefore, that active nitrogen contained little, if any, electrons and  $\text{N}_2^+$  ions. This result appeared to precipitate new interest in the problem and, with the aid of more refined instruments, the nature of active nitrogen began to be more precisely defined.

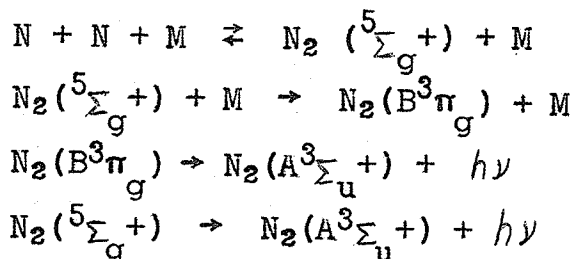
Examination of the paramagnetic resonance spectrum (15) of active nitrogen definitely proved the existence of ground state nitrogen atoms in the afterglow. Mass spectrometric studies conducted by Jackson and Schiff, (16) and by Kistiakowsky and his associates, (17) showed that the appearance potential of the peak for mass 14 was found to be about 14.8 ev. which is very close to the ionization potential of the nitrogen atom

in the ground state (14.545 ev.). This also indicated that the major constituent in active nitrogen, is the ground state nitrogen atom. The vacuum ultraviolet absorption spectrum, studied by Tanaka (18), indicated an appreciable concentration of  $^4S$  ground state atoms together with  $^2D$  and  $^2P$  excited atoms with concentrations of up to 1% of the total atom concentration.

In 1956 Berkowitz, Chupka, and Kistiakowsky (17), proposed a mechanism for the nitrogen afterglow utilizing atom recombination. The original theory (2) was unable to explain the formation of nitrogen molecules in three different electronic states, but this more recent view adequately accounted for this. Two ground state nitrogen atoms with three unpaired p electrons may, on collision, form  $^1\Sigma_g^+$ ,  $^3\Sigma_u^+$ ,  $^5\Sigma_g^+$  and  $^7\Sigma_u^+$  nitrogen molecules, which correspond respectively to 6, 4, 2, and zero paired electrons. If the atoms combine to form  $^1\Sigma_g^+$  or A  $^3\Sigma_u^+$  molecules, a collision with a third body would remove the excess of energy from the  $N_2$  molecule formed, stabilizing it in the X or A state.

Molecules in the B state can be produced from  $^4S$  atoms (19) and, in the nitrogen afterglow, it was postulated that two  $^4S$  atoms collide on the  $^5\Sigma_g^+$  potential energy curve after which a collision with a third body induces a preassociation into the twelfth vibrational level of the B state. Kistiakowsky and

Warneck (20) obtained the population distributions among the vibrational levels of the  $B^3\pi_g$  state at several temperatures. When the normalized population distribution of nitrogen molecules among the vibrational levels of the  $B^3\pi_g$  state was plotted against vibrational energy, the position of the maximum, around  $19000\text{ cm}^{-1}$  at  $100^\circ\text{K}$ , shifted to lower energies with increase in temperature. Extrapolated to  $0^\circ\text{K}$  the position of the maximum is found to coincide with the energy of the  $5\Sigma_g^+$  state (21). These experimental observations were interpreted as being definite proof of the following afterglow mechanism which was originally postulated by Kistiakowsky et al (17).



The work of Broida (22, 23) on the spectra of solid active nitrogen at  $4.2^\circ\text{K}$  gave considerable support to this theory. A band system which is probably emitted in the blue flashes observed when active nitrogen is deposited in the trap, was attributed to the transition  $5\Sigma_g^+ \rightarrow A^3\Sigma_u^+$ . It was thought that the  $5\Sigma_g^+$  state could have been formed either in the discharge or from ground state atom recombination in the trap.

Jennings and Linnett (24) noted in their review on active nitrogen that nitrogen, but neither hydrogen, nor oxygen, has an afterglow. Since the nitrogen atom has three unpaired electrons it can combine with other molecules to form a variety of excited nitrogen molecules. The potential energy curve of the  $^5\Sigma_g^+$  state by chance crosses other potential energy curves, and preassociation is allowed to occur. In the case of hydrogen and oxygen no process similar to preassociation can occur.

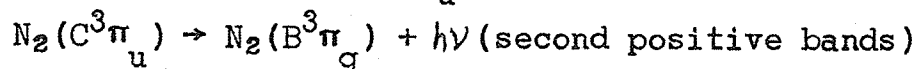
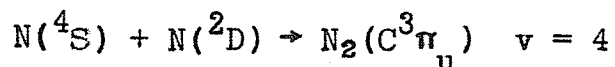
Strong physical evidence for the support of the presence, in active nitrogen, of vibrationally excited  $N_2^+$  molecules was obtained by Kaufman and Kelso (25). In addition, they demonstrated that  $N_2O$  removed the  $N_2^+$  without destroying the nitrogen atoms and that nitric oxide, added in the proper quantity, removed the nitrogen atoms without destroying the vibrationally excited molecules. It was inferred that these  $N_2^+$  molecules could be produced from highly populated triplet states by collisions of the second kind in the discharge.

In a review of the reactive components in active nitrogen, Evans and Winkler (26) proposed that species which could transfer large amounts of energy in collision processes were present in active nitrogen. They suggested that the only species which would be

present in significant concentrations was probably vibrationally excited molecules, (27). It was reasoned, on the basis of energy considerations (28, 29, 30) that electronically excited nitrogen molecules, formed in the discharge by the recombination of atoms, would tend to form ground state nitrogen molecules in the higher vibrational levels.

Le Blanc et al (31), in agreement with the postulated Y bands of Kistiakowsky, observed a new band system which was greatly obscured by the first positive bands. Dieke and Heath (32), in a more detailed investigation of these bands, found that the Y band of nitrogen has exactly the structure expected from a  ${}^3\Sigma_u^- \rightarrow {}^3\Pi_g$  transition.

In a study of the afterglow at liquid nitrogen temperatures, Tanaka et al (33) observed the second positive bands of nitrogen which are not usually present in the afterglow at elevated temperatures. They were about as intense as the first positive system. The excitation of the bands in the low temperature afterglow was explained as a probable inverse predissociation process:



It seems that when the tube is cooled by liquid nitrogen, the wall conditions become favorable for preventing decay of the metastable atoms.



The existence of a short duration afterglow, with characteristics greatly differing from the usual Lewis-Rayleigh glow, was recently discovered by Beale and Broida (34). It occurred rather abruptly, a few milliseconds after a discharge through pure nitrogen was started. The excitation in this "pink afterglow" could not be accounted for on the basis of known constituents of active nitrogen. Emission was found from three species with energy greater than the recombination energy of two ground state nitrogen atoms (9.76 ev (35)). Some of the emission of the first positive band system and all that of the second positive band system was observed to come from levels above 11 ev. Such excitation could occur if there were collisions involving the  $^2P$  or  $^2D$ , as well as the  $^4S$  levels of atomic nitrogen, although this was deemed not too likely because of the small steady state concentration of the metastable atoms. Metastable ( $^1\pi$ ) states of molecular nitrogen were postulated as the best probable source for the short lived species responsible for the emission in the pink region.

In agreement with the work of Dieke and Heath, Wilkinson (36) showed that the upper state of the Y bands is  $Y^3_{\Sigma_u^-}$ . Since the states  $Y^3_{\Sigma_u^-}$  and  $A^3_{\Sigma_u^+}$  have the

same electronic configuration, he indicated that the Y band should have an appearance like that of the first positive group. This similarity consolidated the identification of the Y bands as  $Y^3\Sigma_u^- \rightarrow B^3\Pi_g$ .

Young and Clark (37) investigated the late portion of long afterglows and demonstrated that during 140 sec. of decay no change occurs in the characteristic relative vibrational distribution of the first positive bands of nitrogen. Neither the  $5\Sigma_g^+$  state (17) nor the vibrationally excited ground state molecule (38) has been shown to account for the excitation of low vibrational levels of the  $B^3\Pi_g$  state at rates comparable with that of the  $v = 11, 12$  levels. They observed that the same relative intensity distribution persists for a long time which exceeds the lifetimes of any metastable states which could be expected to be present in active nitrogen. Thus, such states, if initially formed in the discharge, could not be participants in the excitation of selective first positive bands. If metastable particles formed during the decay were necessary to produce the excitation, they would be able to do so only by reacting with stable species. The authors concluded, therefore, that electronic metastable states can play no part, except as intermediaries, in the production of the first positive bands in the afterglow.

The relative intensities in the nitrogen after-glow from 5000 to 10,000 Å°, have been measured by Bayes and Kistiakowsky (39) in pure nitrogen, and in nitrogen diluted with several foreign gases. Most of the bands in the  $Y^3\Sigma_u^- \rightarrow B^3\pi_g$  system were overlapped by  $B^3\pi_g \rightarrow A^3\Sigma_u^+$  bands. They were able to classify the bands into five groups of different kinetic origins by correlating changes in relative intensity with alterations in external conditions. The vibrational levels of the  $B^3\pi_g$  and Y states just below  $D_e$ , the energy of two separated ground state nitrogen atoms, were not populated. At low temperatures, the highest populated levels of the  $B^3\pi_g$  and Y states were observed to tend to a limit at about 850 cm<sup>-1</sup> below  $D_e$ . It was suggested that this is approximately equal to the dissociation energy of the  $^5\Sigma_g^+$  state of the nitrogen molecule. The original after-glow mechanism of Kistiakowsky (et al (17)) was expanded in an attempt to show the mechanism of the entire after-glow emission.

Recently Broida and Tanaka (40) found that electrons and ions are produced in active nitrogen but that the steady state ion concentrations are small compared to the concentrations of active neutral chemical species. It was thought, however, that since the number of charged particles continuously being lost and produced

may be considerably greater, it would be still possible for a significant ionic contribution to the mechanism of atom formation. In the early stages of the afterglow the observed correlation between brightness and amount of ionizations strongly implied a connection between the mechanisms of ionization and atom formation. They speculated that some very energetic non-ionic species leaving the discharge produces the ion concentration maximum and the bright pink glow which contains some emissions necessitating about 19 ev. for excitation.

The nature of the mechanism of the afterglow and the species present in active nitrogen are quite obviously very complex. It is evident, however, that the primary processes occurring in active nitrogen are known with some certainty although the entire mechanism is not yet completely understood.

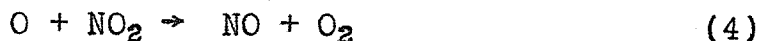
#### Chemical Studies of Active Nitrogen

Lewis (41) investigated the reactions of hydrogen atoms with active and molecular nitrogen and the reaction of molecular hydrogen with active nitrogen. He found that in no case was hydrazine detected and that only when hydrogen atoms and active nitrogen were reacted, did he detect ammonia. He suggested that the most plausible mechanism would involve the reaction of a nitrogen atom

to form an NH radical to which a hydrogen molecule might add to form ammonia.

Steiner (42) confirmed these results and in addition was able to identify traces of hydrazine as a product of the active nitrogen - atomic hydrogen reaction. In the reaction of active nitrogen with molecular hydrogen, hydrazine and traces of ammonia were found as products. It was shown spectroscopically that faint Balmer lines were present in the discharge tube, and that the ammonia produced varied with the intensity of these lines. He proposed the idea of a triple collision (43) for the production of NH radicals and demonstrated that when metals were placed in the path of the mixed atomic hydrogen and active nitrogen stream, the yield of ammonia increased.

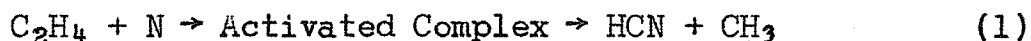
Spealman and Rodebush (44) studied the reaction of active nitrogen with nitrogen dioxide and nitric oxide, and they postulated the following mechanism:



The atomic oxygen formed accounted for the observed bluish glow when nitric oxide was added to active nitrogen. When nitrogen dioxide was added the

bluish glow disappeared probably as a result of oxygen atom consumption by reaction (4).

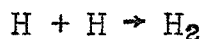
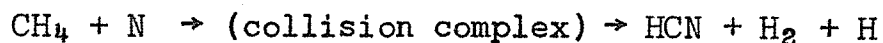
Utilizing the Wood-Bonhoeffer (45) technique, Greenblatt and Winkler studied the reaction of nitrogen atoms and ethylene (46). The nitrogen atom concentrations, measured with a Wrede gauge, were as high as 40% using nitrogen from which oxygen had been removed, and which was saturated with water vapour. The products of the reaction were hydrogen cyanide, ethane and a polymer. The yield of hydrogen cyanide increased linearly with increase in flow rate of ethylene until a maximum, after which the yield of hydrogen cyanide was constant despite a further increase in flow of ethylene. The amount of ethane formed increased from indetectable quantities at low ethylene flow rates to about 30% of the ethylene input at high ethylene flow rates. They proposed the following mechanism to account for their results.



An activation energy of 6.9 kcal./mole as an upper limit was calculated from collision yields with 0.1 assumed as the steric factor.

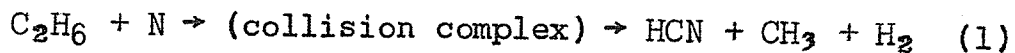
Using the diffusion flame technique (47) the authors estimated that the activation energy was probably not greater than 3 kcal/mole with .01 as the assumed steric factor.

This reaction was re-investigated by Versteeg and Winkler (48) who used a reaction system poisoned with phosphoric acid and dry nitrogen and were able to eliminate the polymer as a primary product. In addition to hydrogen cyanide and ethane, they were able to obtain significant yields of methane, hydrogen, cyanogen and acetylene. The mechanism put forward was again based on the formation of a complex between the double bond of ethylene and the nitrogen atom followed by ejection of a hydrogen atom. The investigation of the reaction of active nitrogen with methane above 300°C was undertaken by Blades and Winkler (49) who found hydrogen cyanide as the only condensable product. They were able to calculate an activation energy of 11 kcal./mole and a steric factor of  $5 \times 10^{-3}$  for the reaction. The suggested mechanism was:



In the reaction of ethane (49) with active nitrogen in the temperature range of 100° to 295°C hydrogen cyanide was the only product found in measureable quantities. Since the atomic nitrogen concentration, indicated by hydrogen cyanide production under conditions of high ethane

flow rate, agreed with the atom concentration measured by a Wrede gauge, it appeared that the only active species in the nitrogen afterglow was atomic nitrogen. The following reactions,



were postulated to account for the products. The obtained activation energy of  $7 \pm 1$  kcal./mole was assumed to be associated with reaction (1). Reaction (2) was presumed to be much faster than (1) in order to account for the absence of methane. Since hydrogen cyanide was the only product obtained it was deemed unlikely that radicals such as NH or nitrogen containing intermediates could be formed.

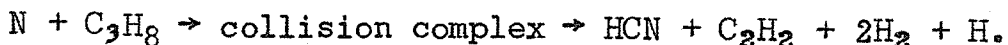
The reaction of active nitrogen with propane was studied by Winkler and co-workers (50) who found that the hydrogen cyanide accounted for 90 to 99% of the propane consumed and that the remainder was recovered as ethylene, acetylene and ethane.

The recovery of ethylene and acetylene, in appreciable amounts, in the presence of excess nitrogen atoms, implied their formation in a primary reaction step rather than from secondary reactions involving hydrogen atoms and free radicals as suggested in the ethane and ethylene reactions. Ethylene could be formed by a reaction

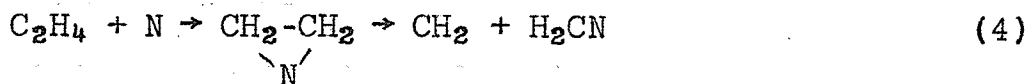
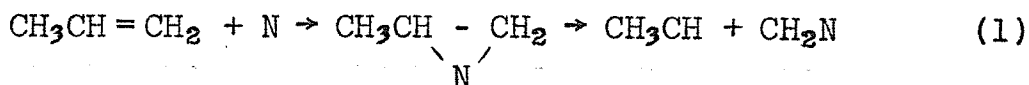


of the type

$N + C_3H_8 \rightarrow \text{collision complex} \rightarrow HCN + CHCH_3 + H_2 + H$ ,  
and the ethylidene radical could then rapidly rearrange to ethylene. The reaction postulated for the formation of acetylene was:



Trick and Winkler (51) investigated the reaction of active nitrogen with propylene and found hydrogen cyanide and ethylene as the main products with smaller amounts of ethane, propane, acetylene and a  $C_4$  hydrocarbon. The nitrogen atoms were completely consumed under conditions of excess propylene and at  $242^\circ C$ , 0.77 mole of ethylene was produced for each mole of excess propylene added. At lower temperatures less ethylene was produced. The relative reactivity of ethane and ethylene led the authors to propose the following mechanism.

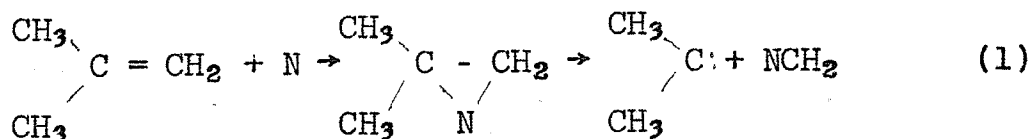


Saturated hydrocarbons formed in this reaction were assumed to be formed by hydrogenation of the corresponding olefin.

The reactions of active nitrogen with butene-1, cis butene-2, and isobutene, studied by Gesser et al (52), were found to produce hydrogen cyanide, propylene, and ethylene as major products along with varying amounts of butane, propane, ethane, methane and hydrogen. The order of reactivity was found to be butene-1 > cis-butene-2 > isobutene. Isobutene reactivity appeared to be temperature independent while butene-1 and cis-butene-2 showed increased activity with increase in temperature.

By analogy with the propylene reaction the authors suggested that butene-1 reacted as propylene did, i.e. the primary reaction of nitrogen atom attack on the double bond resulting in formation of HCN and a propylidene radical which would rearrange to propylene.

For instance the primary reaction step proposed for isobutene was



followed by:

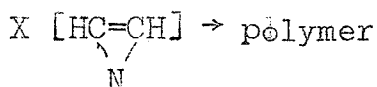
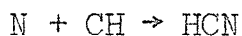
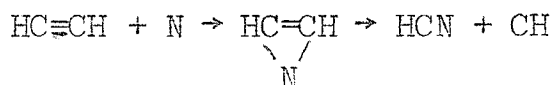


Reaction (2) was based on the fact that sodium atoms react with 2,2 dibromopropane with weak chemiluminescence which was associated with a hydrogen shift, (53).

The primary reaction step for cis-butene-2 with active nitrogen for the formation of propylene could not,

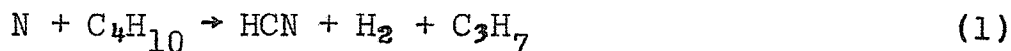
according to the authors, consist of a simple rupture at the double bond, since this would result in the formation of ethylene. Therefore, it was implied that propylene was produced by rearrangement within the complex formed by cis butene-2 and nitrogen atoms, together with simultaneous ejection of a secondary hydrogen atom followed by dissociation into hydrogen cyanide and propylene.

An investigation of the reaction of atomic nitrogen and acetylene was conducted by Versteeg and Winkler (54). The products of the reaction were hydrogen cyanide, methane, hydrogen, cyanogen and considerable formation of polymer on the walls of the reaction flask. The polymer was shown to contain nitrogen and when decomposed by heat it liberated hydrogen cyanide. The mechanism postulated was:

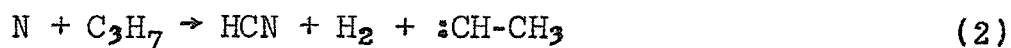


It was found that the main product of the reactions of active nitrogen with n- and iso-butanes (55) at 75° and 250° was, as in all other hydrocarbon-active nitrogen reactions, hydrogen cyanide with ethylene and acetylene in smaller amounts. The occurrence of hydrogen atom abstraction reactions, as in the previous reactions discussed, was assumed to be rare since no nitrogen containing product other than hydrogen cyanide was

detectable. The most probable mechanism in the case of n-butane, as proposed by the authors, was initial attack on the primary hydrocarbon according to the reaction



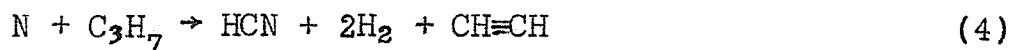
In view of the ethylene produced, the propyl radicals were thought to react according to the following reaction,



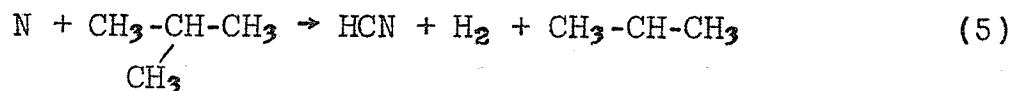
followed by



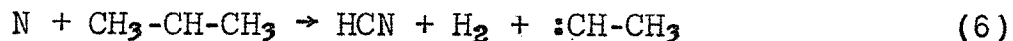
Acetylene could be produced by the reaction



In the isobutane reaction, the primary step was thought to be attack by a nitrogen atom at a primary carbon atom.



The chief source of ethylene would then be the reaction



Trace amounts of ethane, propane and propylene, which were also observed, could be explained by interradsical and hydrogen atom reactions.

In a study on the reaction of ethylene and nitrogen molecules formed in the thermal decomposition of

metallic azides, Back et al (56), detected no reaction. Since nitrogen molecules produced in this manner are electronically excited as are those present in active nitrogen generated by a condensed discharge, it was concluded that excited molecules played only a small part in active nitrogen-hydrocarbon reactions.

In contrast, however, a study of the reaction of active nitrogen with ammonia (57) and active nitrogen with neopentane (58) implied that at least two chemically reactive species were present in active nitrogen and it was likely that the two species were atoms and electronically excited molecules.

Small quantities of ethylene, acetylene, propylene and propane were obtained in addition to large quantities of hydrogen cyanide when neopentane was reacted with active nitrogen. Second order rate constants were calculated for the reaction at several temperatures between  $-40^{\circ}$  and  $350^{\circ}$ , and an Arrhenius plot showed a pronounced curvature with definite indication of two activation energies. The average values of these were 2.0 kcal/mole in the range  $-40^{\circ}$  to  $115^{\circ}$  and 7.1 kcal/mole in the range  $150^{\circ}$  to  $350^{\circ}$ . The conclusion reached by the authors from the observation of the two activation energies was that the overall reaction is composite. Different modes of attack on the neopentane molecule, the presence of two reactive species in the active nitrogen stream, or the influence of hydrogen atom

reactions which produce radicals that react rapidly with active nitrogen, were put forward as possible explanations of the two activation energies.

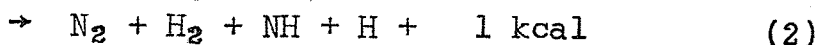
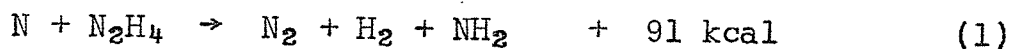
Freeman and Winkler (57) found that ammonia was destroyed by active nitrogen at an optimal rate quite independently of temperature over the range  $-5^{\circ}$  to  $440^{\circ}$ . Active nitrogen, produced under similar conditions, was found to be able to produce hydrogen cyanide from ethylene at a rate 5.7 times greater than it was capable of destroying ammonia.

With regard to the negligible influence of temperature on the ammonia reaction, and to the difference in behaviour of ammonia and ethylene with active nitrogen, the authors concluded that it was nearly impossible to suggest an acceptable mechanism based on a single reactive species in active nitrogen. It was decided, therefore, that there was a strong likelihood of two reactive species; one capable of reacting with ammonia and the other, or both, capable of reacting with ethylene. The ground state nitrogen atom would be one of these and the other could be the excited nitrogen molecule or  $N_2$ .

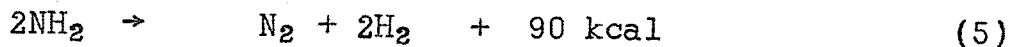
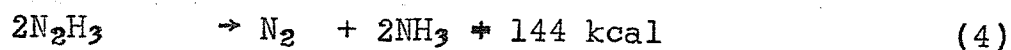
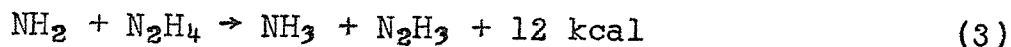
These findings renewed interest in the study of active nitrogen with the object now being the identification of the active species and the study of their chemical reactivity. About this time the investigators involved

in spectroscopic studies of the nitrogen afterglow began their fruitful search of spectra which resulted in the advanced understanding of the physical nature of the nitrogen afterglow and the mechanism by which the glow is produced. It was left to the chemists, then, to find a unified mechanism, for the reactions studied, based on the known physical species present in the active nitrogen stream.

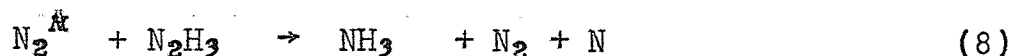
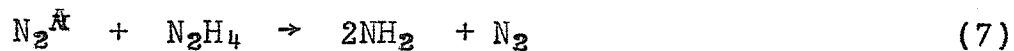
Following the ammonia work, Freeman and Winkler studied the reaction of hydrazine with active nitrogen (59). Hydrazine was completely destroyed at both 150° and 480° with production of small amounts of ammonia. It was concluded that ammonia was formed only by reaction of hydrazine with a product of the hydrazine-active nitrogen reaction. The mechanism postulated for this reaction was:



If  $\text{N}_3$  were the reactive species it would react in a similar manner but the corresponding reactions would be less exothermic. Reactions (1) and (2) would then be followed by:



On the basis that a metastable molecule was the reactive species reactions (7) and (8) would occur:



The nitrogen atom produced in (8) could then react by reaction (1); one hydrazine molecule would be decomposed by each  $\text{N}_2^{\text{A}}$ . A comparison of the rate of hydrazine destruction with the rate of production of hydrogen cyanide from ethylene, however, indicated that excited nitrogen molecules do not make a large contribution to the chemical reactivity of active nitrogen in this particular instance.

Another useful channel of study appeared to be the determination of whether or not the method of production of active nitrogen affected the nature or amount of the reactive species. The two successful methods utilized in the production of active nitrogen have been the condensed discharge and microwave generator methods and, to date, there appears to be a difference only in degree and not in the fundamental nature of the activity in the active nitrogen streams produced. Armstrong and Winkler (60) passed small amounts of nitric oxide, ammonia and nitrogen, diluted with argon, through a condensed discharge and found that active nitrogen was produced in approximately equal amounts from nitrogen and ammonia.



Nitric oxide gave a smaller yield of active nitrogen due to rapid reaction of active nitrogen with nitric oxide. The behaviour observed suggested that all three gases were almost completely dissociated to yield nitrogen atoms as the main reactive species in the active stream.

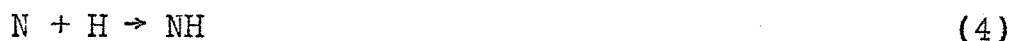
The effect of voltage on the nature of active nitrogen produced by a condensed discharge was also investigated. With constant flash rate, an increase of voltage across the discharge tube resulted in a large increase in the ratio of maximum decomposition of ammonia to maximum hydrogen cyanide production of ethylene. Interpretation of the above behaviour led the authors once more to suggest the presence of two reactive species, only one of which reacts with ammonia while the other, or both, may react with ethylene.

A reinvestigation of the ethane and methane - active nitrogen reactions, prompted by the results of the neopentane and ammonia reactions with active nitrogen, (61), was undertaken with the object of proving whether or not two reactive species were present in the active stream. The authors attempted to attach some positive significance to the two activation energies observed in the neopentane-active nitrogen reaction. In the earlier work (49), hydrogen atoms were assumed to have little importance in

the reaction scheme, but the larger scope of the more recent study revealed that the reaction was carried to an appreciable extent by hydrogen atoms. The following sequence of reactions was suggested as the probable mechanism.



It was found that addition of hydrogen atoms to the active nitrogen stream seemed to deactivate the active nitrogen probably by the reactions



It was concluded that either simultaneous hydrogen atom reactions, or the presence of more than one reactive species in the active stream, could result in the two activation energies observed in the neopentane-active nitrogen reaction.

The reactions of active nitrogen with methyl, ethyl, vinyl, propyl and isopropyl chlorides (62) yielded hydrogen cyanide and hydrogen chloride as the major products, together with smaller amounts of cyanogen and a polymer composed of carbon, hydrogen, nitrogen and chlorine. These reactions appeared, with respect to their rates, to resemble the analogous reactions with unsaturated hydrocarbons. At high flow rates of the organic chlorides

the yields of products approached limiting values and in the case of methyl chloride an increase in limiting yield with increase of temperature was observed. This behaviour was also observed in the reaction of methyl cyanide with active nitrogen (63).

In a review of the reactions of active nitrogen with the various organic molecules discussed above, Evans Freeman and Winkler (64) suggested a reasonably consistent mechanism for most of the reactions of active nitrogen with hydrocarbons. It was assumed that a chemically identical complex was formed in all the reactions. In the case of propylene, propyl chloride and propane, for example, the complex formed would have to be  $\text{N C}_3\text{H}_6$ . Differences observed in chemical reactivity were then ascribed to the increased stability of the complex, the energy content of which decreases from propylene, to propyl chloride, and then to propane, and to differences in ease of formation of the complexes.

The reaction of active nitrogen with phosphine, studied by Wiles and Winkler (65), yielded molecular hydrogen and the  $\alpha$  form of  $(\text{PN})_n$ . It was suggested by the authors that the primary step might be abstraction of hydrogen, with the  $\text{PH}_2$  radicals resulting in this manner reacting further with nitrogen atoms to form the nitride. The results of this study led to the germination of an investigation involving the reactions of "active

phosphorus'' (66). An apparatus similar to that used for nitrogen was tried for phosphorus. Argon, as a carrier gas, was passed through a bulb containing phosphorus and then allowed to flow through the discharge. A definite reaction was obtained between active phosphorus and ethylene, propylene, butene-1, propane, methane, ammonia, and hydrazine. Phosphine was the major gaseous constituent in all cases.

The fact that phosphine was the major product in the reactions mentioned above led to the conclusion that, under the proper conditions, ammonia could be a major product of the reaction of active nitrogen with hydrocarbons. Experimental proof of this conclusion was the principal aim in undertaking a study of the reactions of active nitrogen.

Herron and co-workers (67) investigated the reactions of active nitrogen with acetylene, ethylene, and propylene using a mass spectrometer for the continuous analysis of products. Evidence obtained in the mass spectra of the products pointed strongly to the possible importance of the CN radical in the reactions and suggested that this radical forms several products by displacement reactions. Of special interest was the observation that ammonia was produced in the reactions studied.

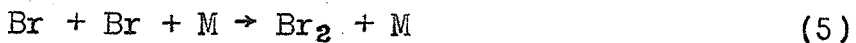
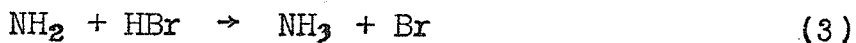
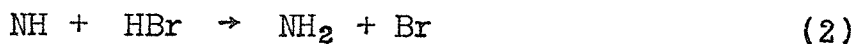
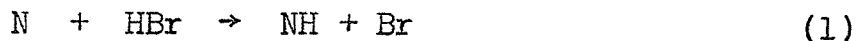
The first report of the formation of significant quantities of ammonia from active nitrogen-hydrocarbon

reactions was made by Dewhurst (68), who found considerable amounts of ammonia formed in the reaction of active nitrogen with neo-pentane, tetra methyl silane, methylamine, ethylamine, benzene and cyclohexane. The author deemed it unlikely that the ammonia could be formed by a series of hydrogen atom abstractions because of the endothermicity involved in the first step. It was suggested, however, that the ammonia could be formed via a nitrogen atom-hydrogen atom recombination reaction.

Dewhurst and Cooper later investigated the reactions of active nitrogen with silane and methylsilanes (69). The only volatile product obtained from silane was hydrogen while the methylsilanes yielded hydrogen cyanide and ammonia in addition to hydrogen. On the basis of bond energies, nitrogen atoms were expected to abstract hydrogen atoms from silane to yield imine radicals which, since no ammonia was produced, could disproportionate to nitrogen and hydrogen. Thus the ammonia produced from the methylsilanes was not formed by way of imine radicals. It was concluded that ammonia was formed directly by some sort of molecular process or that  $\text{NH}_2$  was the radical intermediate involved. The latter view was supported by the fact that ammonia produced from  $\text{CH}_3\text{-SiD}_3$  was principally  $\text{NH}_2\text{D}$ .

Bromine and ammonium bromide were found as the

main products of the reaction of active nitrogen with hydrogen bromide (70, 71). The reaction scheme postulated was:



A possible alternative for the formation of ammonia outlined above was also suggested.



It was observed that chlorine and tetrachlorodiborine were the main products of the reaction of active nitrogen with boron trichloride (72). The reaction, with respect to rate of formation of chlorine, appeared to be temperature independent in the range 100 to 395°C.

$\text{N}_2$  ( $A^3\Sigma_u^+$ ) molecules supposedly initiated the reaction which was then carried by nitrogen atom attack on  $\text{BCl}_2$  radicals.

Hydrogen and germanous nitride were obtained as products of the reaction of active nitrogen with germane (72). The rate of decomposition of germane was observed to increase with increasing temperature. In this particular case the reaction appeared to involve

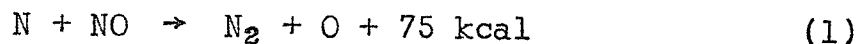
the direct and complete displacement of hydrogen by atomic nitrogen.

The reaction of active nitrogen with nitric oxide has been studied by Kistiakowsky and Volpi (73, 74) who concluded that the primary reaction was

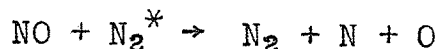


and that the rate constant for this reaction had a lower limit of  $5 \times 10^{13} \text{ cm}^3/\text{mole sec.}$  at ambient temperature. No detectable reaction was observed between nitrogen atoms and nitrous oxide or oxygen molecules. A re-examination, utilizing a mass spectrometer of high sensitivity, was conducted by Herron (75) who found the rate of the above reaction to be  $1.0 \pm .5 \times 10^{13} \text{ cm}^3/\text{mole sec.}$  and also noted that the reactions  $\text{N} + \text{O} \rightarrow \text{NO}$  and  $\text{O} + \text{O} \rightarrow \text{O}_2$  occurred in the ion source of the mass spectrometer.

Verbecke and Winkler (76) studied the reaction of nitric oxide and nitrogen dioxide with active nitrogen. Nitrous oxide was found as a product from the nitrogen dioxide reaction but not from the nitric oxide reaction. The nitrogen dioxide reaction also produced some nitric oxide. Nitric oxide was destroyed mainly by the reaction

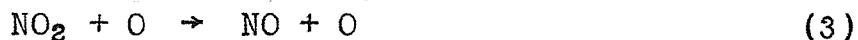
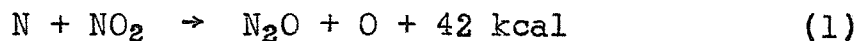


and the collision reaction



where  $\text{N}_2^*$  could probably be the  $\text{A}^3\Sigma_u^+$  state of the nitrogen molecule, was also suggested as a significant mode of

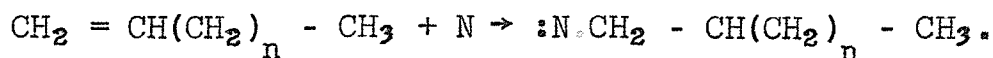
decomposition. The authors concluded that nitrous oxide must be formed from nitrogen dioxide by the following scheme:



In an investigation of the reaction of nitrogen dioxide with active nitrogen, Clyne and Thrush (77), found that the above reaction (1) was the predominant mode of decomposition.

Similar studies involving the reactions of active nitrogen with oxygen and nitric oxide have been conducted (78, 79, 80) primarily because of the importance of such reactions in certain atmospheric phenomena (81) and as a method of studying homogeneous and surface decay of nitrogen atoms.

Polyolefins (82) gave the same gaseous reaction products with active nitrogen as their monomers, or other simple hydrocarbons, in gas phase reactions. Twenty percent of the gaseous products from polyethylene was cyanogen and considerable amounts of ammonia were formed when methyl groups were attached to the polymer chain. A number of reaction complexes could be formed in the primary process and it was suggested that a biradical produced from polyethylene would be most probable.





Thus, nitrogen containing molecules or radicals could be formed by the attack of the nitrogen atom on the carbon-carbon bond:

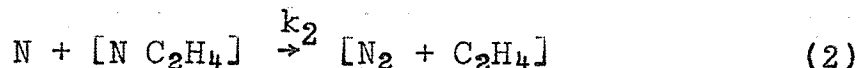
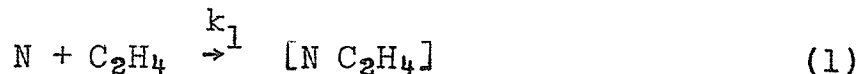


Hydrogen atoms liberated in the reaction could then abstract more hydrogen from the interior of the polymer thus leading to free radical chains with free electrons on secondary carbon atoms which would yield the observed crosslinked and coupled products.

A somewhat similar investigation was undertaken recently by Tsukamoto and Lichtin (83). The reaction of active nitrogen with 1,3-butadiene was found to yield important amounts of pyrrole and cis and trans crotononitrile which were probably produced from addition of a nitrogen atom and loss of a hydrogen atom. Other products produced from degradative processes included cis and trans 1-cyano 1-3 butadiene, 3 cyano-1-butene, cis and trans 1-cyanopentene-3, ethylene, acetylene, propylene and the most abundant product, hydrogen cyanide. A polymeric material,  $(C_4H_6N)_n$  was also found. Since the relative yields of monomeric products depended to a small extent on the partial pressures of reactants, it was suggested that they were all formed by way of the same nitrogenous intermediate.

In a mass spectrometric study of the reaction of nitrogen atoms with ethylene, Herron (84), in order to comply

with his observations, suggested, in agreement with Evans et al (64), the following mechanism:



The species  $[\text{NC}_2\text{H}_4]$  was not detected. This was attributed to the fact that  $k_2 \gg k_1$ . Relative rates of reactions (2) and (3) were not obtained, however, the ratio  $k_3/k_2$  was estimated at about  $10^{-11}$  mole/cc.

Recently (85) a comparison of five methods for terminating the reaction of active nitrogen with ethylene was made, and the rate constants obtained in this manner agreed, within an expected order, with those obtained by Greenblatt and Winkler (46), Milton and Dunford (71), Herron (84), and Wright and Winkler (86). A significant observation was that, since the effect of temperature on the rate constant for the ethylene reaction was negligible, there must be a very low activation energy for the process. A value of  $400 \pm 200$  cal/mole for this quantity was suggested as a reasonable estimate.

The termination of the reaction of active nitrogen with ethylene was utilized in order to enable the reaction time to be estimated with a fairly good degree of accuracy. A problem concurrent with the measurement of rates of nitrogen atom reactions is the manner and rate

with which nitrogen atoms themselves recombine. The recombination rate in the presence of various third bodies has been measured and it was found that in some cases the recombination of atoms is catalyzed by the presence of reactant molecules, (87). The rate constant of recombination was found (88) to be independent of temperature in the range 195-450°K and the reaction was predominantly homogeneous and third order at pressures above 3mm. of mercury. At pressures below 3 mm. of mercury, it was found that wall recombination plays a more significant part in the overall reaction.

Back et al (89) studied the decay of active nitrogen at high temperatures and found rate constants for both homogeneous and heterogeneous recombination. The homogeneous decay was found to have a slight positive temperature coefficient. Recently, Benson and Fueno (90) studied the process of atom recombination in the presence of foreign gases. It was found that the temperature dependence of  $k_r$ , the termolecular recombination rate constant, is not simple and that it varies between light and heavy molecules, but is usually proportional to  $T^{-1}$ . It did not appear that contributions from other electronic states, beyond the ground state, were significant in the recombination process.

In order to examine in detail the chemical methods for estimating nitrogen atom concentrations, and

to resolve more definitely the nature of the reactive species in active nitrogen, a study of the difference between the nitrogen atom content of active nitrogen, as inferred from the maximum hydrogen cyanide production from ethylene, and that obtained by the extent of nitric oxide destruction, was made by Wright, Nelson and Winkler (91, 92). The ratio of nitric-oxide destroyed to hydrogen cyanide produced was found to be independent of both the mode of excitation of the molecular nitrogen and the nitrogen atom concentration. Addition of nitrous oxide and carbon dioxide was observed to have no effect on this ratio.

Experimental results indicated rather definitely that the destruction of ammonia does not proceed by way of nitrogen atoms but was probably due to an excited molecule produced during homogeneous decay of active nitrogen. The authors also concluded that nitric oxide was destroyed not only by nitrogen atoms, but also by an excited molecular species of considerable lifetime produced by both homogeneous and surface decay of nitrogen atoms. It was postulated that ethylene did not react with this excited molecule of nitrogen but was capable of deactivating it. This, then, was suggested as the reason for the observed discrepancy of nitrogen atom estimations using ethylene and nitric oxide as reactants.

It was proposed that the most probable species present in active nitrogen which would be capable of reacting in the manner observed would be  $N_2 (A^3\Sigma_u^+)$  molecules. The half-life of the species assumed capable of reacting with nitric oxide, on the assumption that the decay was first order, was calculated to be  $8.4 \times 10^{-2}$  second. Previous work (93, 94) suggested the half-life of  $N_2 (A^3\Sigma_u^+)$  as  $2.6 \times 10^{-2}$  and .15 second.

Dunford (95) demonstrated that decomposition of ammonia by active nitrogen occurs by two different mechanisms. The predominant mode of decomposition of ammonia was believed to proceed by way of  $N_2 (A^3\Sigma_u^+)$  molecules, accompanied by a somewhat smaller decomposition due to reaction of ammonia with a molecular afterglow precursor. The half-life of the  $N_2 (A^3\Sigma_u^+)$  metastable species was estimated as  $.08 \pm .04$  sec. and the reactive precursor was thought to be the  $\Lambda(5^3\Sigma_u^+)$  state of molecular nitrogen.

### The Imine Radical

Since the imine and amine radicals may be of major importance in the reactions of active nitrogen with hydrocarbons and ammonia, a review of some of the experimental evidence obtained by various workers is perhaps in order at this point.

Rice and Frearno (96, 97) found that when gaseous hydrazoic acid was energized, thermally or electrically, and then condensed at liquid nitrogen temperatures, a blue product was deposited. When this blue deposit was warmed to about 148°K an irreversible transition to ammonium azide occurred. It was postulated that the blue material was the imine radical in the solid state. By illuminating solid hydrazoic acid at liquid nitrogen temperatures with ultraviolet light, Rice and Grelecki (98) showed that the solid could be converted into a blue material.

Mador and Williams (99) subjected hydrazoic acid to an electric discharge and froze the products at 4° and 77°K. Visible spectra bands that disappeared above 148°K were attributed to NH and NH<sub>2</sub> radicals. Dows, Pimentel and Whittle (100) studied the infra red spectrum of hydrazoic acid which had passed through a glow discharge and found that two unidentified intermediates, possibly N<sub>2</sub>H<sub>2</sub> and (NH)<sub>n</sub>, were present at -183°. In a study of free radicals at low temperatures Broida was able to assign spectral lines to the imine radical (23).

In a study of the ultraviolet and visible absorption spectrum of irradiated, solid hydrazoic acid, Papazian (101) found an absorption band at 3400Å° which he interpreted as proof of the existence of the imine radical. He proposed that NH radicals could react to form the radical HN = N which is responsible for the

intense blue color first observed by Rice.

Pannetier et al (102), in an investigation of active nitrogen reactions on simple organic substances, found sufficient experimental evidence to suggest that the imine radical plays a more important role in the active nitrogen - hydrocarbon reactions than it previously was thought. The reaction of active nitrogen with atomic hydrogen was studied spectroscopically by the same group (103). They observed the first and second positive systems of nitrogen and the  $^3\Pi - ^3\Sigma$  system of the imine radical. Ammonia was found to be the only condensible product, and the blue luminescence in the trap at liquid nitrogen temperatures was attributed to a metastable isomer of the ammonia molecule.

Thus, it would appear that ample evidence exists to support the supposition of the presence of the imine radical in active nitrogen-hydrocarbon and ammonia systems.

The present investigation was undertaken in order to find the necessary and sufficient conditions under which ammonia would become a principal product of the reactions of active nitrogen with hydrocarbons. It was also hoped that adequate separation of the active species could be effected in order to restrict the reaction of active nitrogen to one particular species.

## EXPERIMENTAL



## EXPERIMENTAL

### Materials

Helium, nitrous oxide, ammonia, carbon dioxide and all the hydrocarbons used, with the exception of acetylene, were obtained from the Matheson Company. The reactant gases purchased as C.P. grade were simply given a trap to trap distillation, in which the first and last fractions were discarded, before they were stored in the apparatus.

Nitric oxide was prepared by the action of sulphuric acid on a mixture of sodium nitrite and potassium iodide. Acetylene was produced by the action of water on calcium carbide. Hydrogen cyanide, for use as a reactant gas, was prepared by the action of sulphuric acid on potassium cyanide. Phosphine was produced by the reaction of an alkaline water solution on molten white phosphorus in the absence of air. In each case the reactants prepared in the laboratory were given trap to trap distillations, and after discarding first and last fractions were purified by distillation from a LeRoy still (104) over a 20° temperature range at pressures up to thirty microns.

Hydrazine, and formamide, white label grade, were obtained from the Eastman Chemical Company. These reagents were purified in a similar manner to the fractionation of the gaseous reactants.



Argon, 99.99% pure, and nitrogen were obtained from the Linde Company. The nitrogen was purified by passing it through a copper wire furnace at 400° and then through a trap, cooled in liquid nitrogen, which removed the water and carbon dioxide.

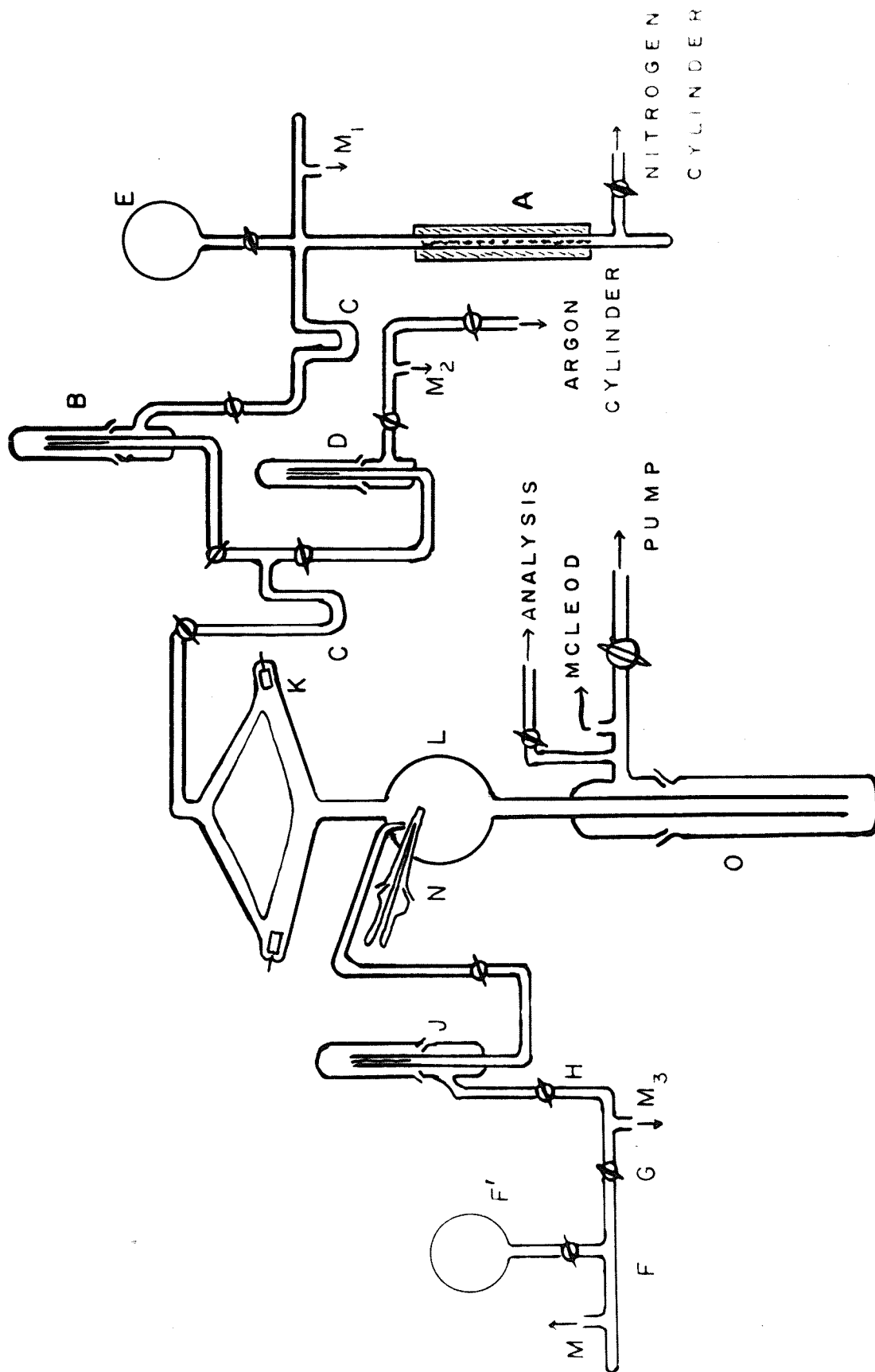
### Apparatus

A diagram of the apparatus is shown in Figure 1. It was constructed entirely of Pyrex glass.

The nitrogen from a cylinder was passed through a reducing valve into the line through a copper furnace A, and a trap, C, cooled by liquid nitrogen. The purified nitrogen, at a pressure given by manometer,  $M_1$ , then passed through a flowmeter, B, which had been calibrated by measuring the rate of evacuation of a known volume under different pressures. A flow system for argon was arranged so that the gas from a cylinder was passed through a reducing valve into the line which was open to a manometer  $M_2$ , placed before a flowmeter, D. The manometer was used to insure a constant pressure head in order that the flow of argon be as nearly constant as possible.

For the experiments in which argon (or helium) was used as a carrier for nitrogen, the purified nitrogen was placed in a known volume of 1250 cc., E, at a specific pressure and then was allowed to pass through flowmeter B, into the argon stream before the discharge.

Figure 1  
Diagram of Apparatus



The flow rate of nitrogen was calculated on the basis of the Ideal Gas Law and the argon flow rate was adjusted at will, in order to obtain the desired reaction pressure.

The flow system for the reactant was arranged in such a way that a continuous range of constant flow rates could be obtained. It consisted of a calibrated volume,  $F$ , adjoined to reservoir,  $F'$ , from which the reactant passed through a scratched stopcock  $G$ , into a ballast volume  $H$ , and then through flowmeter  $J$ . By keeping the pressure in the ballast volume constant during an experiment it was possible to maintain a constant rate of flow of reactant. The reactant flow was determined from the duration of the experiment and the volume of gas used. Gas volumes were calculated from the change in pressure in the calibrated volume with the use of the Ideal Gas Law. When liquids were used as reactants the conventional flow system was found to be useless. In its place a liquid reservoir, which could be weighed before and after an experiment, was attached 20 cm. from the reaction bulb. The 8 mm. connecting tubing, stopcocks, ground glass joint and liquid reservoir were wrapped with an insulated heater. The temperature of the heater and thus the vapor pressure of the liquid was controlled by a variac. If temperatures below room temperature were required the liquid reservoir was surrounded by a dewar filled with the desired coolant.

The discharge tube, K, in the case of the condensed discharge experiments was of 25 mm. diameter (o.d.) tubing and 56 cm. long. A hollowed, cylindrical aluminum block, 2.5 cm. long and 16 mm. in diameter, was attached to a commercial nonex sealed tungsten wire. Electrodes of this kind were sealed into each end of the discharge tube. The argon and/or nitrogen was introduced at each end of the tube.

In the case of the microwave experiments the discharge tube and reaction bulb were replaced by a 30 cm. length of quartz tubing 16 mm. (o.d.) in diameter. The microwave director then was placed as close as possible to the quartz tube.

When the reaction chamber was a 500 ml. spherical bulb, into which the reactant entered at the top through a small jet, the discharge tube and reaction vessel, L, were connected by 15 cm. of 22 mm. tubing. A sheathed thermocouple, N, gave an indication of reaction temperature. All condensible products of the reaction were frozen out in trap, O, which was cooled with liquid nitrogen.

For the experiments conducted at elevated temperatures, the 500 ml. spherical reaction chamber was encased by an asbestos mold in which a 100 ohm resistance had been wound. The low temperature work was carried out in a slightly modified apparatus shown in Figure 2. The discharge tube was connected to a U-trap by 40 cm. of

16 mm. tubing. A 15 cm. section of 8 mm. tubing was utilized as the inlet arm of the U-trap while the other arm was a 20 cm. section of 16 mm. tubing. The reaction trap was followed by a pump-down trap in order to enable trapping of products at  $-211^{\circ}\text{C}$ .

The pumping system consisted of a Welch Duo-Seal vacuum pump, H-1402B, which gave an ultimate vacuum of  $10^{-4}$  mm. of mercury and a Free Air Capacity of 140 liters/min.

#### Electrical Circuit

The active nitrogen was produced by a high voltage condensed discharge, the circuit diagram of which is shown in Figure 3, and a Raytheon Mfg. Co. Microtherm (Model CMD7) unit.

For the condensed discharge method the primary of a variac was connected directly to a 220V line. The secondary of the variac led to the primary of a high voltage transformer. The output voltage across the transformer was thus capable of being varied from 0 to 4500 V. Two 866A mercury-filled radio tubes were used in parallel to rectify the current. The pulsating direct current from these tubes was used to charge a 4  $\mu\text{f}$ . capacitor through two 10,000 ohm resistors. A discharge occurred when the voltage on the condenser was sufficient to discharge through a spark gap (necessary only when argon was

Figure 2  
Diagram of Apparatus



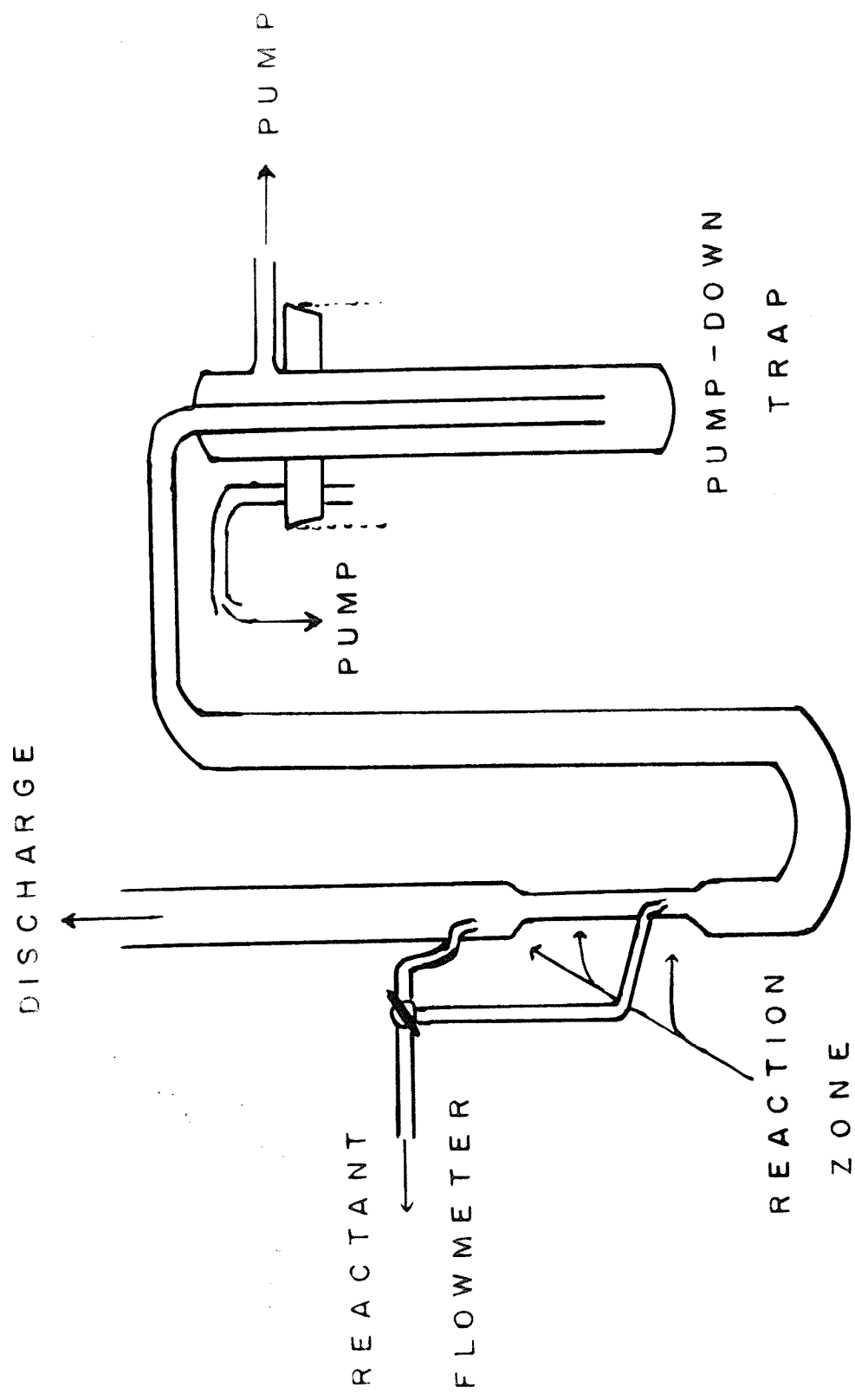
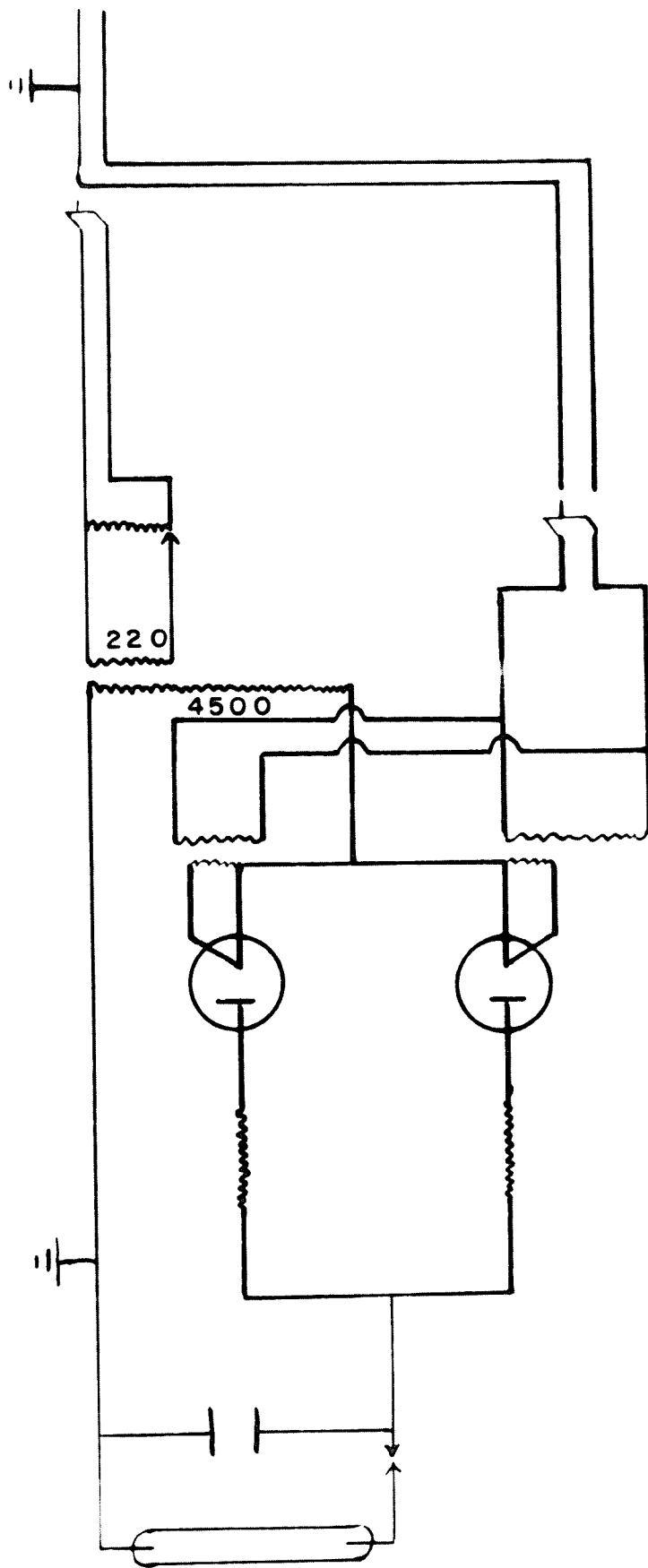


Figure 3  
Circuit Diagram



used as a diluent for nitrogen) and the discharge tube. The rate of discharge was kept constant by keeping the pressure in the discharge tube constant and adjusting the voltage across the discharge tube with the use of the variac.

#### Analysis System

A diagram of the analysis system is given in Figure 4. An indication of the amount of products obtained in a reaction was given by the pressure in a calibrated volume A, open to manometer, M. The condensible products and reactant were analysed and separated by the use of a LeRoy still, B. The products were identified by comparison of the vapour pressure curves with those for the various pure substances which were considered as possible products of the reaction. A mercury diffusion pump, C, aided the speed of separation and a calibrated gas buret and Toepler pump, O, were used to determine the amounts of products.

Ammonia was found to be associated with hydrogen cyanide as ammonium cyanide at low temperatures and was distilled at  $-85^{\circ}\text{C}$ . At room temperature, the ammonium cyanide was an equimolar mixture of ammonia and hydrogen cyanide.

When sufficient product was obtained in any one fraction a Perkin Elmer, Model 21, infrared instrument and a Varian high resolution, 60 megacycle spectrometer were used for identification purposes. Vapour pressure

Figure 4  
Analysis System

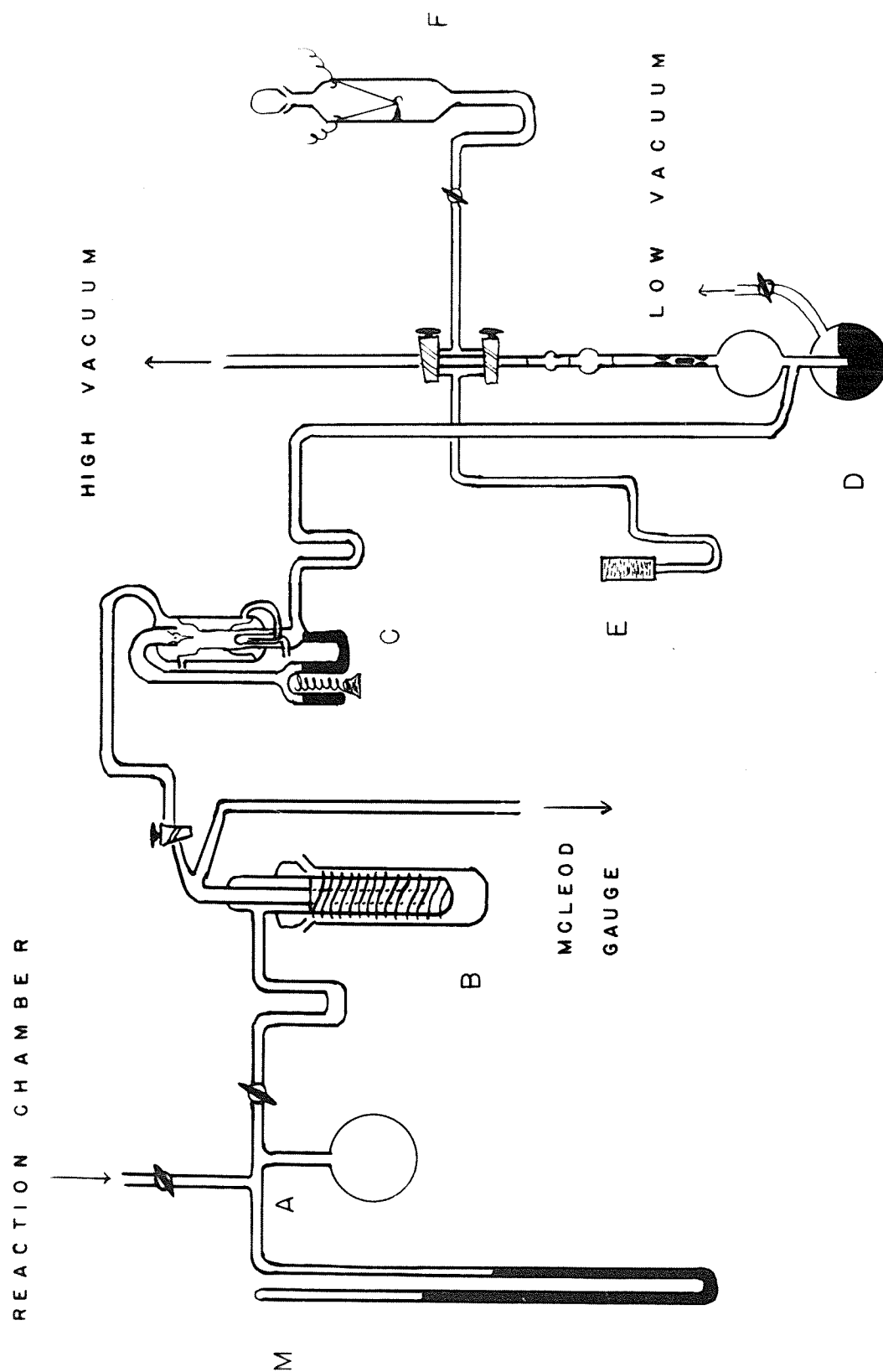
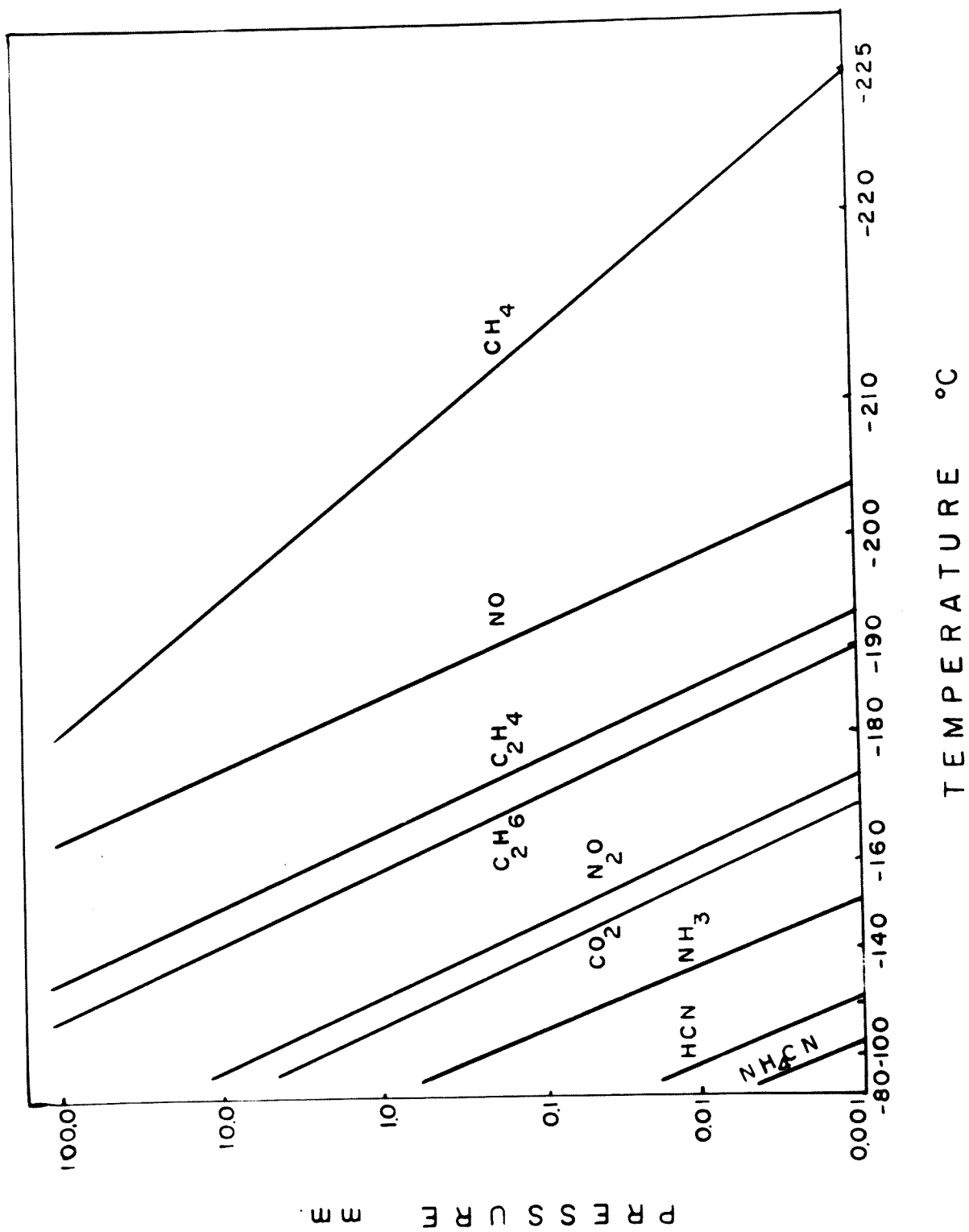


Figure 5  
Vapour Pressure Curves





versus temperature curves shown in Figure 5, were used to indicate the temperature at which good separation could be obtained.

A copper oxide furnace, F, and a platinum wire combustion chamber, F, were used in order to obtain confirming analysis of some of the products. The combustion chamber, F, was connected by a ground glass joint so that it could be replaced by the infrared gas cell or any other product trap.

#### Procedure for Typical Experiment

In the case of the gas phase reactions, trap O, was cooled to liquid nitrogen temperatures after the unpoisoned reaction system was evacuated to  $10^{-3}$  mm. When the liquid nitrogen traps for the removal of carbon dioxide and water from the argon and nitrogen streams were in place, the lines to the reducing valves of both cylinders were then opened to the pump. The argon or nitrogen flow was then started and the discharge was turned on to ensure that the electrical circuit was in order. After a few minutes, the reaction was started by allowing the reactant to flow into the reaction vessel. The flow was maintained constant by manually controlling the pressure differential across the flowmeter with the scratched stopcock. Normally the duration of an experiment was governed by the time needed to introduce sufficient reactant to form a quantity of gaseous products which could be handled comfortably in the Leroy still.

In the argon-nitrogen experiments the nitrogen was not drawn from the cylinder but from reservoir, E, which was filled with pre-purified nitrogen. For all other cases the discharge gases were admitted into the discharge tube in the manner described above. Condensable products formed in the reaction and excess condensable reactant then were removed from trap, O, and enclosed in a calibrated volume open to a manometer. When methane was used as the reactant, the products of the reaction were the only gases present in the trap, O, and when nitric oxide was used as the reactant gas, blank experiments showed that 98% of the nitric oxide was trapped at the temperature of liquid nitrogen. In the experiments in which nitric oxide was involved the pump-down trap shown in Figure 2 was used since at  $-211^{\circ}$  nitric oxide is quantitatively trapped.

At the end of an experiment the system was evacuated to about  $10^{-3}$  mm. and isolated from the pump. After expanding and condensing the gases several times, and pumping to  $10^{-4}$  mm. at liquid nitrogen temperatures, the gases were analysed in the LeRoy still. Fractionation was carried out at temperatures which allowed efficient separation with a minimum of contaminants. From the still the pure fractions were pumped into calibrated volumes by a Toepler pump where their pressure, volume and temperature could be read. These data allowed the

products formed to be calculated in moles and mole percent of total amount of products.

Product gases then could be withdrawn from the Toepler pump into an infrared gas cell, the copper oxide furnace, or into gas storage tubes for wet reagent tests and for proton resonance analysis.

For the heterogeneous trap reactions experimental preparation and method were the same in every respect except for the method of introducing the reactant. Before the discharge was started the reactant was condensed slowly at  $-196^{\circ}$  in a U-trap reaction zone, 40 cm. from the discharge tube, just below the level of liquid nitrogen in the surrounding dewar flask. When diffuse deposits were desired the reactant was swept in with nitrogen, with the liquid nitrogen level at a fixed position.

## RESULTS

## RESULTS

The reactions of active nitrogen with several hydrocarbons, nitrous oxide, ammonia, water, formamide, and phosphine were studied under varying conditions. For the purposes of clarity and ease of comparison, the results of the above studies have been subdivided according to experimental conditions and reactants.

### Reaction of Active Nitrogen with Simple Hydrocarbons

Methane, ethane, and acetylene were reacted with active nitrogen which was produced by passing nitrogen-argon mixtures through a condensed discharge. In each case hydrogen cyanide and ammonia were found as the major gaseous products with little or no polymer formation. Trace amounts of ethane were found when methane was used as the reactant and correspondingly small amounts of butane and cyanogen were found when ethane was the reactant.

In these experiments the only visible reaction was the blue argon discharge. No reaction flame and no nitrogen afterglow was visible. The flow rate of argon in most of the experiments was of the order of  $3.3 \times 10^{-3}$  mole/min. and the flow rate of nitrogen in the argon carrier stream was usually about  $33 \times 10^{-6}$  mole/min. Due to the extremely small concentrations of nitrogen used, no attempt was made to determine a nitrogen atom flow rate by physical or chemical means.

The reaction of methane with active nitrogen produced in a pure nitrogen discharge was also studied for purposes of comparison with the above experiments. The molecular nitrogen flow rate was  $1.6 \times 10^{-3}$  mole/min., corresponding to a reaction zone pressure of 1.30 mm., and the nitrogen atom flow rate as determined by the maximum destruction of ethylene, was  $1.0 \times 10^{-4}$  mole/min. Reaction time or the interval between mixing of reactants and trapping of products was estimated at 0.25 sec in a 500 cc. reaction flask.

On the basis of the hydrogen cyanide formed, about 5% of the methane reacted at 27° when nitrogen was used without a carrier gas. Hydrogen cyanide, ammonia, and traces of both cyanogen and ethane were the only gaseous products trapped. The rate of production of hydrogen cyanide increased rapidly with increase in methane flow but the ammonia remained relatively constant. The hydrogen cyanide and ammonia fractions were identified by their vapour pressures and infrared spectra while the cyanogen and ethane were identified only by their vapour pressures because the trace quantities produced were insufficient for verification by other methods available. No difficulty was encountered in obtaining reproducible results and no pre-conditioning of the apparatus seemed necessary. The results are shown in Figure 6.

Before argon was utilized as a diluent for nitrogen, a few experiments using helium were attempted. Only small amounts of hydrogen cyanide and ammonia were produced. Experimental difficulties in maintaining a steady discharge at different low pressures were encountered and it was found more advantageous to use argon.

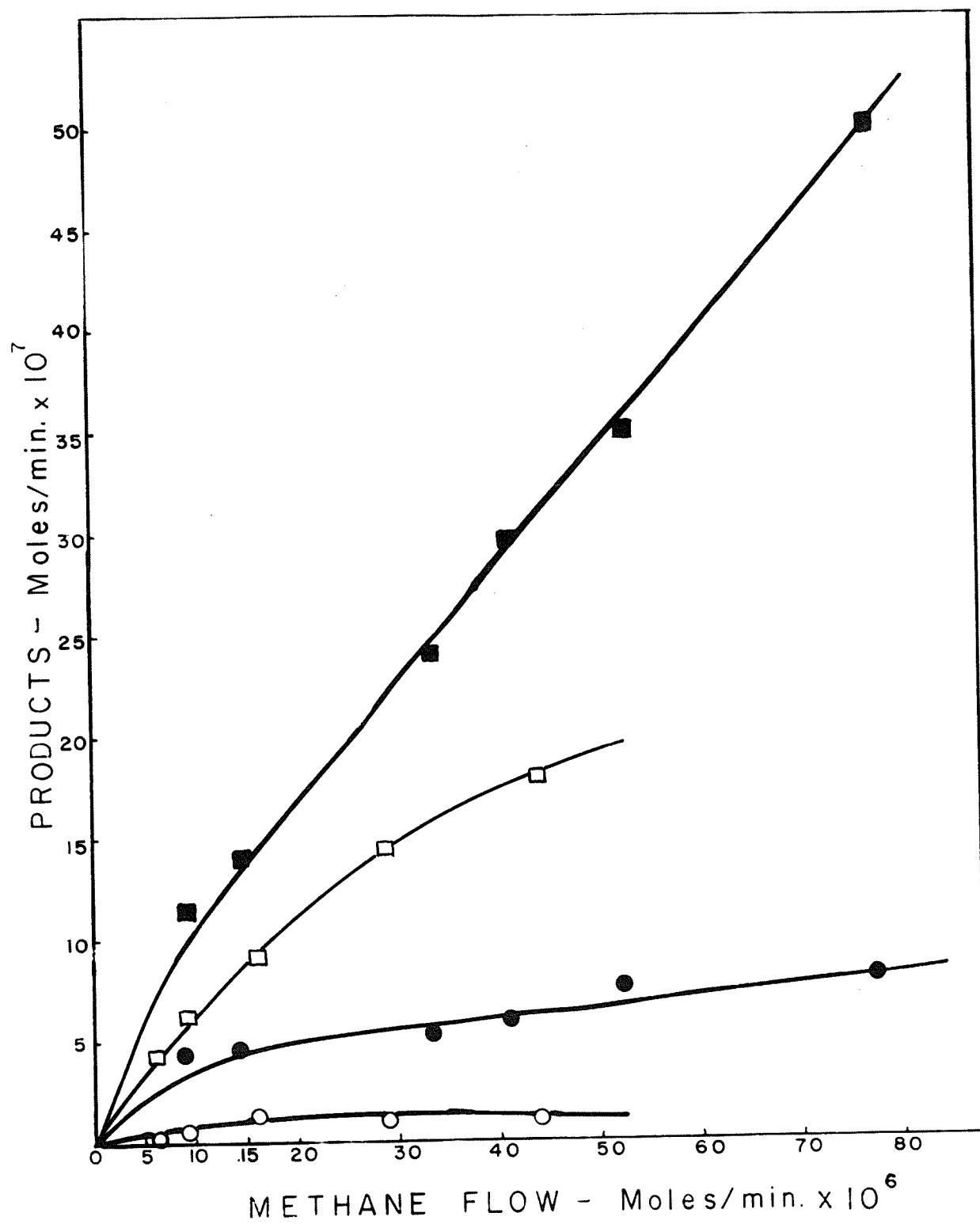
When argon was used as a carrier for nitrogen flowing at a rate of  $33 \times 10^{-6}$  mole/min. ( $A/N_2 > 100$ ) corresponding to a reaction zone pressure of 2.23 mm., the rate of formation of ammonia was increased five fold and the yield of hydrogen cyanide was approximately doubled in comparison with experiments using pure nitrogen. Again the rate of production of hydrogen cyanide increased rapidly with increase in methane flow, but the ammonia remained relatively constant. Blank experiments using only argon in the discharge indicated no hydrocarbon decomposition and blank discharge runs, i.e. passing nitrogen and argon through the discharge, produced no condensible products. The results, for purposes of comparison with the yields obtained using pure nitrogen, are also plotted in Figure 6.

Because oxygen enhances the afterglow of nitrogen in some instances (3), it was thought that the presence of a small amount of oxygen in the nitrogen might act as a catalyst and have an effect on the relative rates of

Figure 6  
Relation between Hydrogen Cyanide  
and  
Ammonia Production  
with  
Methane Flow Rate

- HCN argon-nitrogen mixture
- NH<sub>3</sub> argon-nitrogen mixture
- HCN pure nitrogen system
- NH<sub>3</sub> pure nitrogen system





production of hydrogen cyanide and ammonia. Accordingly, nitrogen was adulterated by the addition of 1/4% of oxygen and was used in an argon-nitrogen discharge for reaction with methane. No change was observed in the ratio of hydrogen cyanide to ammonia and the amounts of product obtained were of the same order of magnitude as those obtained in the absence of oxygen. Considerable amounts of carbon dioxide, nitrous oxide, and water complicated the reaction to such an extent that it seemed useless to continue this kind of experimentation.

When the methane flow was kept constant at about  $20 \times 10^{-6}$  mole/min., and the molecular nitrogen flow in the argon stream was varied, the results obtained were similar to those found when the methane flow was altered. The pressure in the reaction system was 1.45 mm. Ammonia production was constant over a wide range of nitrogen flow rates while the hydrogen cyanide yield increased slightly with increase of nitrogen flow rate. At flow rates of molecular nitrogen of about one micromole/min., about 40% of the nitrogen introduced reacted to form ammonia and hydrogen cyanide. The results are illustrated in Figure 7.

Since active nitrogen, produced in a nitrogen discharge, was found capable of reacting with hydrocarbons and ammonia at  $-196^\circ$  in the product trap, it was necessary

to determine the extent of reaction caused by active nitrogen produced in a nitrogen-argon discharge under similar conditions. When active nitrogen from the argon-nitrogen system was passed over ammonia, ethane, or ethylene at  $-196^{\circ}$  in the product trap, no significant decomposition was observed. The gas phase reaction, at  $-196^{\circ}$ , of methane with active nitrogen, produced from both nitrogen and argon-nitrogen discharges, was found to yield only trace amounts of ammonia and hydrogen cyanide.

In order to find the optimum conditions for the production of ammonia, both nitrogen and methane flow rates ( $33 \times 10^{-6}$  and  $16 \times 10^{-6}$  mole/min. respectively) were kept constant and the reaction pressure was varied by adjusting the flow of argon. The results are illustrated in Figure 8. The yield of ammonia remains nearly constant while the yield of hydrogen cyanide goes through a maximum at about 1.8 mm.

The yields of ammonia and hydrogen cyanide for the active nitrogen reactions with ethane and acetylene, in an argon-nitrogen discharge system, are shown in Figure 9. The reaction zone pressure was 2.23 mm. and the molecular nitrogen flow rate was  $33 \times 10^{-6}$  mole/min. In the ethane reaction about 70% of the ethane destroyed was recovered as hydrogen cyanide. Lower hydrogen cyanide yield and poorer mass balance for the acetylene reaction indicate that there was more polymer formation, although none was observed, than in the ethane reaction.

Figure 7  
Relation Between Product Production and  
Nitrogen Flow Rate in the  
Reaction of Methane with Active Nitrogen

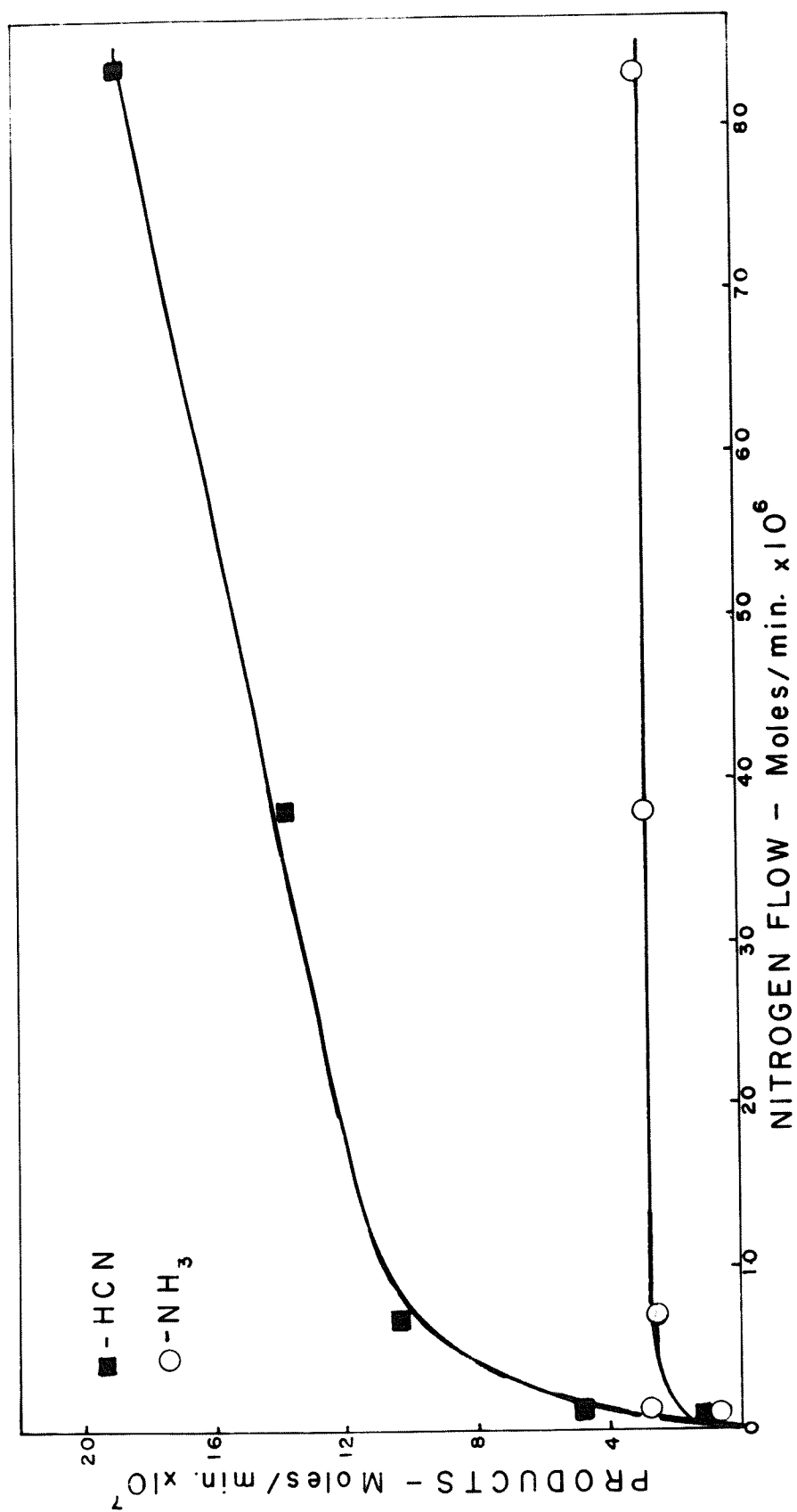


Figure 8

Relation Between Product Production and  
Reaction Zone Pressure for the  
Reaction of Active Nitrogen with Methane

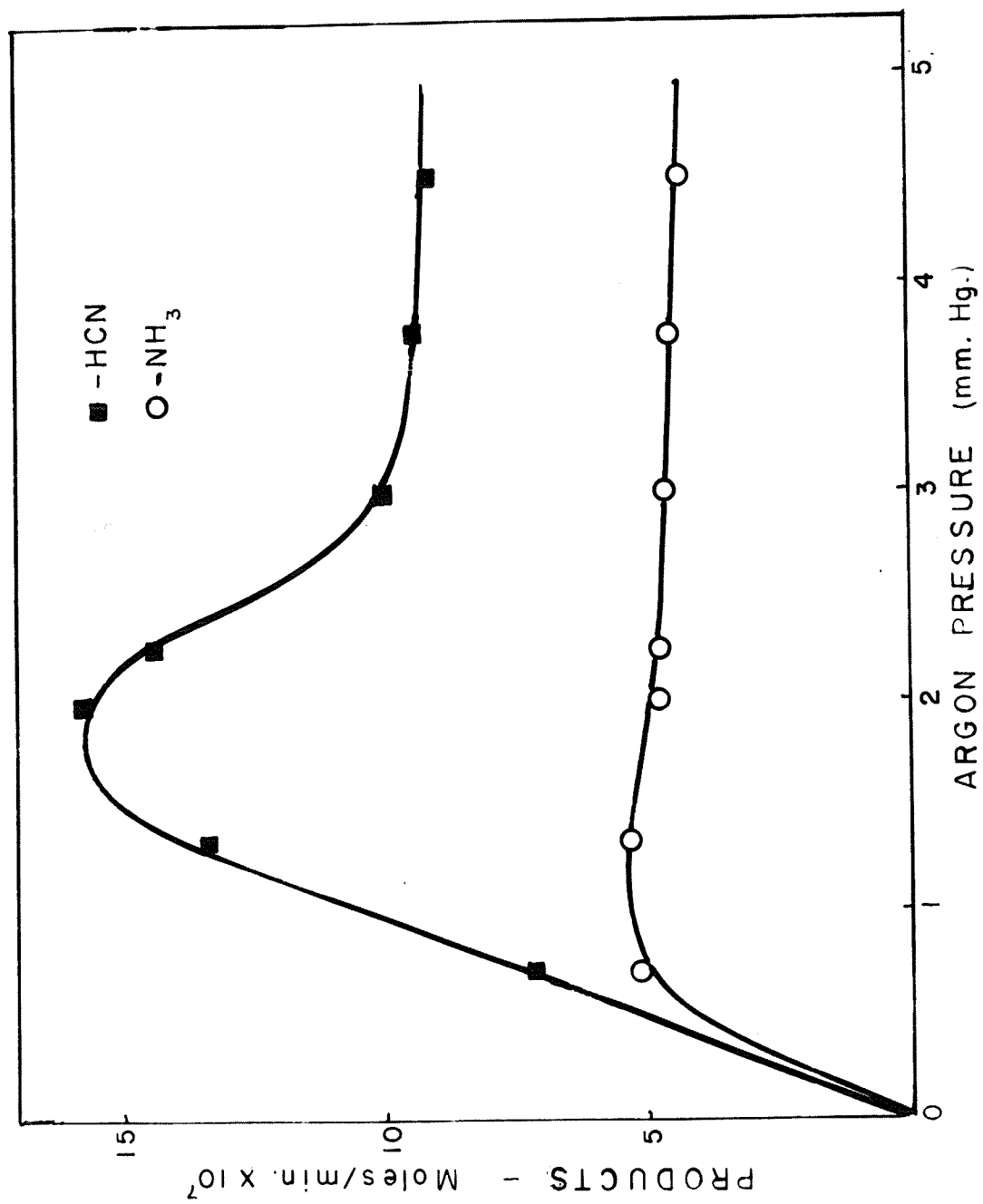
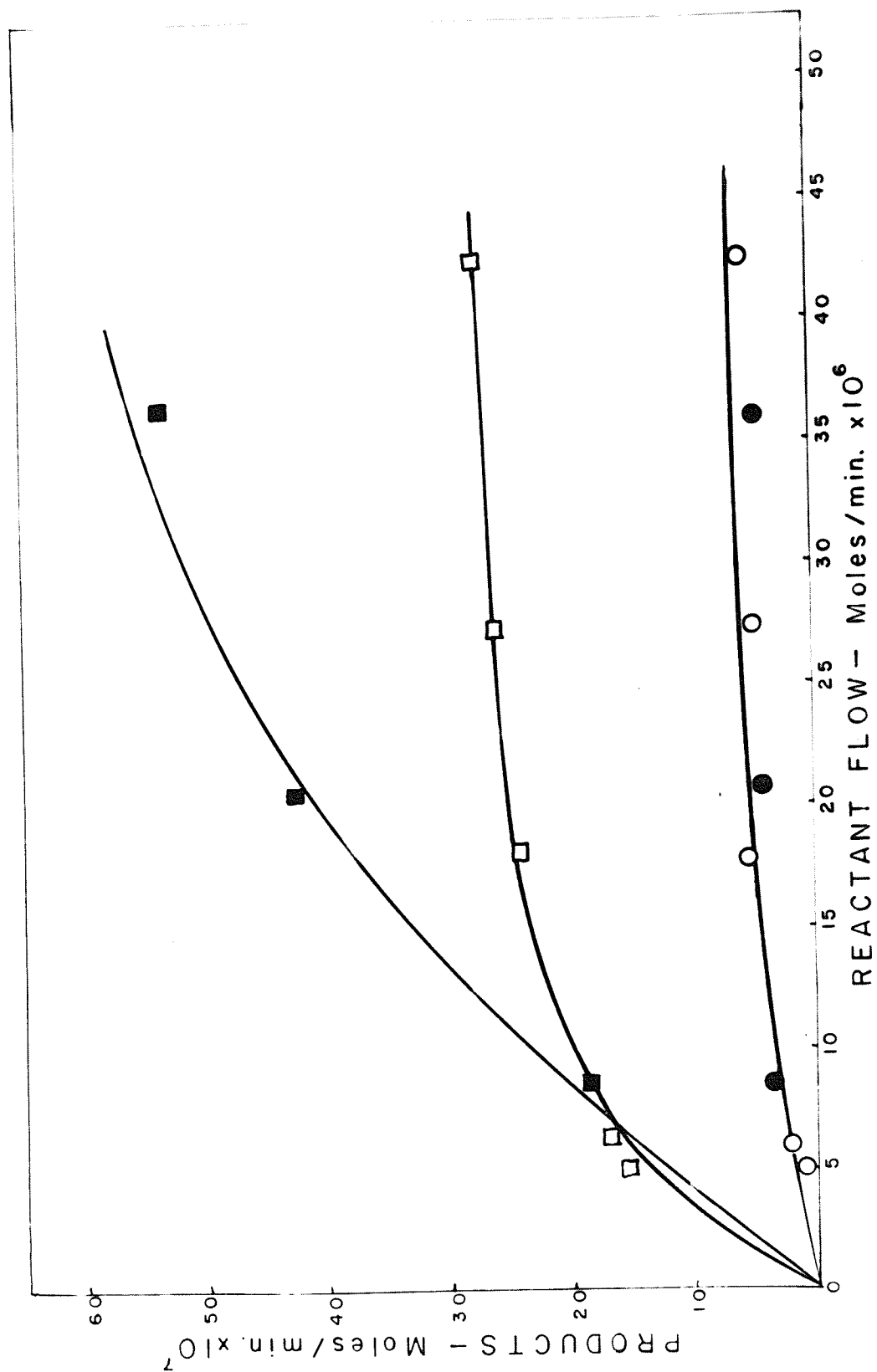


Figure 9  
Relation Between Product Production  
and  
Hydrocarbon Flow Rate

Reactant	HCN	NH <sub>3</sub>
C <sub>2</sub> H <sub>2</sub>	□	○
C <sub>2</sub> H <sub>6</sub>	■	●





Reaction of Active Nitrogen with Simple Hydrocarbons at  $-196^{\circ}$ 

In an attempt to alter the ammonia-hydrogen cyanide ratio so that the production of ammonia would be favoured, the reaction of active nitrogen with methane was studied at  $-196^{\circ}$ . The active nitrogen for this reaction was produced in an electrodeless and a condensed discharge through nitrogen, argon-nitrogen, and helium-nitrogen gas streams. It was found that, regardless whether the methane was pre-cooled or not and whether the reaction was conducted in a 25 cc. bulb or a 16 mm. (o.d.) cylindrical tube, only trace amounts of hydrogen cyanide, ethane, and ammonia were found. In view of the high temperature work of Gartaganis and Winkler (61) and the above observations it was decided that a temperature study of this reaction would not be very fruitful in altering the ammonia-hydrogen cyanide ratio.

The reactions of ethane, ethylene, acetylene and hydrogen cyanide with active nitrogen, produced in a condensed discharge through pure nitrogen, were studied at  $-196^{\circ}$ . Considerable amounts of ammonia and hydrogen cyanide, in contrast to the gas phase methane-active nitrogen at  $-196^{\circ}$ , were produced from ethane and ethylene. Some hydrogen cyanide was produced from acetylene and in the reaction of active nitrogen with hydrogen cyanide, about 15% of the decomposed hydrogen cyanide was recovered

as cyanogen. In all reactions large amounts of polymer were deposited at and beyond the reaction zone. The molecular nitrogen flow rate was  $6.4 \times 10^{-3}$  mole/min. corresponding to a pressure of 1.45 mm. of mercury in the reaction zone, and the flow rate of nitrogen atoms, as determined by the ethylene destroyed in the gas phase reaction with ethylene, was  $2.5 \times 10^{-4}$  mole/min. The results of a time study of the ethane-active nitrogen reaction and a study of the extent of decomposition of ethane as a function of the initial quantity of ethane are listed in Table I.

Since both hydrogen cyanide and ammonia are destroyed by active nitrogen at  $-196^{\circ}$  the quantities produced in the ethane reaction are to be considered as minimum and not the actual amounts produced. Figure 10 shows the trends indicating the maximum extent of decomposition of ethane and ethylene.

When the reactant was deposited about six inches below the level of the liquid nitrogen in the surrounding dewar on a clean baked surface, there was only a slight reaction. After the surface was coated with polymer the extent of reaction increased approximately ten-fold.

TABLE I

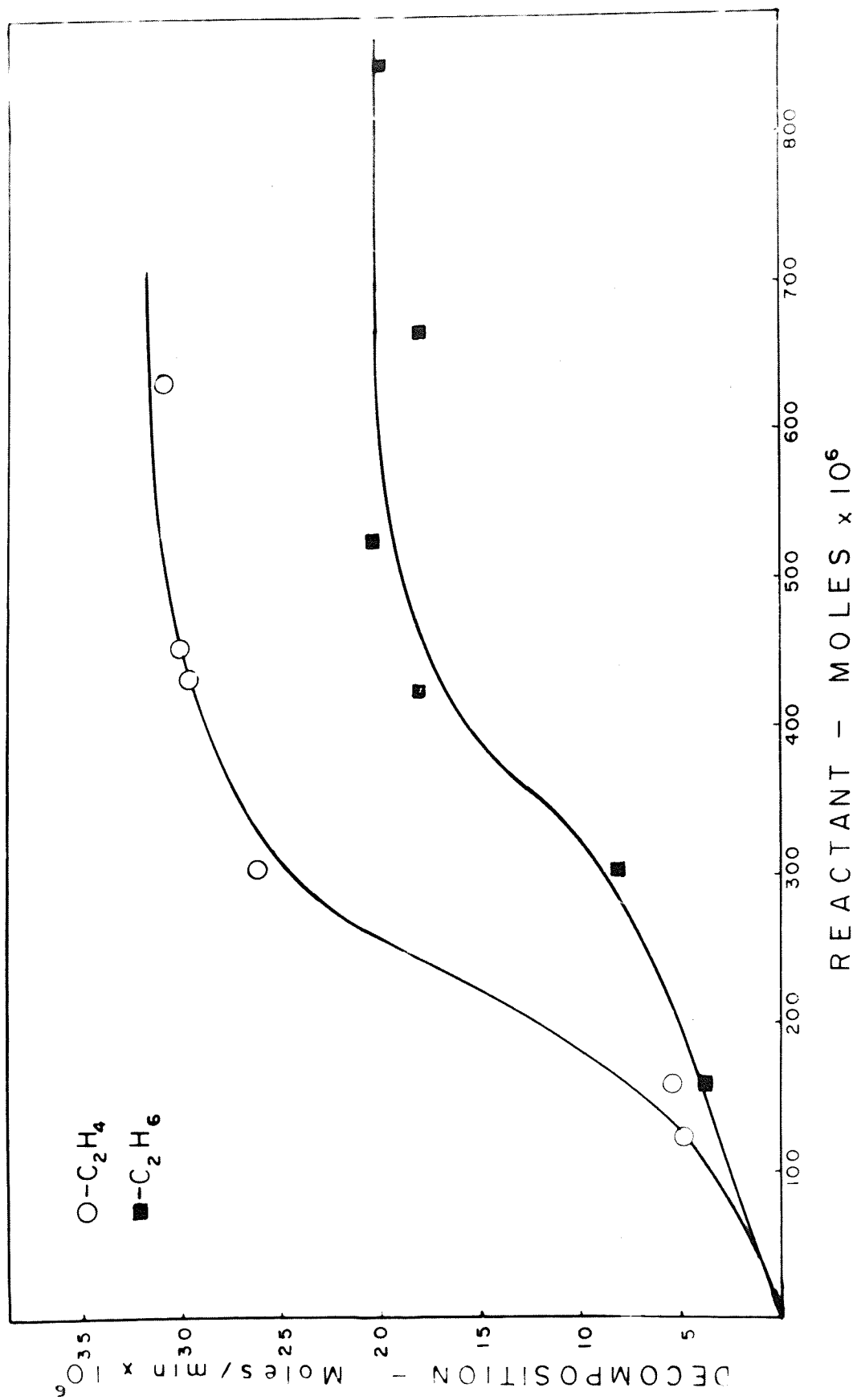
Decomposition of Ethane at -196° by Active NitrogenAll quantities in micromoles

<u>Duration of Experiment</u> min.	<u>C<sub>2</sub>H<sub>6</sub> Reactant</u>	<u>C<sub>2</sub>H<sub>6</sub> Decomposed</u>	<u>C<sub>2</sub>H<sub>6</sub> Decomposed/min.</u>	<u>HCN Produced</u>	<u>NH<sub>3</sub> Produced</u>
5.0	81.5	23.2	4.6	11.2	0.5
10.0	81.0	42.5	4.2	16.8	3.8
20.0	73.5	41.9	2.1	20.8	2.8
30.0	78.0	73.6	2.4	28.6	2.4
40.0	74.5	56.6	1.4	28.8	2.4
5.0	154	18.1	3.6	3.4	1.0
"	231	14.0	2.8	5.0	1.0
"	303	39.0	7.8	12.1	2.9
"	423	91.0	18.2	40.7	11.7
"	657	90.0	18.0	36.8	8.1
"	522	107	21.4	63.8	19.3
"	846	101	20.2	43.7	13.5

Figure 10  
Relation between Decomposition Rate at  $-196^{\circ}$   
and  
Initial Amount of Reactant for Ethane and Ethylene

O -  $C_2H_4$

■ -  $C_2H_6$



The reaction of active nitrogen with acetylene at  $-196^{\circ}$  gave extremely erratic and irreproducible results, as is evident from the data shown in Table II. The reason for this was found to be that acetylene was apparently incorporated in the polymer. When active nitrogen was reacted with the polymer produced in the acetylene reaction, as much as 30% of the supposedly decomposed acetylene from the preceding acetylene reaction, was recovered. Only small amounts of hydrogen cyanide were produced.

In the reaction of active nitrogen with hydrogen cyanide at  $-196^{\circ}$ , as much as 20% of the decomposed hydrogen cyanide was recovered as cyanogen. Table III gives the extent of decomposition of hydrogen cyanide and the amounts of cyanogen produced. No other gaseous product was found. Figure 11 shows the extent of decomposition of acetylene and hydrogen cyanide with a nitrogen atom flow rate of  $250 \times 10^{-6}$  mole/min.

Table IV shows the results of a time study of the ethylene-active nitrogen reaction and a study of the extent of destruction of ethylene as a function of the initial quantity of ethylene.

When ethylene was deposited on a clean glass wall about six inches below the level of the liquid nitrogen in the dewar surrounding the reaction chamber,

virtually no reaction was observed. Less than 2% of the ethylene was decomposed during a 15.0 minute experiment when 630 micromoles were used as the reactant surface. Three micromoles of cyanogen and 0.75 micromoles of ammonium cyanide were the only gaseous products obtained and no visible polymer was produced. After the clean glass had been coated with the polymer associated with active nitrogen-hydrocarbon reactions, the extent of ethylene decomposition increased until a somewhat reproducible maximum was obtained (see Figure 10 and Table IV).

Some evidence was obtained that ethylenimine was produced besides ammonia and hydrogen cyanide. Titration of the hydrogen cyanide formed from the active nitrogen-ethylene reaction showed that about 2% of the hydrogen cyanide fraction was in fact not hydrogen cyanide but a compound with almost identical vapour pressures. A positive determination could not be obtained, however, because of the minute quantity produced, but it seemed not unreasonable to suspect that this small fraction was ethylenimine.

Some experiments were done in attempting to make larger amounts of ethylenimine using active nitrogen and hydrogen atoms to react with ethylene. Nitrogen and hydrogen were passed through the discharge simultaneously to produce atomic hydrogen and active nitrogen. The molecular hydrogen flow rate was  $1 \times 10^{-3}$  mole/min. and



TABLE II

Decomposition of Acetylene at -196° by Active NitrogenAll quantities in micromoles

<u>Duration of Experiment</u> (min.)	<u>C<sub>2</sub>H<sub>2</sub> Reactant</u>	<u>C<sub>2</sub>H<sub>2</sub> Decomposed</u>	<u>C<sub>2</sub>H<sub>2</sub> Decomposed/min.</u>	<u>HCN Produced</u>	<u>NH<sub>3</sub> Produced</u>
10.0	57.6	21.9	2.2	9.7	trace
"	116.2	24.4	2.4	5.7	"
"	174.0	18.0	1.8	4.1	1.9
"	231.0	11.0	1.1	2.5	1.5
"	290	7.0	0.7	4.4	trace
5.0	116.0	23.7	4.8	9.7	trace
10.0	116.5	18.3	1.8	6.1	"
15.0	115.8	40.1	2.6	12.9	"
20.0	116.2	35.6	1.8	16.2	"
10.0	234	7.5	0.7	trace	trace
"	282	20.0	2.0	5.4	"
"	447	12.3	1.2	2.1	"
"	562	109.1	10.9	51.7	"
"	573	14.0	1.4	2.9	"

TABLE III

Decomposition of Hydrogen Cyanide at -196° by Active NitrogenAll quantities in micromoles

<u>Duration of Experiment</u> (min.)	<u>HCN Reactant</u>	<u>HCN Decomposed</u>	<u>HCN Decomposed/min.</u>	<u>C<sub>2</sub>N<sub>2</sub> Produced</u>
10.0	58.6	23.6	2.4	1.4
"	115.1	36.0	3.6	6.8
"	176.0	41.5	4.2	5.1
"	230.5	45.5	4.6	4.7
"	345.0	46.0	4.6	6.1
5.0	174.0	24.0	4.8	2.4
10.0	173.5	49.5	5.0	5.0
15.0	174.0	46.5	3.1	2.9
20.0	174.0	54.5	3.6	2.2
30.0	174.5	59.5	2.0	1.5

Figure 11

Relation between Decomposition Rate at  $-196^{\circ}$   
and

Initial Amount of Reactant for  
Hydrogen Cyanide and Acetylene

O - HCN

■ -  $C_2H_2$

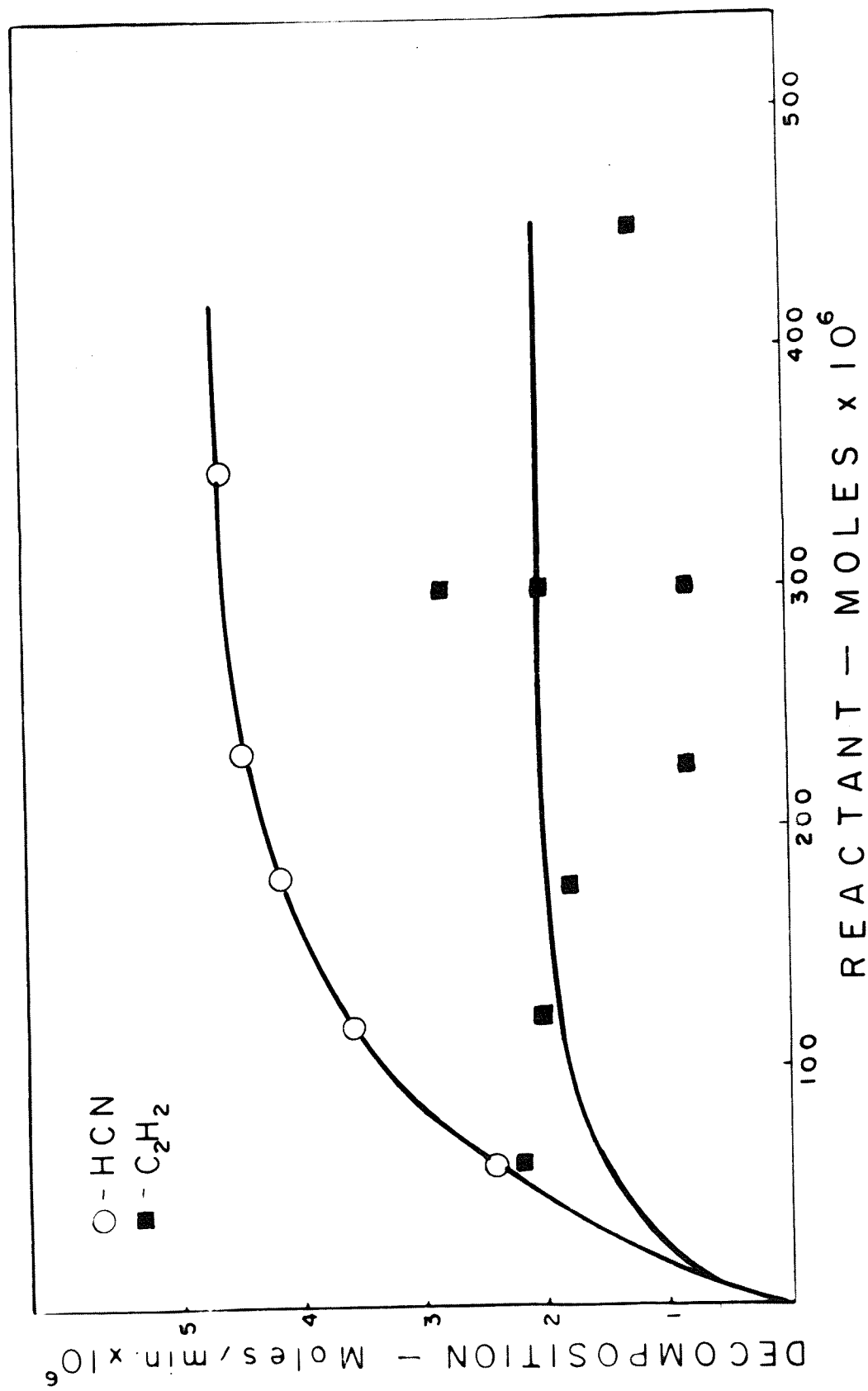


TABLE IV

Decomposition of Ethylene at -196° by Active NitrogenAll quantities in micromoles

<u>Duration of Experiment (min.)</u>	<u>C<sub>2</sub>H<sub>4</sub> Reactant</u>	<u>C<sub>2</sub>H<sub>4</sub> Decomposed</u>	<u>C<sub>2</sub>H<sub>4</sub> Decomposed</u>	<u>C<sub>2</sub>H<sub>4</sub> Decomposed/min.</u>	<u>HCN Produced</u>	<u>NH<sub>3</sub> Produced</u>
5.0	122.7	24.8	5.0	7.9	0.8	
10.0	125.7	56.2	5.6	16.9	1.1	
10.0	124.3	51.8	5.2	18.4	1.1	
15.0	126.2	41.0	2.7	16.1	1.6	
15.0	123.0	39.0	2.6	15.9	2.2	
15.0	125.2	32.2	2.1	13.4	1.2	
20.0	124.1	48.1	2.4	23.1	2.3	
30.0	124.2	61.0	2.0	24.6	2.7	
40.0	122.8	86.7	2.2	36.6	3.3	
5.0	122.7	24.8	5.0	7.9	0.8	
"	155.0	130	26.0	35.1	5.0	
"	308.2	130	26.0	56.5	8.5	
"	449.0	75.2	15.0	29.5	4.6	
"	450.0	151	30.2	62.5	9.0	
"	632.8	159	31.8	64.0	13.0	

the molecular nitrogen flow rate was  $6.5 \times 10^{-3}$  mole/min. corresponding to a reaction pressure of 1.61 mm. A considerable amount of ammonia together with a small amount of hydrazine were formed when nitrogen and hydrogen were passed through the discharge without any reactant. When this active stream was passed over solid ethylene at  $-196^{\circ}$ , ammonia, hydrogen cyanide, butene, hydrazine, and a gaseous product with the vapor pressure of ethylenimine were found.

In one experiment where 440 micromoles of ethylene were used only 8.5 micromoles of ethylenimine were produced. The maximum rate of production of ethylenimine was in all experiments less than 2 micromoles/min. At discharge times in excess of five minutes the yield was considerably less than 2 micromoles/min. presumably because the ethylenimine can itself react. Again, however, due to the difficulty of separating the imine from ammonia and hydrogen cyanide and the small yields obtained, a definite spectral identification could not be made.

An interesting observation made in the ethylene-active nitrogen work was that the extent of reaction with ethylene changed when the volume and shape of the reaction chamber was altered. Table V gives the rate of destruction of ethylene in three different reaction chambers. The importance of reaction vessel shape and size has been noted

TABLE VRate of Destruction of Ethylene at 25° inDifferent Reaction VesselsAll Quantities in micromoles/min.

<u>Reaction Chamber</u>	<u>C<sub>2</sub>H<sub>4</sub> Decomposed</u>	<u>HCN Produced</u>	<u>NH<sub>3</sub> Produced</u>
16 mm (o.d.) cylinder	62.2	67.0	8.5
25 cc. sphere	155	130	7.0
250 cc. sphere	210	252	6.1

by other workers (91, 92), and it appears that the effect is not simply a surface phenomenon.

#### Reaction of Active Nitrogen with Nitrous Oxide

The reaction of nitric oxide with active nitrogen was done at  $-196^{\circ}$  and at  $-211^{\circ}$  and in each case the amount of reactant decomposed was about 2 micromoles/min. when the discharge was run for 5 minutes over 250 micromoles of nitric oxide. No other gaseous product was produced. Nitrous oxide, however, showed surprising reactivity but with little or no nitric oxide formation. Table VI lists the results of a time study of the reaction of active nitrogen with nitrous oxide at  $-196^{\circ}$ . The maximum rate of destruction of nitrous oxide was found to be about 12 micromole/min.

Nitrous oxide was also reacted in the gas phase at  $25^{\circ}$  in a 16 mm. (o.d.) cylindrical reaction chamber. Table VII gives the results for the rate of destruction of nitrous oxide with variation of flow rate at  $25^{\circ}$ .

A similar study of the reaction of active nitrogen with carbon dioxide was attempted but, under the above experimental conditions, no reaction was observed.



TABLE VIReaction of Active Nitrogen With Nitrous Oxide at -196°All quantities in micromoles

<u>Duration of Reaction</u> (min.)	<u>N<sub>2</sub>O Reactant</u>	<u>N<sub>2</sub>O Decomposed</u>	<u>N<sub>2</sub>O Decomposed/min.</u>
2.5	167.5	28.5	11.4
5.0	167.5	49.5	9.9
7.5	170.0	63.0	8.4
10.0	168.2	83.0	8.3
20.0	167.1	157.1	7.9
10.0	348	92.3	9.2
10.0	265	105.5	10.5
10.0	492	128.0	12.8
5.0	148	28	5.6
5.0	213	40	8.0
5.0	290	58	11.6
5.0	328	50	10.0
5.0	220	44	8.8

### Reaction of Active Nitrogen with Ammonia

In the reaction of active nitrogen with ammonia at  $-196^{\circ}$ , the yellow nitrogen afterglow was replaced by an intense blue reaction flame over the solid ammonia deposit. When the discharge was turned off the blue luminescence disappeared immediately. The results of many experiments indicated that the reaction was extremely dependent on the condition of the walls, the amount of reactant and the surface area of the reactant. For example, there was a three-fold decrease in the extent of reaction when the deposit was just below the level of liquid nitrogen as compared with experiments in which the ammonia was deposited at the level of liquid nitrogen in the surrounding dewar vessel. The extent of decomposition of ammonia varied with the amount of reactant as shown in Table VIII.

When constant quantities of ammonia were used the decomposition showed a regular time dependency. The results for two different initial quantities of ammonia are recorded in Table IX.

Hydrazine was identified by its vapour pressure, infrared analysis, and the identification of ammonia among the products of its decomposition. The potassium iodate carbon tetrachloride test also was used but with limited success.

TABLE VIIRate of Destruction of Nitrous Oxide at 25°All quantities in micromoles

<u>Duration of Experiment</u> (min.)	<u>N<sub>2</sub>O Reactant</u>	<u>N<sub>2</sub>O Decomposed</u>	<u>N<sub>2</sub>O Decomposed/min.</u>	<u>NO Produced</u>
5.0	187	37.4	7.5	2.9
5.0	191	57.8	11.6	trace
5.0	386	59.3	11.8	3.2
2.5	341	39.0	15.6	2.5
2.5	214	40.5	16.2	2.9
2.5	186	38.0	15.2	2.9
4.0	219	39.7	9.9	2.4
* 4.0	214	24.8	6.2	nil

\* This reaction was carried out at -90°

TABLE VIIIDecomposition of Ammonia at -196° by Active NitrogenDuration of experiments 5.0 min.All quantities in micromoles

<u>NH<sub>3</sub> Reactant</u>	<u>NH<sub>3</sub> Decomposed</u>	<u>NH<sub>3</sub> Decomposed/min.</u>	<u>N<sub>2</sub>H<sub>4</sub> Produced</u>
37.8	8.4	1.7	2.4
78.0	11.6	2.3	2.6
117	20.4	4.1	14.4
152	14.0	2.8	2.5
192	17.5	3.5	4.2

TABLE IXDecomposition of Ammonia at -196° by Active NitrogenAll quantities in micromoles

<u>Duration of Experiment</u>	<u>NH<sub>3</sub> Reactant</u>	<u>NH<sub>3</sub> Decomposed</u>	<u>NH<sub>3</sub> Decomposed/min.</u>	<u>N<sub>2</sub>H<sub>4</sub> Produced</u>
2.5(min.)	63.0	6.6	2.6	4.5
5.0	62.4	18.6	3.7	7.8
5.0	62.6	12.4	2.5	2.0
7.5	63.2	28.4	3.8	1.7
7.5	61.8	16.2	2.2	5.0
10.0	62.6	18.3	1.8	1.7
10.0	63.2	17.5	1.8	1.3
15.0	63.5	28.0	1.9	1.6
20.0	62.3	43.9	2.2	0.5
2.5	188.2	37.7	15.1	3.9
5.0	186.3	48.1	9.6	15.8
7.5	186.3	70.1	9.3	5.6
10.0	187.1	87.8	8.8	6.3
15.0	187.3	111.6	7.4	4.5
20.0	186.3	117.9	5.9	4.0

The hydrazine production goes through a maximum, thus indicating that the hydrazine is produced and subsequently destroyed by active nitrogen. This was verified by reacting active nitrogen with hydrazine at  $-196^{\circ}$ . Ammonia was produced but the rate of decomposition of hydrazine, on the basis of ammonia produced, was not significantly greater than the rate of decomposition of ammonia, indicating that the weak nitrogen-nitrogen bond probably plays no preferentially important part in the reaction scheme. Hydrogen atoms failed to decompose ammonia at  $-196^{\circ}$  but reacted with hydrazine to yield ammonia to about the same extent as did active nitrogen.

On the basis of a nitrogen atom flow rate of  $2.5 \times 10^{-4}$  mole/min. between 1 and 15% of the available nitrogen atoms lead to ammonia destruction. In two successive experiments in a 16 mm. cylindrical reaction chamber, one at  $-196^{\circ}$  and the other at  $25^{\circ}$ , the rates of destruction of ammonia were  $15.1 \times 10^{-6}$  mole/min. and  $12.7 \times 10^{-6}$  mole/min. respectively. For the experiment at  $25^{\circ}$  the products were trapped six inches below the entry position of ammonia into the active nitrogen stream. The gas phase reaction and the low temperature solid reaction must therefore occur at similar rates in such a system.

It was found that the position of solid reactant surface, as in the ethylene reaction, in relation

to the level of liquid nitrogen in the surrounding dewar, had a marked influence on the extent of decomposition. When the ammonia was deposited six inches below the level of the liquid nitrogen surface the rate of decomposition was  $2.6 \times 10^{-6}$  mole/min., but when the reactant surface was just at the level of the liquid nitrogen the rate increased to  $8.2 \times 10^{-6}$  mole/min. With the reactant surface diffusely spread over six inches of the 8 mm. reaction tube, the rate was found to be  $7.4 \times 10^{-6}$  mole/min. There was no polymer formation and the reaction chamber appeared to need no conditioning.

#### Reaction of Active Nitrogen with Water

Water was reacted with active nitrogen produced in an argon-nitrogen discharge system. With the flow rate of water estimated at about  $15 \times 10^{-6}$  mole/min. a reaction pressure of 1.42 mm. and a nitrogen flow rate of  $36.8 \times 10^{-6}$  mole/min. ammonia was found to be the principal product produced at  $1.4 \times 10^{-6}$  mole/min. Smaller amounts of nitrous oxide were also formed. Both ammonia and nitrous oxide were identified by their infrared spectra.

Unfortunately it was found that ammonia could not be completely recovered from the excess reactant and subsequently, reproducible results were unattainable. A sufficient number of experiments were done, however, to

indicate that a decrease of flow rate of water resulted in a decrease of rate of production of ammonia. The rate of production of nitrous oxide appeared to be relatively constant.

Some preliminary results of the reaction of water with active nitrogen, produced from a pure nitrogen discharge, are given in Table X. The reaction pressure was 2.2 mm., the molecular nitrogen flow rate  $6.4 \times 10^{-3}$  and the nitrogen atom flow rate was about  $2.5 \times 10^{-4}$  mole/min. Although the results were difficult to reproduce because of the nature of the reactant and the difficulty of controlling its flow rates, it is evident that the reaction of water with active nitrogen, produced from a condensed discharge through nitrogen, is temperature dependent. Ammonia was not found as a product under these conditions.

Of particular interest in the water-active nitrogen reaction was the production of a white solid. It was thought that the solid, soluble in acetone, might be hydroxylamine, however, a proton magnetic resonance spectrum proved that the unknown product was not hydroxylamine, but that it did contain hydrogen. This white solid could be the NOH polymer obtained by Serewicz and Noyes (105) in their photolysis study of ammonia in the presence of nitric oxide.



TABLE XReaction of Active Nitrogen with Water at 230°Quantities in micromoles/min.

<u>Duration of Experiment</u> (min.)	<u>H<sub>2</sub>O Reactant</u>	<u>N<sub>2</sub>O Produced</u>
10.0	2.0	1.4
10.0	4.5	4.5
4.0	45	30.1
1.0	190	15.5
1.0	8000	20.9
* 1.0	135	8.6
** 20.0	135	0.3

\* Reaction temperature 140°

\*\* Reaction temperature 27°

The flow rate of water was estimated by weighing the water reservoir before and after each experiment. The measurement of excess water trapped in the product trap was not attempted.

#### Reaction of Active Nitrogen with Formamide

For the reaction of active nitrogen with formamide at  $-196^{\circ}$ , the products were predominantly nitrous oxide, water, and a white solid, with smaller amounts of ammonia and hydrogen cyanide. Nitrous oxide was identified by its infrared spectrum, water by its proton resonance spectrum, and the ammonia and hydrogen cyanide were identified by their vapour pressures. The infrared spectrum of the white solid in a potassium bromide pellet indicated that  $C=O$  ( $1700\text{ cm}^{-1}$ ),  $=C-N=O$  ( $1450\text{ cm}^{-1}$ ),  $CH$  ( $3100\text{ cm}^{-1}$  and  $1180\text{ cm}^{-1}$ ), and  $OH$  ( $3400\text{ cm}^{-1}$ ) groupings were present in the solid.

When a 500 cc bulb was used as the reaction vessel nitrous oxide and water were the principal products at low formamide flow rates but at higher flow rates of formamide hydrogen cyanide and water became the principal products. Table XI shows some preliminary results of the formamide-active nitrogen reaction. The excess formamide was not measured.

TABLE XI

Reaction of Active Nitrogen with FormamideAll quantities in micromoles/min.

<u>Reaction Temperature</u>	<u>Reactant</u>	<u>N<sub>2</sub>O Produced</u>	<u>HCN Produced</u>	<u>NH<sub>3</sub> Produced</u>	<u>H<sub>2</sub>O Produced</u>
60°	140	4.7	2.2	1.2	1.7
81°	51.2	6.9	0.9	0.3	19.3
98°	120	18.0	3.1	nil	10.2
95°	148	5.2	5.1	1.6	4.4
95°	478	17.2	56.5	12.9	21.6
97°	1500	20.8	222	1.8	170
160°	117	15.1	trace	nil	trace
230°	3040	52.5	371.4	nil	≈200

### Reaction of Active Nitrogen with Phosphine

The reaction of active nitrogen with phosphine at  $-196^{\circ}$  proved to be considerably different than the gas phase reaction conducted by Wiles and Winkler (65). Products of the reaction were ammonia, biphosphine, hydrazine, a white solid and an unknown substance the vapour pressure of which was between that of biphosphine and hydrazine. This substance is believed to be  $\text{PH}_2\text{NH}_2$ . Large quantities of the white solid were deposited in the reaction chamber but each of the gaseous products were obtained in small yields (between one and five micromoles) in a ten minute reaction period.

When the white solid was heated, considerable amounts of gas were evolved and a much smaller white residue, which was insoluble in acid, base, and the usual organic solvents, and which was stable to at least  $600^{\circ}\text{C}$ , remained. Analysis of the gases evolved showed that small amounts of phosphine, biphosphine, hydrazine and probably  $\text{NH}_2\text{PH}_2$  were present, together with a large amount of ammonia. In one experiment 70 micromoles of phosphine were decomposed and 40 micromoles of ammonia were found associated in the initial white solid product. This corresponds to about 60% conversion of phosphine to ammonia.

Attempts to prepare and separate larger quantities of the substance contended to be  $\text{PH}_2\text{NH}_2$ , proved unsuccessful. Mixtures of ammonia and phosphine were condensed simultaneously and used as a reactant surface at  $-196^\circ$  for active nitrogen, but only small amounts of hydrazine and biphosphine were obtained, in addition to a large amount of polymer deposited in the reaction chamber. Phosphine and ammonia were identified by infrared analysis and the other products were identified only by their vapour pressure,

## DISCUSSION

## DISCUSSION

Originally the purpose of this work was to demonstrate the importance of ammonia production from hydrocarbon-active nitrogen reactions and clearly, the results presented in this thesis show that under some conditions ammonia formation is of prime importance. For purposes of continuity, the results are discussed under the same subheadings as they have been presented.

### Reaction of Active Nitrogen with Simple Hydrocarbons

The increase in the rates of formation of products, demonstrated by the results illustrated in Figure 6, can be attributed to the fact that argon decreases the rate of recombination of nitrogen atoms which effectively increases the nitrogen atom concentration (88). This, however, cannot be the entire explanation, since the nitrogen atom flow rate in the pure nitrogen system was greater than twice the molecular nitrogen flow rate in the nitrogen-argon system. Therefore, it is concluded that ground state atoms do not directly react with hydrocarbons to form ammonia and that a species other than ground state atoms must be responsible for the initial process resulting in ammonia formation.

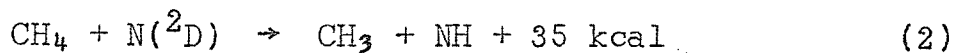
Since blank experiments using only argon in the discharge indicated no hydrocarbon decomposition,

the increase in the rates of formation of products in the argon-nitrogen system, as compared to the pure nitrogen system, must be due to collisions between excited argon atoms and nitrogen atoms and molecules. Excited atoms, which are known to exist in active nitrogen in very small concentrations may very well be present in much larger concentrations in active nitrogen produced in an argon-nitrogen discharge, and may therefore be responsible for the increase in yields of hydrogen cyanide and ammonia.

Since ammonia is formed as a product in the gas phase reaction of active nitrogen with acetylene in a nitrogen-argon system, it seems very likely that one of the fundamental processes in active nitrogen-hydrocarbon reactions in this type of system, is a hydrogen atom abstraction to form an imine radical. The reaction (a)



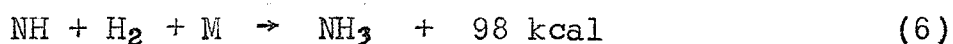
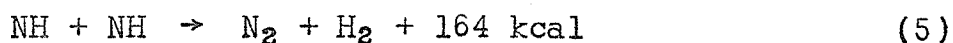
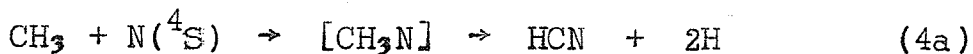
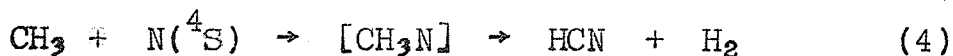
has a minimum activation energy of 20 kcal for ground state nitrogen atoms. It therefore becomes necessary to assume that either excited nitrogen atoms or molecules are responsible for the initial reaction. If  $^2\text{D}$  or  $^2\text{P}$  excited atoms (33, 34) were produced in large concentrations they could react with methane by the reaction



(a) See Appendix 1 for energy values.

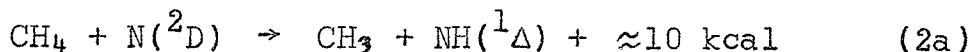


The products of the overall reaction can then be accounted for in the following manner:



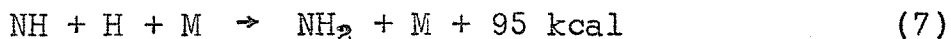
The heat of reaction for reaction (2) is based on the formation of a ground state NH radical. With increase in concentration of NH radicals reaction (5) would be favoured over reaction (6). The fact that reactions (5) and (6) are competitive probably results in the observed constancy of ammonia production. According to the preceding mechanism, the hydrogen yield would be at least as great as that of hydrogen cyanide, which is always greater than the yield of ammonia.

If the NH radicals are produced in the ground state ( $^3\Sigma^-$ ) then reaction (6) does not conserve spin and must be considered to be very slow. The imine radical may also be produced in the  $^1\Sigma^+$  or  $^1\Delta$  states which have the same electronic configuration as the  $^3\Sigma^-$  state (106). Reaction (2) could then be written



Production of the  $\text{NH}(^1\Sigma^+)$  radical would probably render reaction (2) endothermic (107).

An alternative mode of formation of ammonia by way of ground state imine radicals could occur by the reactions



In considering the results shown in Figures 6 and 8, the initial reaction,



where  $[\text{CH}_4\text{N}]$  is an associated complex, undoubtedly also occurs (61). In a nitrogen discharge system, reaction (9) would be the predominant first step leading to the observed high ratio of hydrogen cyanide to ammonia production. The small amounts of ammonia produced in this system may be considered to be the result of hydrogen-nitrogen atom recombination reactions.

For the nitrogen-argon discharge system, however, reactions (2) and (9) would become competitive since the concentration of excited species is probably greatly increased. This would result in the increased rate of production of ammonia and the decrease in the ratio of hydrogen cyanide to ammonia production shown in Figure 6.

Reaction (2), as suggested by Figure 7, would also be favoured with decrease in molecular nitrogen flow rate. Presumably with lower molecular flow rates the nitrogen atom to molecule ratio in the system would

increase as would the excited to ground state atom ratio. For example when flow rates of molecular nitrogen of about one micromole/min. were used in a nitrogen-argon discharge about 40% of the nitrogen appeared in the form of ammonia and hydrogen cyanide. Under these conditions reaction (2) would certainly predominate since it appears that a high percentage of the nitrogen is in the form of atoms. In the case of the pure nitrogen discharge, the direct attack of ground state nitrogen atoms on carbon occurs perhaps almost exclusively, as suggested by Winkler<sup>(64)</sup>. Thus all molecular nitrogen concentrations intermediate with the pure nitrogen system and the nitrogen-argon system ( $N_2$  flow of 1 micromole/min.) would yield products depending on a different degree of occurrence of reactions (2) and (9).

Perhaps the best evidence for the existence of these simultaneous processes is the results illustrated in Figure 8. It is difficult to visualize a single process which would lead to the formation of ammonia and hydrogen cyanide and which would be pressure dependent only with respect to hydrogen cyanide. Nitrogen atom concentrations have been observed to exhibit a maximum with respect to pressure (88). The absence of a maximum in the ammonia production immediately suggests that ground state atoms are responsible only for the formation

of hydrogen cyanide while another species, less pressure dependent over the range studied, is responsible for the formation of both hydrogen cyanide and ammonia. The reaction time is also pressure dependent and may have some effect on the rates of production of products. Spectroscopic measurements of atom and excited molecule concentrations as a function of pressure in an argon-nitrogen discharge system could resolve this hypothesis but the very small concentrations of the species involved would, at present, make a study of this kind exceedingly difficult.

If hydrogen atom abstraction was responsible for the formation of imine radicals and subsequently ammonia, the rate of production of ammonia would be expected to exhibit some dependence on the number of hydrogen atoms in the reactant molecule. The results shown in Figure 9 indicate that no such dependence exists. More work of this kind, however, would have to be done before any definite conclusions could be drawn. Particular attention would have to be given to the determination of whether or not the constancy of ammonia production is fortuitous.

Reaction (3) must be postulated to account for the trace amounts of ethane found in the present work. Reactions (4) and (4a) explain the formation of hydrogen cyanide and hydrogen atoms and molecules. They occur

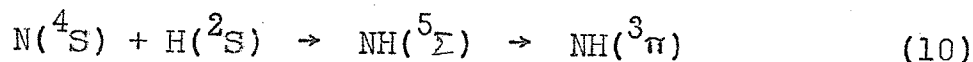
much more readily than reaction (3) because the nitrogen atom concentration is in excess (hydrogen cyanide production increases with increasing flow rate of hydrocarbon). The minute quantities of ethane formed are, of course, partly due to the fact that ethane reacts with active nitrogen somewhat faster than does methane.

If the production of hydrocarbon radicals by reaction (2) is indeed significant then reactions (4) and (4a) contribute more to the production of hydrogen cyanide than reaction (9), since the reaction of nitrogen ( $^4S$ ) atoms with free radicals is known to be faster than the nitrogen atom reaction with the parent hydrocarbon (64).

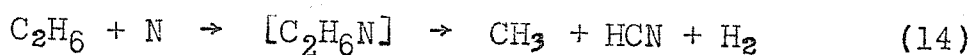
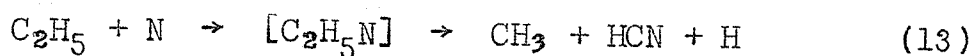
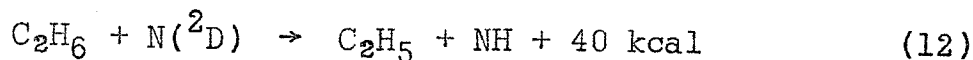
Reactions (5) and (6) constitute the most direct path for ammonia formation but, as mentioned above, reaction (6) does not conserve spin for the  $^3\Sigma^-$  ground state of NH and therefore would be very slow. The alternative mode of formation utilizing  $NH(^3\Sigma^-)$  radicals given by reactions (7) and (8) is much more acceptable although an extra step is involved. In view of the results of Gartaganis and Winkler (61) it would seem that reaction (4a) predominates over reaction (4), thus supplying a high hydrogen atom concentration which would be necessary for ammonia production by reactions (7) and (8).

Ammonia could also be formed to a smaller extent by recombination of nitrogen and hydrogen atoms

by the reactions



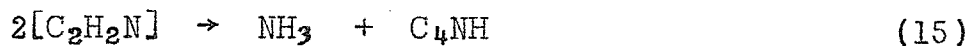
where  $\text{NH}_3^*$  is a metastable intermediate of the ammonia molecule (103), which could be deactivated on collision with a third body. The mechanism for the ethane reaction would involve similar steps.



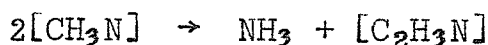
Reactions corresponding to reactions (4) and (9), in the acetylene-active nitrogen reaction, unfortunately cannot be written. This of course would mean that the hydrogen produced in reaction (5) is the only hydrogen available for production of ammonia. Thus the small differences in the rates of formation of ammonia shown in Figures 6 and 9 would seem to indicate that ammonia production is dependent to a greater extent on reaction (5) than on the hydrogen atom concentration in the system.

Formation of an imine radical is not entirely necessary in the production of ammonia even in the acetylene reaction. A complex of the type  $[\text{C}_2\text{H}_2\text{N}]$  might, on interaction with itself, yield ammonia in a one-step reaction without intervention of the imine radical. The nitrogen atom, however, is far removed from the hydrogen

atoms and the reaction



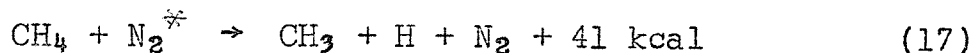
seems very unlikely if the radical models are considered. If reactions of this type did occur to a significant extent it might not be necessary to assume hydrogen atom abstraction. Radical reactions of the type



may occur in the methane-active nitrogen reaction but certainly only to a small extent since the lifetime of the  $[\text{CH}_3\text{N}]$  radical would be very short.

It may well be that not only are excited atoms produced by collision with excited argon atoms but excited nitrogen molecules may be formed which could, on collision with hydrocarbon molecules, produce hydrogen cyanide and ammonia, without the primary formation of an imine radical.

The  $\text{A}^3\Sigma^+ \text{u}^+$  state of the nitrogen molecule, frequently suggested as the "second reactive species in active nitrogen" (92, 108), may react with methane in the following manner:

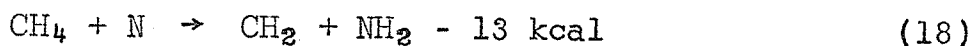


Ammonia and hydrogen cyanide could then be produced by reactions (10, 11) and (4, 4a). In a discharge of pure nitrogen, where reasonably large concentrations of  $\text{A}^3\Sigma^+ \text{u}^+$  molecules are known to exist, this method of attack is probably quite significant. For low concentrations

of molecular nitrogen in an argon discharge, however, since much of the nitrogen appears in the form of ammonia and hydrogen cyanide, reaction (2) probably would occur more frequently than reaction (17).

Excited atom reactions would be expected to have little if any temperature dependency. Consequently, the fact that methane reacted only slightly with active nitrogen from an argon-nitrogen system at  $-196^{\circ}$  opposes the hypothesis of excited species in this system. This fact, however, cannot be construed as valid evidence against the proposed mechanism since these experiments were performed in a small cylindrical reaction chamber rather than in a large sphere and at a much greater distance from the discharge.

Another possibility for the mechanism of formation of ammonia is that the amine, instead of the imine radical, may be produced in the first step as suggested by Dewhurst and Cooper (69). Thus the reaction



may occur, but in view of its endothermicity and the results of the reactions of active nitrogen with acetylene and water, it is difficult to arrive at a mechanism based on reaction (18), which would be consistent with the observations.



### Reaction of Active Nitrogen with Nitrous Oxide

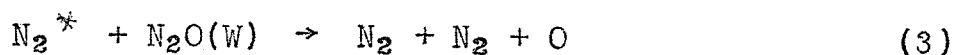
Kistiakowsky has reported (73) that active nitrogen does not react with nitrous oxide in the temperature range 25° to 280°C. In the reactions of active nitrogen with nitric oxide and nitrous oxide in the present investigation, nitric oxide did not decompose readily at -196° or -211° but nitrous oxide did decompose at -196°C. The failure to find nitric oxide as a product would appear to rule out the reaction



as the principal mode of decomposition. Recombination of nitrogen atoms on the nitrous oxide surface by the reaction



could cause the decomposition, but since nitric oxide showed comparatively little reactivity (2 micromole/min.), it is very likely that this mode of decomposition is not significant. The most likely active species responsible for the reaction is the excited nitrogen molecule, probably in the  $A^3\Sigma_u^+$  state, since, in an active nitrogen stream produced from pure nitrogen, ground state atoms and excited molecules are essentially the only chemically reactive species present. The decomposition is probably caused by the reactions



The trace of nitric oxide produced may be formed by recombination of nitrogen and oxygen atoms or by the direct decomposition of nitrous oxide.



The reaction



is endothermic and would not be expected to occur at  $-196^\circ$ . Therefore if nitric oxide was produced in the active nitrogen-nitrous oxide reaction it would not undergo decomposition. Thus reaction (3) must be the predominant primary reaction. Both reactions (3) and (6) are exothermic on the basis of a mean bond energy value of 132 kcal./mole in nitrous oxide.

For the reaction of nitrous oxide with active nitrogen at  $25^\circ$  the occurrence of reactions which produced nitric oxide increased. The rate of decomposition at  $25^\circ$ , however, was not significantly greater than the rate at  $-196^\circ$  and, therefore, the reaction likely proceeds by a similar mechanism. It is also possible that the nitrous oxide reaction at  $25^\circ$  takes place almost entirely at the walls and is therefore also a heterogeneous reaction.

Another possible mode of decomposition could be the formation of a complex by the reaction



followed by

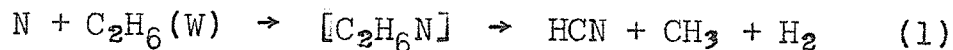


If reaction (8) did occur to any extent nitrous oxide would be expected to be a product of the reaction of active nitrogen with nitric oxide at  $-196^\circ$ . The similarity of the decomposition rates in the heterogeneous and homogeneous reactions and consideration of the reactants and products, lead to the conclusion that an excited molecular species and not nitrogen atoms are responsible for the greater part of decomposition of nitrous oxide by active nitrogen at  $-196^\circ$ . Thus the 12 micromole/min. decomposition of nitrous oxide would be the total of 10 micromoles/min. decomposed by excited molecules and 2 micromoles/min. decomposed via nitrogen atom recombination.

#### Reaction of Active Nitrogen with Simple Hydrocarbons at $-196^\circ$

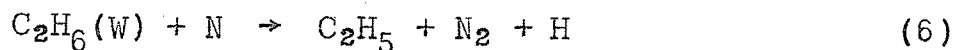
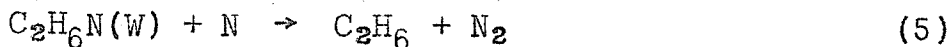
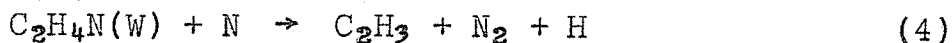
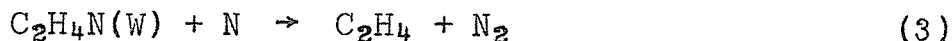
Several fundamental reactions could conceivably be responsible for the production of ammonia and hydrogen cyanide from ethane and ethylene at  $-196^\circ$ . As in the case of nitrous oxide, a small part of the decomposition is due, likely, to nitrogen atom recombination. Ground state nitrogen atoms could react according to the following

reactions.



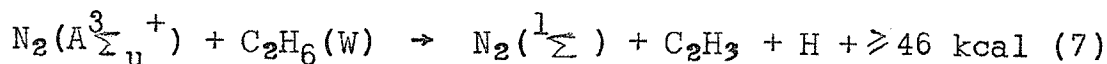
Complex radicals such as  $[\text{C}_2\text{H}_4\text{N}]$  and  $[\text{C}_2\text{H}_6\text{N}]$  would be expected to have some degree of stability at  $-196^\circ$ .

Therefore reactions of the type,

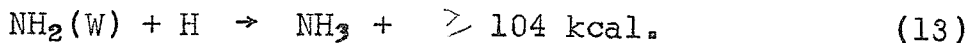
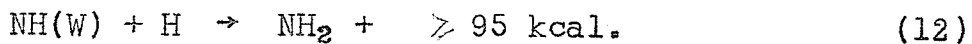
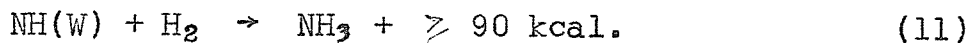
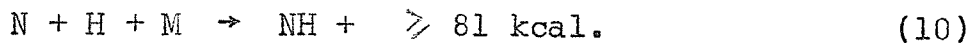


probably occur on the walls producing hydrocarbon radicals and hydrogen atoms. On the assumption that the radicals are sufficiently stable, reactions (3) to (6) will predominate over reactions (1) and (2).

Decomposition by means of  $\text{A}\sum_u^3$  molecules may be represented by the equation



The radicals produced by nitrogen atom recombination and by reaction (7) could then undergo reactions of the type

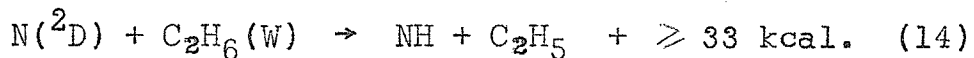


The process represented by reactions (3) to (6) probably accounts for a large percentage of the total decomposition, since the maximum extent of decomposition is greater in the case of ethylene ( $\sim 30$  micromole/min.), and ethane ( $\sim 20$  micromole/min.), than for either nitrous oxide ( $\sim 12$  micromole/min.), or ammonia ( $\sim 10$  micromole/min.). Further, the relative ease of formation and stability of the complexes  $[C_2H_4N]$  and  $[C_2H_6N]$ , likely results in the fact that the maximum extent of decomposition of ethylene is about 50% greater than the maximum extent of decomposition of ethane. This would seem to indicate that the ease of formation and stability of a nitrogen atom-reactant complex determines, to some degree, the extent of decomposition. Complex formation between nitrogen atoms and hydrogen cyanide, acetylene, or nitric oxide would be expected to occur readily. In view of the low reactivity of hydrogen cyanide ( $\sim 4$  micromole/min.), acetylene ( $\sim 2$  micromole/min.), and particularly nitric oxide, a general mechanism which involves reactions based only on the formation and dissociation of nitrogen atom-reactant complexes, appears to be inadequate. Until evidence of the existence of complexes of this nature is obtained, it would seem more reasonable to assume that the decompositions at  $-196^\circ$  are due in part to nitrogen atom recombination ( $\sim 2$  micromole/min.), excited nitrogen

molecules ( $\sim 10$  micromole/min.), and nitrogen atom-reactant complex formation and dissociation.

Reactions (7) and (8) need not occur at the wall and in fact must occur to some extent in the gas phase because polymer deposits were observed downstream from the original reactant surface. For this to occur, radical fragments would have to escape from the reactant surface and undergo reaction in the gas phase, or at the wall downstream from the reactant surface. Radicals which escape from the reactant surface would of course be swept downstream by the nitrogen flow.

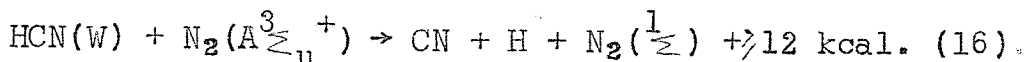
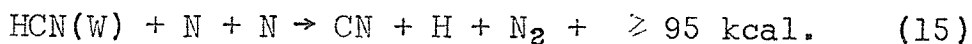
In view of the results of Tanaka et al (33) the reaction



probably occurs to a small extent in this system, but the low concentration of excited atoms in active nitrogen precludes their importance. Formation of ammonia under these conditions likely does not occur via primary formation of NH radicals, as postulated for the methane-active nitrogen reaction in an argon-nitrogen system. The most probable mode of production of ammonia would be that represented by equations (10) to (13), but complex radicals of the type  $[\text{C}_2\text{H}_4\text{N}]$  might, on interaction with another radical, yield ammonia in a one-step rearrangement process thereby eliminating the necessity for successive atom recombination reactions.

Of the reactive species available in sufficient concentrations, metastable  $A^3\Sigma_u^+$  nitrogen molecules seem to be the only species, in addition to ground state nitrogen atoms, capable of effecting the decomposition of the hydrocarbon molecules at  $-196^\circ\text{C}$ . If  $A^3\Sigma_u^+$  nitrogen molecules are indeed entirely responsible for the decomposition of ammonia (92) and nitrous oxide, then the rate of decomposition of the hydrocarbons due to  $A^3\Sigma_u^+$  should be approximately 12 micromoles/min. under the conditions specified in the results. Decomposition over and above this value would then necessarily be the result of reactions corresponding to reactions (4) and (6). Decompositions of ethane and ethylene are apparently not propagated by hydrocarbon radical attack, since no hydrocarbon products were obtained.

Some additional support for the view that excited nitrogen molecules are the species in active nitrogen responsible for a part of the decompositions observed, is found in the results obtained for the hydrogen cyanide-active nitrogen reaction. Since cyanogen was found as a product, CN radicals must have been formed from hydrogen cyanide. Thus, either reaction (15) or (16) should occur.



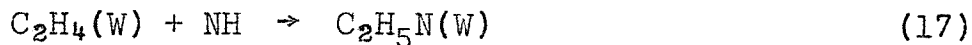
From a comparison of the maximum rates of decomposition of the gases studied reaction (16) certainly would be favoured on the basis of relatively low reactivity of hydrogen cyanide. The maximum extent of decomposition of all the reactants investigated would not be expected to vary considerably, if nitrogen atom recombination was principally responsible for the observed reaction. If nitrogen atom-reactant complex stabilization is required for decomposition via nitrogen atom recombination, this conclusion would not be entirely valid. Since there is no absolute evidence for complex formation in systems of this type, the mechanism of decompositions induced by active nitrogen at  $-196^{\circ}$  must be considered as tentative.

The absence of ammonia in the products of the active nitrogen-acetylene reaction at  $-196^{\circ}$ , indicates that the fundamental process in these circumstances is not the same as the initial process for the acetylene reaction with active nitrogen in an argon-nitrogen system at  $25^{\circ}$ . It would seem likely that hydrogen atom abstraction does not occur to any significant extent in active nitrogen reactions conducted at  $-196^{\circ}$ . The formation of ammonia from hydrocarbons at  $-196^{\circ}$ , therefore, probably occurs through nitrogen-hydrogen atom recombination. The possibility, however, of primary formation of an amine radical, or of one-step ammonia displacement through radical interaction is greatly enhanced in this system



because of the possibility of formation of relatively stable nitrogen atom-hydrocarbon complexes which could conceivably yield either  $\text{NH}_2$  or ammonia on decomposition.

The possible existence of ethylenimine among the products of decomposition in the ethylene-active nitrogen reaction indicates that imine radicals probably exist in systems of this kind as is suggested by Pannetier et al (102, 103). Ethylenimine could be produced by the reaction



One of the most difficult aspects of these surface reactions at  $-196^\circ$  is the effect of the wall on the reactions. In the case of ammonia no polymer formation occurred and decomposition, although less than when the reactant was at the liquid nitrogen level, was observed even when the reactant surface was well below the liquid nitrogen level. Apparently, as would be expected, the liquid nitrogen cooled active stream is deactivated to some extent.

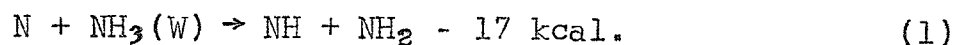
In the case of ethylene, however, the formation of a polymer surface apparently removes this deactivating effect by either preventing atom recombination or catalyzing the reaction. The most plausible explanation is that nitrogen atoms gravitate to the liquid nitrogen cooled wall and easily recombine on a clean glass surface, but

recombine less readily on a polymer surface. This of course is pure conjecture, and before positive proof could be obtained a considerable amount of surface effect studies would have to be done.

#### Reaction of Active Nitrogen with Ammonia

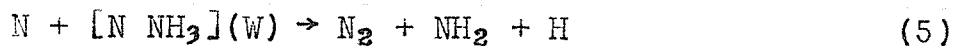
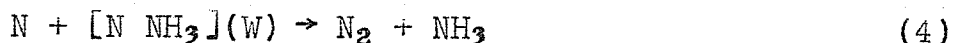
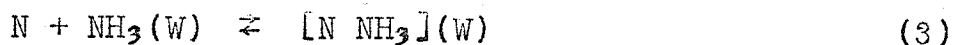
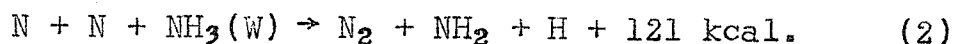
A mechanism similar to that proposed in the explanation of the nitrous oxide reaction may be used to explain the decomposition of ammonia at  $-196^{\circ}$ .

The reaction



can definitely be eliminated since it would have a minimum activation energy of 17 kcal. and would not occur to a significant extent at  $-196^{\circ}$ . This is in agreement with the gas phase reaction (59).

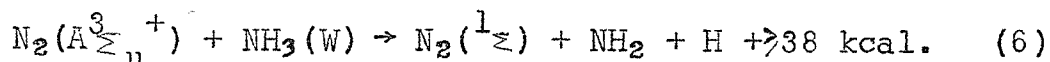
The reactions



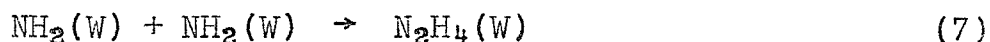
probably occur on the walls where ammonia can be destroyed by the energy of recombination of nitrogen atoms. Reaction (2) would be expected to occur to the same extent as in the nitric oxide reaction. Since ammonia is approximately as reactive as nitrous oxide, reaction (4) probably occurs much more readily than (5) and the overall decomposition

would be slight. The reactivity of hydrogen atoms with ammonia and hydrazine at  $-196^{\circ}$  is consistent with the energetics involved.

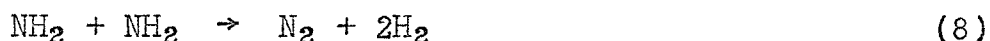
Decomposition induced by excited atoms undoubtedly does not occur to any marked extent because of the low concentration of excited atoms in active nitrogen produced from a pure nitrogen discharge. Metastable  $A^3\Sigma_u^+$  nitrogen molecules, which have been postulated as the species in active nitrogen which is responsible for the destruction of ammonia in the gas phase, however, can account for the major portion of decomposition of ammonia at  $-196^{\circ}$ .



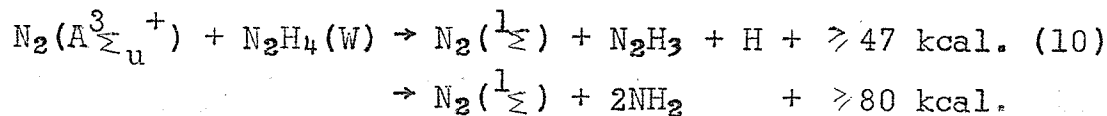
Hydrazine undoubtedly is formed by the recombination of amine radicals on the walls;



but these radicals may also be destroyed by the reactions

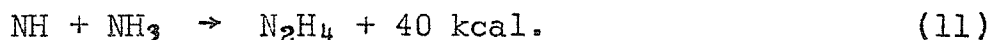


Hydrazine may also undergo decomposition by the reaction



In some cases more hydrazine is produced than that equivalent to one-half of the ammonia decomposed. This would seem to indicate that hydrazine may be formed by some process, other than reaction (7), which incorporates

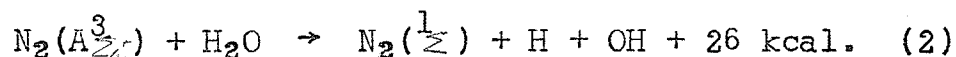
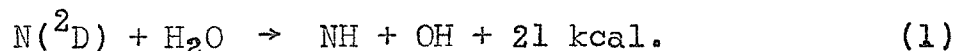
nitrogen from the discharge, possibly by a reaction such as



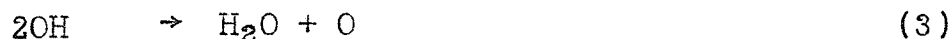
which has been proposed by Pannetier et al (103). The imine radical could be formed by atom recombination and by the small extent of hydrogen atom abstraction caused by excited nitrogen atoms.

#### Reaction of Active Nitrogen with Water

The mode of formation of nitrous oxide and ammonia in the active nitrogen-water reaction in an argon-nitrogen system is most interesting. As in the methane reaction in an argon-nitrogen system at 25°, the initial process is likely initiated by excited atoms or molecules according to equations (1) and (2).

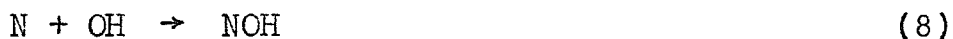


Ammonia may be produced then by imine radical reactions with hydrogen or by nitrogen and hydrogen atom recombination. Nitrous oxide could be produced by the following sequence:



Equations (3) and (4) are necessary for the production of oxygen atoms and nitric oxide which react

with ground state nitrogen atoms by reactions (5), (6) and (7) as suggested by other workers (73, 76, 77). Nitric oxide is known to react very rapidly with nitrogen atoms by reaction (7) and, therefore, reaction (6) probably occurs to an insignificant extent. If the reaction of nitrogen atoms and hydroxyl radicals produced the intermediate NOH (105), the nitrous oxide could form via the reactions



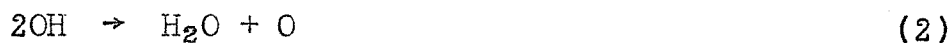
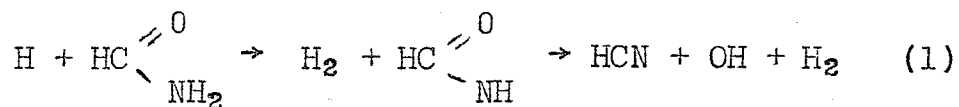
Since ammonia was produced in the water-active nitrogen reaction in an argon-nitrogen system but not in a pure nitrogen system two different mechanisms must occur in the different systems. This may be construed as partial proof of the excited atom mechanism proposed for the methane-active nitrogen reaction which takes place in an argon-nitrogen system.

In a pure nitrogen discharge system, the production of nitrous oxide in the water-active nitrogen reaction was temperature dependent. Reaction (1) would contribute little to the destruction of water in this system, but reaction (2) could proceed quite readily. If reaction (2) was the primary reaction, either reaction (8) or (9) would have to be temperature dependent and therefore rate controlling, since reaction (2) presumably would have a very low activation energy.

The temperature dependence of active nitrogen reactions, as suggested by Wright et al (92), may be peculiar to spherical reaction flasks. Therefore, this reaction would probably have to be conducted in both a cylindrical and a spherical reaction chamber, over a wide range of temperature, before the mechanism and activation energy could be known with any degree of certainty.

#### Reaction of Active Nitrogen with Formamide

Some exploratory work with oxygen containing organic molecules was done with the aim of elucidating the mode of formation of nitrous oxide. The most likely reactant, formaldehyde, unfortunately could not be used because of its tendency to polymerize. Formamide was then chosen as a reactant principally because results of the reaction of hydrogen atoms with formamide were known (109). The mechanism suggested for this reaction was,

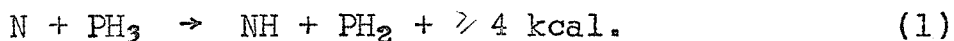


Reaction (2) was postulated since no peroxides were found and (1) was considered the only possible first step because the hydrogen cyanide produced was equal to the hydrogen atom concentration.

Since considerable nitrous oxide and water formation was observed in the reaction of active nitrogen with formamide at low flow rates of formamide, the existence of oxygen atoms and hydroxyl radicals in the reaction mixture is indicated. Although the reaction is of interest because of the possibility of determining which hydrogen atoms are preferentially abstracted or displaced, the nature of the reactant and the complexity of the products make it a difficult system to study. A mass spectrometric study with labeled formamide would solve some of the difficulties of analysis and would enable clarification of the mechanism.

#### Reaction of Active Nitrogen with Phosphine

For the reaction of active nitrogen with phosphine the primary reaction, as suggested by Wiles and Winkler (65), is likely the reaction



The radicals produced would be expected to have some degree of stability and could rearrange to form a stable nitrogen-phosphorus hydride which on heating could decompose into a phosphorus hydride and ammonia.

The small amounts of gaseous hydrides could be accounted for by the following scheme.



The composition of the decomposable and stable white solids would have to be known before a complete mechanism could be contemplated. The gaseous hydrides are quite probably the result of hydrogen atom abstraction reactions, followed by radical recombinations. Decomposition induced by atom recombination, excited molecules, and nitrogen atom-reactant complex formation could also occur, but a more detailed study would have to be undertaken to determine which processes are principally responsible for the observed reaction.



## SUMMARY

The reactions of methane, ethane, and acetylene with active nitrogen, produced in an argon-nitrogen discharge were studied in an unheated reaction vessel. Hydrogen cyanide and ammonia were the principal products. Results of these reactions, together with the results of the preliminary investigation of the reaction of active nitrogen with water, indicate that hydrogen atom abstraction by nitrogen atoms probably occurs. It is concluded that excited argon atoms increased the chemical reactivity of active nitrogen by augmenting the percentage of excited species in active nitrogen.

Methane, ethane, ethylene, acetylene, hydrogen cyanide, nitrous oxide, nitric oxide and ammonia were reacted at  $-196^{\circ}$  with active nitrogen produced from a nitrogen discharge. Methane showed little reactivity but considerable amounts of hydrogen cyanide and ammonia were produced from ethane and ethylene. Some hydrazine was produced in the ammonia reaction. The order of reactivity at  $-196^{\circ}$  with active nitrogen is ethylene > ethane > nitrous oxide > ammonia > hydrogen cyanide > acetylene > nitric oxide. Four different processes have been postulated as responsible for the decompositions observed: (a) nitrogen atom recombination at the reactant surface; (b) energy transfer at the reactant surface from excited nitrogen molecules and (c) from excited nitrogen

atoms; (d) nitrogen atom-reactant complex formation followed by decomposition. The extent to which each mode of decomposition occurs in any particular reaction is not known with any degree of certainty.

APPENDIX

Heats of reaction are based on:

D(N-H) = 81 kcal.	}	M.A.A. Clyne and B.A. Thrush, Proc. Chem. Soc., 227 (1962).
D(NH-H) = 95 kcal.		
D(NH <sub>2</sub> -H) = 104 kcal.	}	M. Swarc, Chem. Revs. <u>47</u> , 75 (1950).
D(NH <sub>2</sub> -NH <sub>2</sub> ) = 60 kcal.		
D(H-N <sub>2</sub> H <sub>3</sub> ) = 95 kcal. -		G.R. Freeman and C.A. Winkler, Can. J. Chem., <u>33</u> , 692 (1955).
D(N <sub>2</sub> ) = 225 kcal. -		J.M. Hendric, J. Chem. Phys. <u>22</u> , 1503 (1954).
N( <sup>2</sup> D) = 55 kcal.	}	"Atomic Energy Levels," Natl. Bur. Standards. Circ. No. 467
N( <sup>2</sup> P) = 82.5 kcal.		
N <sub>2</sub> (A <sub>u</sub> <sup>3+</sup> ) = 142 kcal. -		K.D. Bayes, Can. J. Chem. <u>39</u> , 1074 (1961)
D(HCN) = 130 kcal.	}	Natl. Bur. Standards. Circ. No. 500 (1952). Selected values of chemical thermodynamic properties.
D(N-N-O) = 264 kcal.		
D(CH <sub>3</sub> -H) = 101 kcal.	}	T.L. Cottrell "The Strengths of Chemical Bonds," Sec. Ed. Butterworths, London (1958).
D(CH <sub>2</sub> -H) = 88 kcal.		
D(PH <sub>2</sub> -H) = 77 kcal.		
D(HO-H) = 116 kcal.		
D(NO) = 162 kcal.		

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