REACTIONS OF ACTIVE NITROGEN
WITH
AMMONIA, HYDRAZINE AND METHYLAMINE

FREEMAN

REACTIONS OF ACTIVE NITROGEN WITH AMMONIA, HYDRAZINE AND METHYLAMINE

by

Gordon Russel Freeman, M.A.

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TABLE OF CONTENTS

INTRODUCTION

It is now well established that free radicals play an important part as intermediates in many chemical reactions. However, until 1929 the existence of free radicals was the subject of a vehement controversy. As early as 1834, the possible isolation of alkyl radicals through the action of potassium on their chlorides or iodides was predicted (1). In 1900 Gomberg (2) attempted to prepare hexaphenylethane by the reaction of triphenylchlormethane with metallic magnesium, and obtained an unusually reactive material which he concluded was free triphenylmethyl. However, other chemists denied the existence of free radicals and Richter's textbook "Organic Chemistry" (1915) contains the statement: "The assumption of the existence of radicals, capable of existing alone and playing a special role in molecules, has long been abandoned."

In 1918 Nernst (3) postulated an atomic chain reaction to explain Bodenstein's observation that much more hydrogen chloride was formed during the photolysis of hydrogen-chlorine mixtures than was predicted by Einstein's law of photochemical equivalence (4). Some time later (1925), Taylor suggested that organic chain reactions involving free radicals might occur in a similar way (5), and four years later the classical metallic mirror experiments of Paneth and coworkers (6, 7) demonstrated that free methyl and ethyl radicals are indeed capable of an individual existence. There followed a series of investigations by F.O. Rice and his colleagues which culminated in the suggestion that the majority of organic substances decompose by mechanisms involving free radicals (8), and that free radical mechanisms could be devised which would lead to simple rate laws and to overall activation energies which were much below the C-C bond dissociation energy (9).

Atomic and free radical reactions have been comprehensively reviewed (10 to 15) and soundly integrated into the framework of chemical kinetics, particularly by Steacie, whose new book (15) provides a critical and authoritative treatment of the pertinent literature up to 1954. A brief discussion only of certain hydrogen atom and radical reactions is necessary in this thesis to provide a background for, and to facilitate the discussion of the reactions of active nitrogen.

SOME RELEVANT REACTIONS OF HYDROGEN ATOMS

The reactions of atomic hydrogen have probably been more extensively studied than those of any other atomic species. Several methods have been used to obtain hydrogen atoms in sufficient concentration to permit studies of their reactions.

A relatively high concentration of hydrogen atoms can be produced by the passage of a high voltage electric discharge through hydrogen gas at low pressures in a Wood-Bonhoeffer fast-flow apparatus (16, 17).

In a static system hydrogen atoms can be generated, in low concentration, by the mercury-photosensitized decomposition of molecular hydrogen (18, 19). Mercury vapor is mixed with the gaseous reactants and excited with resonance radiation from a mercury lamp. With hydrogen, the reaction is generally represented as

$$Hg(^3P_1) + H_2 \longrightarrow Hg(^1S_0) + 2H$$

Low concentrations of hydrogen atoms may be produced by dissociation of molecular hydrogen on a hot filament. Le Roy et al (20, 21) modified the method originally described by Langmuir (22, 23) to obtain pressures of atomic hydrogen in the range 10^{-3} to 10^{-2} mm. Hg in a fast flow system.

The photochemical decomposition of hydrogen sulfide (24) has also been used to produce hydrogen atoms in static systems. The decomposition reaction was thought to proceed by:

$$H_2S + h\nu \longrightarrow H + HS$$
$$H + H_2S \longrightarrow H_2 + HS$$

The primary process in the mechanism for hydrogen atom reactions with many saturated organic compounds is generally thought to be abstraction, while the corresponding process with unsaturated compounds is thought to be addition.

Hydrogen Atoms and Methane

Early investigations of this reaction (25 to 27) found methane to be inert to hydrogen atom attack at temperatures up to 183°C. The possibility that a series of reactions which would produce no net change in the chemical constitution of the system, such as

$$H + CH_4 \longrightarrow CH_3 + H_2 \qquad (1)$$
$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (2)$$

was ruled out by an investigation by Geib and Steacie (28) using deuterium atoms. They found no detectable reaction up to 100°C, indicating an activation energy of not less than 11 kcal., if a steric factor of 0.1 was assumed.

From an investigation in which deuterium atoms were produced by mercury photosensitization, Morikawa et al (29) concluded that the reaction chain represented by reactions (1) and (2) became significant at temperatures around 300°C.

Several investigations (15) were consistent with reaction (1) as the initial process, with an activation energy of 13±2 kcal., assuming a steric factor of 0.1.

Majury and Steacie (30) calculated an activation energy of 7.0±1.5 kcal. and a steric factor between 10^{-3} and 10^{-4} for reaction (1), using the measured activation energy for the reverse reaction and known bond dissociation energies of methane and hydrogen.

Recent work by Berlie and Le Roy (31) in the temperature range 99° to 163°C led the authors to conclude that the main reactions are

$$H + CH_4 \longrightarrow CH_3 + H_2 \qquad (1)$$

$$H + CH_3\ (+M) \longrightarrow CH_4\ (+M) \qquad (3)$$

An activation energy of 4.1 kcal. with a steric factor of 10^{-5} was obtained for reaction (1).

Hydrogen Atoms and Ethane

Early experiments with deuterium atoms indicated that there was some doubt concerning the nature of the initial reaction and the mode of methane formation (15). The two main possibilities were

$$C_2H_6 + D \longrightarrow CH_3 + CH_3D \qquad (1)$$

or

$$C_2H_6 + D \longrightarrow C_2H_5 + HD \qquad (2)$$

$$C_2H_5 + D \longrightarrow CH_3 + CH_2D \qquad (3)$$

followed by recombination of methyl radicals with deuterium atoms.

The occurrence of reaction (1) is contrary to the Rice theory (9), because all the Rice mechanisms are based on the idea that reactions of the type

$$R + HX \longrightarrow RH + X$$

occur readily, but that hydrocarbon chain-splitting reactions of the type

$$R + CH_3(CH_2)_nCH_3 \longrightarrow RCH_3 + CH_3(CH_2)_n$$

never occur to an appreciable extent. Rice and Teller (32) also concluded that from the standpoint of the principle of least motion, reaction (2) would occur much more readily than reaction (1).

From measurements of the rate of consumption of hydrogen atoms and of ethane with improved experimental methods, Berlie and Le Roy (33) conclude that the reaction mechanism is

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5 \qquad (1)$$
$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (2)$$
$$H \longrightarrow \tfrac{1}{2}H_2$$
$$H + C_2H_5 \longrightarrow C_2H_6$$
$$H + CH_3 \longrightarrow CH_4$$

They obtained an activation energy of 6.8 kcal. and a steric factor of 4.8×10^{-3} for reaction (1).

Strong evidence for the occurrence of reaction (2) came from Steacie and Parlee's investigation of the hydrogen atom-propane reaction (34, 35), in which the only product at room temperature was methane. At higher temperatures, ethane was produced in increasing amounts. The only possible mechanism which would explain the large amount of methane was

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2$$
$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5$$
$$H + C_2H_5 \longrightarrow 2CH_3$$
$$H + CH_3 \longrightarrow CH_4$$

Work on the reaction of hydrogen atoms with butane (36) led to a similar conclusion.

Thus it appears that reaction of hydrogen atoms with saturated hydrocarbons involves hydrogen abstraction followed by "atomic cracking" of the alkyl radicals to smaller radicals.

Hydrogen Atoms and Ethylene

The reaction of ethylene with hydrogen atoms which were produced by the discharge-tube method was accompanied by chemiluminescence and produced large quantities of ethane, with a little acetylene (37, 38). This suggested that both hydrogenation and dehydrogenation occur, i.e.,

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (1)$$

$$H + C_2H_5 \longrightarrow C_2H_6 \qquad (2)$$

$$H + C_2H_4 \longrightarrow C_2H_3 + H_2 \qquad (3)$$

$$H + C_2H_3 \longrightarrow C_2H_2 + H_2 \qquad (4)$$

The formation of ethane when ethylene and hydrogen atoms are mixed at liquid air temperature (39) points to an activation energy for reaction (1) of less than 5 kcal. (15). Darwent and Roberts (24) obtained a value of 4.1 kcal. The production of acetylene during the reaction at room temperature indicates an activation energy of about 10 kcal. for reaction (3).

When hydrogen was in large excess during the mercury photosensitized reaction, ethane was virtually the sole product (40), but with relatively more ethylene, C_4 hydrocarbons and a liquid of molecular weight about 230 were formed. Some methane was formed in both cases. Reaction (1) was suggested as the initial reaction, followed by

$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H \qquad (5)$$

to produce ethane. Butane could be formed by

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (6)$$

and methane by

$$\left.\begin{array}{l} H + C_2H_5 \longrightarrow 2CH_3 \\ H + CH_3 \longrightarrow CH_4 \end{array}\right. \qquad (7)$$

More recent investigations (41 to 43) have established that, at temperatures below 200°C the mechanism is probably

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (1)$$

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (6)$$

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \qquad (8)$$

while at higher temperatures the additional reactions

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \qquad (5)$$

$$C_4H_9 \longrightarrow CH_3 + C_3H_6 \qquad (9)$$

$$C_4H_9 \longrightarrow C_2H_4 + C_2H_5 \qquad (10)$$

may occur. Activation energies of about 11 kcal. and 1 kcal. have been assigned to reactions (5) and (8) respectively (42).

Hydrogen Atoms and Propylene

The mercury-photosensitized reaction of hydrogen-propylene mixtures produced hexane and propane in the ratio 5:2 as the main products (44). Hydrogen was in sixfold excess over propylene. The reactions considered to be most significant were

$$H + C_3H_6 \longrightarrow C_3H_7 \qquad (1)$$

$$2C_3H_7 \longrightarrow C_6H_{14} \qquad (2)$$

$$H + C_3H_7 \longrightarrow C_3H_8 \qquad (3)$$

$$\text{or} \qquad 2C_3H_7 \longrightarrow C_3H_6 + C_3H_8 \qquad (4)$$

Moore (45) reinvestigated the reaction using a mass spectrometer for product analysis. The only C_6 compound in the products was 2,3-dimethyl butane except for a trace of 2,2-dimethylbutane so reaction (1) appears to produce isopropyl radicals exclusively.

The reaction of propylene with hydrogen atoms from a discharge-tube produced 0.45 mole methane, 0.68 mole ethane, and 0.33 mole propane per mole of propylene reacted, and the amounts were independent of temperature over the range 30 - 250°C (46). The initial step is undoubtedly

$$H + C_3H_6 \longrightarrow C_3H_7 \qquad (1)$$

but the propyl radicals thus formed did not react in the same manner as those produced from propane, at least at room temperature. The reaction mechanism suggested included the participation of "hot radicals", in which the radicals formed by the addition of a hydrogen atom to an olefin retained some of the energy of the reaction, and thus would undergo, at room temperature, reactions which would normally be expected only at high temperatures:

$$H + C_3H_6 \longrightarrow C_3H_7^* \qquad (1)$$

$$C_3H_7^* + H_2 \longrightarrow C_3H_8 + H \qquad (5)$$

$$C_3H_7^* \longrightarrow C_2H_4 + CH_3 \qquad (6)$$

$$H + C_2H_4 \longrightarrow C_2H_5^* \qquad (7)$$

$$C_2H_5^* + H_2 \longrightarrow C_2H_6 + H \qquad (8)$$

An activation energy of 5 kcal. was estimated for reaction (1). This value was also obtained using photolysis of D_2S as a source of atoms (24). Methane formation was attributed to the reactions

$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5$$

$$H + C_2H_5 \longrightarrow 2CH_3$$

$$H + CH_3 \longrightarrow CH_4$$

Hydrogen Atoms and Acetylene

In the presence of acetylene it was found that the recombination of hydrogen atoms was strongly catalysed, heat and light were emitted, but practically all the acetylene was recovered unchanged (26, 37). The reaction of acetylene with deuterium atoms results in the almost complete deuteration of the acetylene (28). Essentially no ethylene was formed. Apparently the acetylene is alternately hydrogenated and dehydrogenated, either by

$$C_2H_2 + H \longrightarrow C_2H + H_2 \qquad (1)$$

$$C_2H + H \longrightarrow C_2H_2 \qquad (2)$$

or

$$C_2H_2 + H \longrightarrow C_2H_3 \qquad (3)$$

$$C_2H_3 + H \longrightarrow C_2H_2 + H_2 \qquad (4)$$

Ethane, butane and a partially hydrogenated polymer were produced in the mercury-photosensitized reaction (47). The rate of hydrogenation increased with increasing temperature in the range 25° - 300°C. It seems necessary for vinyl radicals to be formed before any hydrogenation can occur, and these may be formed by reaction (3) or by reaction (1) followed by

$$C_2H + H_2 \longrightarrow C_2H_3 \qquad (5)$$

Ethyl radicals could then be produced by

$$C_2H_3 + H_2 \longrightarrow C_2H_5 \qquad (6)$$

and recombination and disproportionation of these would produce butane and ethane.

Since hydrogenation reactions were absent with the higher atom concentrations in the discharge tube experiments (26, 28, 37), reactions (2) or (4) were assumed to occur much more readily than reactions (5) or (6).

Dingle and Le Roy (21) assigned an activation energy of about 1.5 kcal. and a steric factor of about 4×10^{-4} to reaction (1) or (3).

Hydrogen Atoms and Ammonia

Boehm and Bonhoeffer (25) found that ammonia was inert to hydrogen atoms produced in a Wood discharge tube. Dixon (48) found a small amount of decomposition which was independent of temperature over the range 25° - 260°C. However, they used 3% water in the hydrogen as a wall poison, and when the water concentration was doubled, the amount of ammonia decomposition doubled. It thus appears that the ammonia was reacting with the dissociation products of water (10% dissociation of the water was sufficient to explain the results).

No addition product was formed between ammonia and hydrogen atoms at liquid air temperatures (39).

The photodecomposition (direct and sensitized) of ammonia has been extensively studied (49 to 66). The quantum yield at 20°C is about 0.2 and is between 0.5 and and 1 at 500°C. Molecular hydrogen inhibits the reaction at 400°C but not at room temperature (49, 51), while atomic hydrogen inhibits the decomposition at room temperature (55).

It has been noted that the hydrogen atom concentration present during the photolysis of ammonia is smaller than would be expected if every ammonia absorbing a quantum immediately decomposed, assuming that the only method for hydrogen atom removal was their recombination. Although various mechanisms have been postulated to explain these facts, the increase in quantum yield and the inhibition by molecular hydrogen at high temperatures seems to indicate that the reactions

$$H + NH_3 \longrightarrow NH_2 + H_2$$

and

$$NH_2 + H_2 \longrightarrow NH_3 + H$$

occur at high temperatures.

Hydrogen Atoms and Hydrazine

Hydrogen atoms produced in a discharge tube react rapidly with hydrazine to produce nitrogen, hydrogen and ammonia (48). The ratio of ammonia produced to hydrazine destroyed was about 0.85. The reaction was found to be independent of temperature over the range 0° - 22°C. The mechanism proposed was

$$H + N_2H_4 \longrightarrow H_2 + N_2H_3 \qquad (1)$$

$$2N_2H_3 \longrightarrow 2NH_3 + N_2 \qquad (2)$$

with a smaller amount of N_2H_3 destroyed to nitrogen and hydrogen in a side reaction.

Birse and Melville (67) studied the photosensitized reaction of hydrogen atoms with hydrazine and proposed the mechanism

$$Hg(^3P_1) + H_2 \longrightarrow Hg(^1S_o) + 2H$$

$$H + N_2H_4 \longrightarrow NH_3 + NH_2 \qquad (3)$$

$$NH_2 \longrightarrow \tfrac{1}{2}N_2 + H_2 \qquad (4)$$

for two reasons: (a) when enough energy is available, hydrogen atoms do not dehydrogenate ammonia, but exchange positions (61), so reaction (1) would probably not occur; (b) by analogy with hydrocarbon reactions, since the reaction $H + C_2H_6 \longrightarrow CH_4 + CH_3$ occurs, reaction (3) would be expected. However, it is now known that the initial step in the reaction of hydrogen atoms with ethane is

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2$$

Also, according to this mechanism, the ratio of ammonia produced to hydrazine destroyed would always have to be at least 1, and would be greater than one if the reaction

$$2NH_2 \longrightarrow N_2H_4 \qquad (5)$$

occurred. Since the ratio is never greater than, and is usually less than one, reaction (3) probably does not occur to an appreciable extent.

Hydrogen Atoms and Methylamine

It appears that the reaction between hydrogen atoms and methylamine has never been studied in detail. It has been shown to occur at 100°C with hydrogen atoms produced by Wood's discharge tube method (69), and has been postulated as a step in the photochemical and thermal decompositions of methylamine (68 to 71). Although most authors have assumed the process to be

$$H + CH_3NH_2 \longrightarrow CH_3NH + H_2$$

Watson and Darwent (71) assumed that

$$H + CH_3NH_2 \longrightarrow CH_2NH_2 + H_2$$

was equally likely.

Each mole of methylamine photodecomposed produced one mole of hydrogen, one-half mole of ammonia, about 0.04 mole methane and a polymer. There has been no general agreement upon the exact composition of the polymer nor its method of formation. The composition appears to vary between C_2H_5N and C_2H_3N, the amount of hydrogen decreasing as the length of the experiment increases. Johnson and Taylor (70) described the polymer as an initially colorless liquid deposit on the walls which darkened as the experiment progressed and eventually became dark brown. The polymerization has been variously ascribed to interaction of the CH_3NH (or CH_2NH_2) radicals with themselves, or to rearrangement of these radicals to methyleneimine ($CH_2{=}NH$) followed by

$$CH_2{=}NH + CH_3NH_2 \longrightarrow CH_3{-}N{=}CH_2 + NH_3$$

$$CH_3{-}N{=}CH_2 \longrightarrow \frac{1}{n}(C_2H_3N)_n + H_2$$

SOME RELEVANT FREE RADICAL REACTIONS

Alkyl Biradicals

Bawn and his coworkers (72 to 74) have used the diffusion flame technique of Hartel and Polanyi (75) for the preparation of alkyl biradicals by the reaction of sodium vapor with the appropriate dihalide.

Methylene radicals, prepared from methylene dibromide and sodium (73, 74), yielded only ethylene at 300°C in the absence of hydrogen. The reaction was presumably

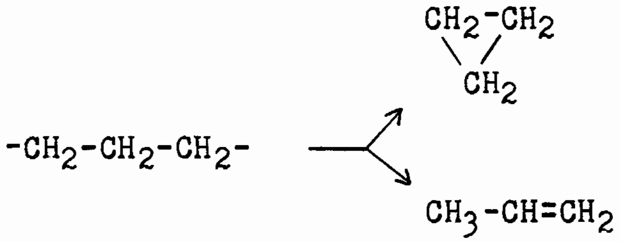
$$2CH_2 \longrightarrow CH_2{=}CH_2$$

In the presence of hydrogen, methane was the major product, which indicated hydrogenation of the methylene radical

$$CH_2 + H_2 \longrightarrow CH_4$$

An attempt to produce ethylidene radicals in a similar way yielded ethylene only, both in the presence and absence of hydrogen (74). Since some dimerisation or hydrogenation of the ethylidene radicals might have been expected in the reactions in the absence or presence of hydrogen respectively, it was suggested that rearrangement to ethylene took place in the activated complex.

Trimethylene radicals rearranged to form cyclopropane and propylene in the ratio 9:1 (72).



The rearrangement to propylene was shown to be mainly a wall reaction, while cyclization was considered to be a homogeneous reaction.

Methyl Radicals and Methylamine

The reaction

$$CH_3 + CH_3NH_2 \longrightarrow CH_4 + CH_3NH \qquad (1)$$

has been suggested as a step in the thermal decomposition of methylamine (68). Trotman-Dickenson and Steacie (76) studied reaction (1) using acetone as a radical source and obtained an activation energy of 8.4 kcal. and a steric factor of 8×10^{-4}.

ACTIVE NITROGEN

When a condensed (77) or high frequency electrodeless (78) electric discharge is passed through nitrogen at low pressures, a bright golden-yellow color is produced which may persist for a considerable time after the discharge is shut off. This color is therefore called the nitrogen afterglow. The glowing gas possesses peculiar physical and chemical properties and is called "active nitrogen". The spectrum of the afterglow was first measured by Lewis (77) who found four bands which he identified with the spectrum of molecular nitrogen. It is now known that the afterglow is generated by transitions from the 10, 11 and 12th vibrational levels of the $B^3\Pi_g$ state to the metastable $A^3\Sigma_g$ state of nitrogen molecules.

For many years, the optimum conditions for producing active nitrogen were hotly disputed. Some workers (79, 80, 86 to 89) maintained that production of the afterglow was favored by the absence of even the smallest traces of impurities, while others (77, 90 to 93) claimed that a small amount of oxygen was necessary for its production. It was eventually determined that small quantities of certain impurities (such as oxygen or water) were indeed beneficial to the production of the afterglow and that they probably acted to poison the walls against deactivation of active nitrogen (79, 94).

The Behavior and Properties of Active Nitrogen

It has been observed that active nitrogen is very sensitive to the condition of the walls of the containing vessel (81). Bonhoeffer and Kaminsky (94) showed that although about one part per thousand of foreign gas was needed to produce a bright nitrogen afterglow, the added gas had no influence on the spectrum of the afterglow and thus could not be of importance in the production of luminosity directly. They concluded that the impurity "poisoned" the glass surface, thus helping in the production of the afterglow.

Herzberg (95) found that thoroughly baked-out vessels do not allow the afterglow to form by electrodeless discharge even in mixtures of nitrogen and oxygen. He found that a clean quartz surface was a good catalyst for non-luminous atom recombination.

Lewis (96) observed that with untreated vessels, the duration and intensity of the afterglow increased as pressure and temperature decreased, while the reverse was true with specially cleaned vessels.

In a 22 litre untreated Pyrex flask, Knipp (97) was able to obtain, by high-frequency electrodeless discharge, an afterglow which increased in duration as more and more experiments were made. After one year, he obtained an afterglow which lasted three hours.

Lord Rayleigh (81) obtained an afterglow which lasted nearly six hours in a large glass bulb wetted with sulfuric or phosphoric acid.

It is thus evident that the duration of the afterglow is very dependent on wall conditions.

Strutt noticed very early in his study of active nitrogen that this material possesses a great chemical reactivity. He showed that active nitrogen reacts with metals to form nitrides, with nitric oxide to form the dioxide, with hydrocarbons to form cyanogen and hydrogen cyanide, with white phosphorus to form red phosphorus, with carbon disulfide to form polymers which were identified as $(NS)_x$ and $(CS)_x$, and with many other compounds (79, 82). Most of the reactions were accompanied by luminosity which is different in constitution from the spectrum of the afterglow (e.g., hydrocarbon reactions were accompanied by the cyanogen flame). Phosphorescence can be induced by active nitrogen impinging on a variety of substances, such as uranium nitrate and aluminum chloride (100, 101). Willey and Rideal observed that ammonia and several other substances were decomposed (102). Active nitrogen reacts with atomic hydrogen to produce small quantities of ammonia (103 to 105) and with molecular hydrogen to produce hydrazine (104, 105) in small amounts.

Most of the early investigations of the chemical activity of active nitrogen were made in a very qualitative manner. Recently, a series of quantitative investigations was undertaken in the McGill laboratories. These, with some of the more detailed early studies, are discussed later (Kinetics of Active Nitrogen Reactions).

In his early investigations, Strutt (82, 83) showed that a strong ionization current can be observed between electrodes immersed in the nitrogen afterglow. The current was much smaller than would correspond to the electrochemical equivalent of the active material, as determined by chemical methods. It was shown that this current is not due to the survival of ions from the generating discharge, nor is the afterglow affected appreciably by the removal of the ions (78, 83). The removal of charged particles also has no effect upon the chemical reactivity of active nitrogen (98). Constantinides (99) found that the ionization current was proportional to the area of the negative collecting electrode and concluded that the effect must either be photoelectric or due to active nitrogen impinging upon the electrodes. It was found by Lord Rayleigh (83) that, since the ionization was completely stopped when the testing vessel was separated from the afterglow by a silica wall, the ionization was not due to a photoelectric effect on the electrodes. The ionization current was roughly independent of the electrode material and decayed according to a rate law which was first order with respect to active nitrogen concentration and to inactive nitrogen concentration. It was therefore concluded that ionization results from single collisions between active centres and nitrogen molecules.

Lewis (106) observed metallic lines of mercury and of aluminum (from the electrodes) in the spectrum of the afterglow. Strutt and Fowler (107) found that active nitrogen could excite the spectra of various substances, such as sodium and mercury iodide, and that it emits its energy more quickly at lower temperature and on compression, which indicates that the process is polymolecular (81). Ruark et al (108) stated that mercury atoms can receive 10 ev. of energy from active nitrogen, whereas Okubo and Hamada (109) found no mercury lines above 9.56 ev. Carbon monoxide bands of excitation energy 8.2 and 9.0 ev. can be produced, but hydrogen (first excited level at 11.1 ev.) is unaffected (110). Constantinides (99) observed that ions were produced in iodine vapor but not in mercury vapor or hydrogen and concluded that active nitrogen contained 9.4 - 10.4 ev. of energy. Lord Rayleigh showed that active nitrogen heats metals which are placed in it (84).

It is evident that active nitrogen is able to impart approximately 10 ev. to single atoms or molecules with which it comes in contact.

The rate of decay of the nitrogen afterglow has been extensively studied (81, 85, 94, 111 to 115) and all workers found that the decay was second order with respect to the active species, but there was considerable disagreement about the effect of normal nitrogen. Some authors maintain that the decay is first order with respect to normal nitrogen, which means that the process giving rise to the afterglow is a three-body collision, whereas others claim that normal nitrogen is without effect, i.e., the afterglow results from collisions which involve two active centres only.

Rudy (112) observed that the afterglow decay has a small negative temperature coefficient.

Willey (114) observed considerable deviation from second order decay in very clean vessels, which indicated that glowless deactivation was occurring on the walls. The presence of small amounts of certain substances, such as oxygen, returned the decay to second order, which again indicated that the influence of small amounts of foreign gases on the afterglow constitutes a wall effect.

When active nitrogen is passed through a heated tube or through a weak auxilliary discharge, the afterglow is quenched but the chemical activity, determined by reaction with nitric oxide, is unaffected (116). Kaplan and Cario (117) demonstrated that when the afterglow had been destroyed by heating, the glowless modification of active nitrogen could still excite the D lines of sodium. Okubo and Hamada (118) obtained the same spectrum of mercury from the dark modification of active nitrogen (i.e. heated to 600°C) as from active nitrogen that had not been heated and the highest energy level excited was 9.51 ev. in either case. They observed, however, that when the afterglow was destroyed by an auxilliary discharge, the activity was destroyed simultaneously.

Thus it appears that nitrogen which produces the afterglow is always 'active', but nitrogen which is 'active' need not necessarily produce the afterglow.

The Constitution of Active Nitrogen

For nearly forty years there has been a controversy over the precise constitution of active nitrogen. The unusual physical and chemical reactivity has been variously attributed to nearly everything, within reason, that it is possible to construct out of nitrogen, viz., N, N^*, N_2^*, N_2^+, and N_3. The fact that the problem still has no definite solution demonstrates very emphatically the complex nature of active nitrogen. There are several reviews of the subject available in the literature (119 to 121), and a large number of papers have been published in which the authors postulate theories in an attempt to correlate the various phenomena that have been discussed briefly in the previous section. Most of these theories, however, start with an assumption as to the identity of the active component (or components) and attempt to explain the various phenomena on the basis of that assumption. The theories often vary widely even when they assume the same active component. To illustrate: one author explained the dark modification of active nitrogen, produced by heating, by assuming that metastable molecules are destroyed by heat and metastable atoms are unaffected (117), while another author explained the phenomenon by assuming that the metastable levels of both atoms and molecules are sensitive to heat (122).

The evidence which seems to indicate the presence of the various possible active species in active nitrogen will be outlined. Only the considerations and observations which are relevant to the argument whether or not a particular species is present will be presented, and the details of the individual theories which attempt to explain the various phenomena will be omitted, since most of them necessarily include considerable speculation.

The initial observation of the great chemical reactivity of active nitrogen led Strutt to assume that it was atomic nitrogen (79). This assumption seemed to be strengthened by the fact that the afterglow was weakened by heating and intensified by cooling or compression, which would be expected if it were produced by the recombination of atoms (81, 83).

The second order dependence of the afterglow on concentration of the species which generates it seems to indicate that atoms are that species. However, Lord Rayleigh (84) found that only a small fraction of the energy contained in active nitrogen is emitted as light, hence the afterglow would not require a large concentration of atoms.

Shortly after Wood and Bonhoeffer (16, 17) had shown that hydrogen atoms could be produced in a discharge tube, and that impurities such as oxygen and water "poisoned" the walls against atom recombination, Sponer (123) reasserted that active nitrogen was atomic nitrogen and showed a marked similarity between its behavior and that of atomic hydrogen. Both substances heat metals which are placed in them, both have relatively long life, which is probably due to the necessity of triple collisions in the gas phase for atom recombination, if the walls are poisoned, and both are capable of collisions of the second kind, since atomic hydrogen can also excite the D-lines in sodium.

From the fact that no ammonia is obtained from a mixture of nitrogen and hydrogen unless both gases are activated, Lewis believed that atomic nitrogen was present in active nitrogen (103).

Kaplan and Cario (117) said that the long life of active nitrogen (many minutes in some cases) precluded the possibility of only metastable molecules being present. The long life and behavior toward wall catalysts seemed to be more rationally explained by atoms. To account for all the varied phenomena, they supposed that metastable atoms and molecules as well as normal atoms were present.

Direct proof for the presence of atoms in active nitrogen was obtained by Herzberg (124), who found atomic nitrogen arc lines in the electrodeless discharge used for the production of the afterglow. If the discharge was so modified that no afterglow was obtained, then the atomic lines were absent. However, Herbert, Herzberg and Mills (125) found an upper limit of 1/6000 per cent for the stationary concentration of metastable atoms.

Wrede (126) claimed that direct pressure measurements indicated several per cent of atoms in active nitrogen. He used a small orifice on one side of which he placed a metal catalyst for the recombination of atoms. The diffusion of molecules and atoms through the orifice, followed by recombination of the atoms, created a pressure differential across the orifice. With the assumption of isothermal conditions, he was able to calculate the atom concentration by kinetic theory. He found that an increased capacitance in the discharge circuit increased the atom concentration. Although the assumption of isothermal conditions is undoubtedly the source of some error, it should be noted that Wrede gauge measurements have been accepted as a direct method for measuring hydrogen atom concentrations (127) where non-isothermal conditions doubtless also prevail.[☆]

The atomic arc lines of nitrogen were observed by Bay and Steiner (128) when they applied an additional high-frequency discharge external to the condensed discharge which produced active nitrogen.

Jackson and Broadway (129) performed a Stern-Gerlach experiment on active nitrogen and obtained visible evidence of nitrogen atoms. The atoms were detected on a plate of silver nitrate and the traces were interpreted to indicate the presence of nitrogen atoms in the $^2P_{\frac{1}{2}}$ state.

However, Hamada (130) observed no resonance enhancement

[☆] Versteeg and Winkler estimated that as much heat was produced with hydrogen atoms as with active nitrogen at a Wrede gauge. (private communication).

of spectral lines with term values equal to 2.36, 3.56 and 8.2 ev., which correspond to the levels of metastable atoms in the ^2D or ^2P states respectively and to metastable molecules in the $A^3\Sigma$ state, and concluded that these species were present in active nitrogen in only very small concentrations.

Debeau (131) obtained a marked increase in the pressure of a static system containing nitrogen by applying a high frequency discharge. He found that the pressure nearly doubled as the afterglow appeared, although the temperature of the walls of the system increased only slightly. The increase in pressure was attributed therefore to an almost complete dissociation into atoms. The disappearance of the afterglow was accompanied by a return to the original pressure.

Jackson and Schiff (152) have compared the mass spectra of ordinary and active nitrogen. The mass 14 peak was greater and the mass 28 peak was smaller in active nitrogen than in ordinary nitrogen. The ion currents at masses 28 and 14 were measured versus the energy of the bombarding electrons in the mass spectrometer with inactive and active nitrogen. Comparison showed that while the mass 28 peaks were superimposable, those at mass 14 were quite different. The mass 14 curve of active nitrogen also showed an inflection which indicated that the ionization process generating it was composite. The appearance potentials of the constituents of the mass 14 peak were 14.7 and 16.1 ev. The 14.7 ev. appearance potential was definitely due to the presence of ^4S atoms in active nitrogen, although an unequivocal explanation of the 16.1 ev. appearance potential could not be offered.

Very recently the spectrum for N^4S has been observed in active nitrogen using the microwave absorption method (132). The authors used a condensed discharge and coated the walls of the vessel with metaphosphoric acid. However, they obtained a greatly enhanced resonance spectrum for N^4S when the nitrogen was bubbled through water previous to admission to the discharge. The enhanced spectrum was accompanied by a greatly enhanced afterglow. With dry nitrogen, the intensity of both the visible afterglow and of the magnetic resonance spectrum from the ^4S state were greatly diminished, but were immediately restored and sustained upon introduction of water vapor. No trace of the resonance spectra from the metastable ^2D or ^2P states were obtained with wet or dry nitrogen using a number of different types of discharge. It thus appeared that the N^4S concentration and afterglow intensity run parallel to each other, although their dependence on significant amounts of water vapor does not seem to agree with the results of Lord Rayleigh (81).

A certain amount of evidence has been reported which contradicts that given above. Rudy (147) was able to observe no atomic nitrogen lines in active nitrogen. Bonhoeffer and Kaminsky (94) failed to obtain a more intense afterglow while increasing the pressure of ordinary nitrogen as would be expected from triple collision theory. Kichlu and Basu (138) found no change in the relative intensity of the infra-red lines of nitrogen belonging to the electronic configurations $2L_2M_1 \leftarrow 2L_2M_2$ by exciting first nitrogen and then active nitrogen with an uncondensed discharge under identical conditions. This indicated that no appreciable density of atoms was present in the active nitrogen.

One of the first attempts to explain the behavior of active nitrogen in terms of modern quantum concepts was made by Saha and Sur (133), who believed that active nitrogen consisted of excited molecules having about 9 ev. of energy. They claimed that foreign substances would prevent the emission of light from the excited molecules by producing radiationless transfers.

Birge (134) attempted to give a more detailed picture. Since the afterglow bands are part of the first positive group of nitrogen, and the main vibrational levels involved in the initial state of the transition have vibrational numbers 10, 11 and 12, he supposed that this initial state was metastable for 10, 11 and 12 units of vibrational energy. Rotational energy does not seem to be important in determining the initial or final states of the nitrogen molecule when it gives out the afterglow. Birge believed the long life of active nitrogen to be due to metastability of the initial excited state. However, he later realized that his theory had shortcomings and agreed that Sponer's atomic theory was better (134).

Foote and Ruark (135) concluded that active nitrogen consists of metastable molecules because (a) the afterglow is part of the spectrum of molecular nitrogen and the same bands had been found to be excited well below the ionization potential of the molecule, and (b) no appreciable current flows between sounding electrodes (unless these are in actual contact with the luminous vapor), indicating that active nitrogen is not ionized. The production of current when active nitrogen was in contact with the electrodes was explained by the Holst-Oosterhuis hypothesis: excited molecules upon encountering a metal surface may liberate electrons.

Willey and Rideal (102) claimed that active nitrogen particles contained only about 45 kcal.(2ev.) energy and therefore must be molecules. They measured the energy calorimetricaly and inferred it also from the fact that they observed ammonia, hydrogen bromide, hydrogen iodide and nitric oxide to be destroyed by active nitrogen whereas hydrogen, oxygen, water, carbon dioxide, hydrogen chloride, and several other compounds were unaffected. This low energy value was severely criticized (136) on the basis of the large amount of energy (>150 kcal.) required to excite the various spectra observed when various substances were immersed in active nitrogen, or even the spectrum of active nitrogen itself. Willey therefore proposed that two active species of different energies were present: atoms produced the luminous phenomena by impacts of the second kind, while the chemical activity was due to another modification with an energy content of about 45 kcal. (116). He showed that luminosity and chemical activity are not concomitant by producing the dark modification discussed earlier.

It was observed by Kaplan (137) that the fourth positive group of nitrogen could be excited by passing a weak discharge through active nitrogen. This suggests that there exist in the active gas some metastable molecules which are easily raised to the higher energy levels from which the fourth positive group is known to originate.

By conditioning the walls of the experimental tube Kaplan (139) and Jones and Grubb (140) were able to produce a strong afterglow in nitrogen by an uncondensed discharge. The first negative bands of nitrogen (due to N_2^+) were produced in the exciting discharge itself, indicating that the conditions of this discharge simulated the auroral conditions where these negative bands are found. Kaplan considered the excitation of the N_2^+ bands to be due to large concentrations of metastable nitrogen molecules in the $A^3\Sigma$ state.

Gaydon (141) pointed out that the $a'\ {}^1\Sigma_u$ state may be metastable and therefore may be of importance in active nitrogen.

From a study of active nitrogen in an aerodynamic shock tube, Benson (142) concluded that the response of the afterglow to shock waves was evidence that molecules in metastable levels adjoining the $B^3\Pi$ state were present in active nitrogen.

The photoelectric decay studies of Kaplan, Kash and Brooks (143) led them to consider metastable molecules ($A^3\Sigma$ and $X^1\Sigma$ in high vibrational levels) as the energetically active particles in the afterglow.

The theory of active nitrogen involving nitrogen positive ions proposed by Mitra (120) was based to a substantial degree on an analogy with processes in the night sky and the ionosphere. New experimental data on the upper atmosphere show that this analogy is rather remote

(144) and experiments to detect N_2^+ ions in active nitrogen have yielded negative results (145, 146), so the theory has been discarded. Quite recently, Mitra (120) proposed a 'metastable atom' theory of active nitrogen in which the metastable atoms are produced in the discharge tube by dissociative recombination of N_2^+ ions and electrons.

The formation of H_3 by passage of hydrogen at low pressures through an electric discharge (148, 149) and the similar formation of ozone has led certain authors to propose that an active component in active nitrogen is N_3.

Strutt (83) believed that the bimolecular decay of the afterglow limited the possible active species in active nitrogen to monatomic and triatomic nitrogen, and he favored the monatomic form.

Trautz (150) postulated the mechanism

$$N + N_2 \rightleftarrows N_3$$
$$N_3 + N \longrightarrow 2N_2$$

for active nitrogen decay because he found that the temperature coefficient for the decay was not constant, and he believed that ordinary binary recombination would predict a life time at least one hundred times smaller than was observed. Since, however, this simple suggestion did not explain the various phenomena observed with active nitrogen, it was discarded.

Willey (116) thought that his 45 kcal. species of active nitrogen might be either excited molecules or N_3.

The failure of Herzberg to observe N_1 resonance lines in the absorption spectrum of active nitrogen in the vacuum ultra-violet led Uri (151) to propose that N_3 might be responsible for "active" nitrogen. Uri has shown that N_3 radicals are formed in solution by photo-excited electron transfer in the ion pair complex $Fe^{3+}N_3^-$ which would induce polymerization, or lead to the evolution of molecular nitrogen in the absence of a substrate. It was suggested that in the gas phase N_3 radicals could be formed via the equilibrium

$$N_2 + N \rightleftarrows N_3$$

It was early observed by Strutt (82) that active nitrogen was not condensed at liquid air temperatures, and he therefore concluded that large molecular complexes were not present. This lack of condensability need not be too serious an objection however, because nothing is known about the behavior of N_3 and the possibility exists that it would simply recombine to form N_2 rather than condense at low temperatures. This possibility is supported by the negative temperature coefficient of the afterglow.

It is evident from the preceding outline that one definite statement concerning the constitution of active nitrogen is possible, viz., it is not simple. Strutt's observation that active nitrogen reacts with phosphorus vapor only after its own afterglow has died out, while the glowing form reacts with many substances, such as hydrocarbons and certain metals, gave the first hint that there may be more than one reactive species present in active nitrogen, although he did not postulate more than one. Willey postulated two species to reconcile his views of a low energy species and the atomic theory of active nitrogen. Many of the theories which have been postulated to correlate the various phenomena observed with active nitrogen assume the presence of normal atoms, excited atoms and excited molecules. It is now generally accepted that both atoms and excited molecules are present but their relative abundance and chemical activity is still a matter of debate.

In most, if not all, of the quantitative chemical studies of active nitrogen, atomic nitrogen has been assumed as the only reactive species. This is because, in addition to the experimental evidence for the presence of atoms, atoms seem to provide the simplest interpretation of the observed results.

Kinetics of Active Nitrogen Reactions

In 1946 a series of kinetic investigations of the reactions of active nitrogen with hydrocarbons was undertaken in this laboratory. More recently a series of organic halides was also studied. Prior to 1946, the only reactions investigated quantitatively were those with hydrogen and with nitric oxide. The reaction with ammonia had been studied semi-quantitatively. A review of the kinetics of these reactions is presented to provide a background for the present work.

A Wood-Bonhoeffer type apparatus was used in all the investigations to be discussed except that with the oxides of nitrogen, in which case active nitrogen was produced in an electrodeless discharge.

Hydrogen

Lewis (153) found that active nitrogen reacted with atomic hydrogen to form ammonia, and that no reaction resulted with molecular hydrogen. These systems were more thoroughly investigated by Steiner (104) who found that ammonia and traces of hydrazine were formed in the hydrogen atom reaction and that small amounts of hydrazine were formed in the molecular hydrogen reaction. He postulated the mechanisms

$$N + H + X \longrightarrow NH + X \qquad (1)$$

$$NH + H_2 + X \longrightarrow NH_3 + X \qquad (2)$$

and

$$N + H_2 + X \longrightarrow NH_2 + X \qquad (3)$$

$$2NH_2 + X \longrightarrow N_2H_4 + X \qquad (4)$$

where X represents a third body.

The necessity of a third body in these reactions was tested by Dixon and Steiner (105) who reacted active nitrogen with hydrogen atoms in the presence of a metal surface. The yield of ammonia increased fourfold, thereby confirming the necessity for a three body collision to stabilize the products. The yield of hydrazine decreased, however, which led them to believe that hydrazine was formed by reaction (1) followed by

$$NH + H + X \longrightarrow NH_2 + X \qquad (5)$$

followed by reaction (4). They found ammonia production to be first order with respect to hydrogen atom concentration. They failed to detect the NH radical spectroscopically which seemed to indicate that this radical reacted rapidly and had a low steady state concentration. Recently Rice and Freamo (154) also failed to detect the NH radical in a system containing active nitrogen and hydrogen atoms.

Oxides of Nitrogen

Spealman and Rodebush (155) reacted active nitrogen with nitric oxide and nitrogen dioxide and observed that the characteristic yellow afterglow of active nitrogen changed to the faint bluish afterglow of atomic oxygen. An excess of nitric oxide did not influence this glow, but a sufficient excess of nitrogen dioxide quenched it completely. When they substituted atomic oxygen for active nitrogen in the reactions they again found that excess nitric oxide did not quench the oxygen afterglow though excess nitrogen dioxide did. They therefore suggested the mechanism

$$N + NO \longrightarrow N_2 + O \qquad (1)$$

$$N + NO_2 \longrightarrow 2NO \qquad (2)$$

$$O + NO \longrightarrow NO_2 \qquad (3)$$

$$O + NO_2 \longrightarrow NO + O_2 \qquad (4)$$

The disappearance of the yellow nitrogen afterglow was attributed to reaction (1). The appearance of the blue glow of atomic oxygen was associated with reaction (3) and this reaction was assumed to be the rate-controlling step because the oxygen afterglow persisted when the yellow afterglow had ceased. Excess nitrogen dioxide would quench the bluish glow because of reaction (4), whereas an excess of nitric oxide would tend to intensify the glow owing to an increase in the rate of reaction (3).

Ammonia

It was noted qualitatively by Willey and Rideal (102) that ammonia was rapidly decomposed by active nitrogen. Dixon and Steiner (105) examined the reaction in a fruitless attempt to detect the NH radical spectroscopically. Although their results were not very precise, they noted a low reactivity in spite of a marked weakening of the afterglow. They observed from about $0.04 - 1.55 \times 10^{-6}$ mole/sec. ammonia destroyed and from about $2 - 4 \times 10^{-9}$ mole/sec. hydrazine formed as the ammonia flow rate increased from about $6 - 41 \times 10^{-6}$ mole/sec. From consideration of the possible reactions

	ΔH(kcal.)
$NH_3 + N(^4S) \longrightarrow NH_2 + NH$	6
$NH_3 + N(^4S) \longrightarrow N_2 + H_2 + H$	-22
$NH_3 + N(^2P) \longrightarrow NH_2 + NH$	-76
$NH_3 + N_2(^3\Sigma) \longrightarrow NH_2 + H + N_2$	
$NH_3 + 2N \longrightarrow NH_2 + H + N_2$	

they concluded that exothermic reactions are sometimes slow.

Methane

Blades and Winkler (156) found methane to react with active nitrogen at temperatures above 300°C to produce hydrogen cyanide. An activation energy of 11 kcal. and a steric factor of 5×10^{-3} were estimated for the reaction, which was assumed to proceed by

$$CH_4 + N \longrightarrow \begin{matrix}\text{activated}\\ \text{complex}\end{matrix} \longrightarrow HCN + H_2 + H$$

Ethane

Hydrogen cyanide was the only detectable product from the reaction of active nitrogen with ethane at temperatures up to 295°C (156). The reaction was shown to be second order. An activation energy of 7±1 kcal. and a steric factor between 10^{-1} and 10^{-3} were estimated from an Arrhenius plot. The assumed mechanism was

$$C_2H_6 + N \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCN + CH_3 + H_2$$

$$CH_3 + N \longrightarrow HCN + H_2$$

Since methane was not observed in the products, it was concluded that the second reaction was much faster than the first.

A close correspondence was obtained between the values of the active nitrogen concentration determined by Wrede gauge and estimated from the maximum amount of hydrogen cyanide produced from ethane. This observation was interpreted as evidence in support of atomic nitrogen as the reactive species in active nitrogen.

Propane and Cyclopropane

Active nitrogen reacted with propane and cyclopropane to produce hydrogen cyanide with smaller amounts of ethylene and acetylene and traces of ethane (157, 158). Propane reacted more rapidly than cyclopropane. The variation in the rate of recovery of ethylene and acetylene with propane or cyclopropane flow rate led to the assumption that they were produced as primary products and removed by subsequent reaction with excess active nitrogen.

The mechanism suggested for the propane reaction was

$$N + C_3H_8 \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCN + CH_3CH{:} + H_2 + H \quad (1)$$

$$CH_3CH{:} \longrightarrow CH_2{=}CH_2 \quad (2)$$

$$N + C_3H_8 \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCN + C_2H_2 + 2H_2 + H \quad (3)$$

followed by reaction of the ethylene and acetylene with active nitrogen as described in the discussion of those reactions. It was deduced from the temperature coefficient of second order rate constants that the over-all reaction has an activation energy of about 5.6 kcal. and a steric factor between 10^{-2} and 10^{-4}.

The mechanism postulated for the cyclopropane reaction was

$$N + \text{cyclo}(C_3H_6) \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \begin{array}{ll} \longrightarrow CH_2{=}CH_2 + HCN + H & (4) \\ \longrightarrow CH{\equiv}CH + HCN + H_2 + H & (5) \end{array}$$

with subsequent reaction of the ethylene and acetylene as above. An activation energy of about 3.6 kcal. and a steric factor of 10^{-3} to 10^{-5} were assigned to the over-all reaction.

Both of these mechanisms contain reactions which appear to be prohibitively endothermic. Reactions (1), (3) and (5) are endothermic by approximately 59, 54 and 15 kcal. respectively.[*] If it were assumed that ethylene

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[*] The heats of reactions mentioned in this thesis have been calculated from the heats of formation of the reactants and products. For conciseness and convenience, the heats of formation of the relevant materials are grouped together in Appendix A. Sample calculations are also included.

were generated directly from the activated complex in reaction (1), the reaction would be endothermic by only about 6 kcal. In any case, the mechanisms postulated seem to be inadequate.

The Butanes and Cyclobutane

As in the analogous propane and cyclopropane reactions, it seemed necessary to postulate the formation of acetylene and ethylene as primary products of the reactions of active nitrogen with n-butane, isobutane, and cyclobutane. Back and Winkler (159) studied n-butane and isobutane and postulated the following mechanisms. For n-butane:

$$N + C_4H_{10} \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCN + C_3H_7 + H_2$$

$$\begin{aligned} N + C_3H_7 &\longrightarrow HCN + C_2H_4 + H_2 \\ &\longrightarrow HCN + C_2H_2 + 2H_2 \\ &\longrightarrow HCN + C_2H_5 + H \end{aligned}$$

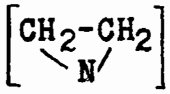
Ethyl radical formation, if it occurred, was believed to be a minor reaction. For isobutane, the most probable mechanism appeared to be

$$N + iso\text{-}C_4H_{10} \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCN + CH_3CHCH_3 + H_2$$

$$\begin{aligned} N + CH_3CHCH_3 &\longrightarrow HCN + C_2H_4 + H_2 \\ &\longrightarrow HCN + C_2H_2 + 2H_2 \\ &\longrightarrow HCN + 2CH_3 \end{aligned}$$

Activation energies of about 3.1 and 3.6 kcal. were assigned to the isobutane and n-butane reactions respectively, and the steric factor was about 5×10^{-4} for both reactions. Although the reactions suggested for ethylene and acetylene formation seem to violate the Rice-Teller principle of least motion, it was pointed out that this principle was tested mainly for reactions involving 100 kcal. of energy or less, whereas the active nitrogen reactions release about 175 kcal. with the formation of the $C\equiv N$ bond. A much more drastic rearrangement within the collision complex might therefore be possible.

The cyclobutane reaction was studied by Onyszchuk (158) who postulated the mechanism

$cyclo\text{-}C_4H_8 + N \rightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \rightarrow CH_2{=}CH_2 +$  (1)

$$[C_2H_4N] \rightarrow CH_2 + [CH_2N] \rightarrow CH_2 + HCN + H \qquad (2)$$

$$cyclo\text{-}C_4H_8 + N \rightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \rightarrow -CH_2CH_2CH_2- + HCN + H \qquad (3)$$

$$-CH_2CH_2CH_2- + N \rightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \rightarrow CH_2{=}CH_2 + HCN + H \qquad (4)$$

$$\rightarrow C_2H_2 + HCN + H_2 + H \qquad (5)$$

$$-CH_2CH_2CH_2- \longrightarrow CH_2{=}CHCH_3 \qquad (6)$$

$$CH_2{=}CHCH_3 + N \rightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \rightarrow CH_3CH{:} + HCN + H \qquad (7)$$

$$\rightarrow C_2H_2 + HCN + H_2 + H \qquad (8)$$

with the ethylidene radicals transforming rapidly to ethylene. It was assumed that most of the trimethylene biradicals, propylene, ethylene and acetylene formed were subsequently removed by reaction with active nitrogen. The over-all reaction was found to have an activation energy of 5.5 kcal. and a steric factor between 10^{-2} and 10^{-4}. However, thermodynamic calculations show that the series of reactions represented by (1)+(2) is endothermic by about 47 kcal., and reactions (3), (7) and (8) are endothermic by about 28, 27 and 22 kcal. respectively. Direct generation of olefins instead of biradicals in reactions (3) and (7) would make these reactions exothermic by over 20 kcal. (about 22 and 27 kcal. respectively). In view of the high endothermicity of some of the reactions postulated it appears that the mechanism is not adequate.

Neopentane

The active nitrogen-neopentane reaction was studied over the temperature range -40° - +250°C (158, 160). An Arrhenius plot of the second order rate constants calculated for HCN production showed a distinct break, and the two nearly-linear portions of the curve corresponded to activation energies of 2.3 and 9.2 kcal., with respective steric factors of about 10^{-5} and 10^{-3} to 0.5.

The obvious inference to be drawn from the existence of two activation energies was that the over-all reaction was composite. Several possible causes of this were considered, viz., different modes of active nitrogen attack on neopentane molecules, the presence of two reactive species in active nitrogen, or simultaneous hydrogen atom reactions which might produce radicals that would react rapidly with active nitrogen. From comparison with the rather unusual behavior of the neopentane-hydrogen atom reaction (161, 162), and in view of the fact that the change of composition of the secondary products with temperature was small, it was concluded that no choice could be made among the three possibilities.

The composition of the products led to the postulation of a reaction mechanism which involved a step-wise degradation of neopentane in units containing one carbon atom.

Ethylene

The reaction of ethylene with active nitrogen was first investigated by Greenblatt and Winkler (163), who found the products to be hydrogen cyanide with smaller amounts of ethane and a polymer. Complete consumption of active nitrogen was obtained above a critical limit of ethylene flow rate. At lower flow rates ethylene was completely consumed. The yield of ethane increased as the excess of ethylene over active nitrogen increased. The mechanism suggested to account for this behavior was

$$C_2H_4 + N \longrightarrow \begin{matrix}\text{activated}\\ \text{complex}\end{matrix} \longrightarrow HCN + CH_3$$

$$CH_3 + N \longrightarrow HCN + 2H$$

$$C_2H_4 + H \longrightarrow C_2H_5$$

$$C_2H_5 + H \longrightarrow C_2H_6$$

$$2CH_3 \longrightarrow C_2H_6$$

Polymer formation was probably due to polymerization of hydrogen cyanide, catalysed by the water vapor used as a wall poison. An activation energy of 6.9 kcal. was calculated from collision yield data with an assumed steric factor of 0.1.

A study of this reaction by the same authors with a diffusion flame technique over the temperature range $273^\circ - 373^\circ K$ yielded an activation energy of about 3 kcal. and a steric factor of about 10^{-2}.

A further investigation of the ethylene reaction by

Versteeg and Winkler (164) with metaphosphoric acid instead of water vapor as a wall poison to eliminate polymer formation, confirmed hydrogen cyanide to be the principal product. In addition, small quantities of ethane, methane, cyanogen and acetylene were found. The observed variation of the amounts of these products with ethylene flow rate was attributed to the reactions

$$\begin{array}{rcl}
C_2H_4 + H & \longrightarrow & C_2H_3 + H_2 \\
C_2H_3 + H & \longrightarrow & C_2H_2 + H_2 \\
C_2H_4 + N & \longrightarrow & [C_2H_4N]^* \\
[C_2H_4N]^* + N & \longrightarrow & [C_2H_4N_2]^* \\
[C_2H_4N_2]^* & \longrightarrow & C_2N_2 + 2H_2
\end{array}$$

A possible alternative initial step suggesting the formation of a methylene radical was also proposed:

$$C_2H_4 + N \longrightarrow \begin{array}{c}\text{activated}\\ \text{complex}\end{array} \longrightarrow CH_2 + CH_2N$$

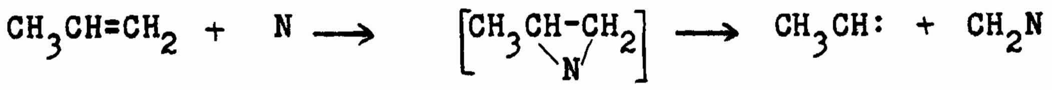
$$CH_2N \longrightarrow HCN + H$$

However, this combination of reactions is endothermic by about 28 kcal. (see Appendix A) and probably does not occur to an appreciable extent.

Propylene

The products of the active nitrogen-propylene reaction were hydrogen cyanide and ethylene with small amounts of ethane and propane and traces of acetylene and a C_4 hydrocarbon (165). Active nitrogen was completely consumed in the presence of excess propylene at 96° and 242°C, and propylene was completely consumed with an excess of active nitrogen. The rate of recovery of ethylene increased sharply at propylene flow rates greater than that corresponding to complete removal of active nitrogen. Ethylene production increased with temperature.

Olefins react more rapidly than paraffins with active nitrogen (156), and it appears that this is due to the ease with which active nitrogen can attack a double bond. Therefore, the mechanism postulated for the propylene reaction assumed the formation of an activated complex by active nitrogen attack at the C-C double bond of propylene with subsequent decomposition into radicals.



$$CH_3CH{=}CH_2 + N \longrightarrow \left[\begin{array}{c} CH_3CH{-}CH_2 \\ \diagdown N \diagup \end{array}\right] \longrightarrow CH_3CH\colon + CH_2N \qquad (1)$$

which could be followed by

$$CH_2N \longrightarrow HCN + H \qquad (2)$$

$$CH_3CH\colon \longrightarrow CH_2{=}CH_2 \qquad (3)$$

The ethylene produced could react further if active nitrogen were available.

Hydrogenation reactions of the type

$$C_nH_{2n} + H \longrightarrow C_nH_{2n+1}^{*}$$
$$C_nH_{2n+1}^{*} + H_2 \longrightarrow C_nH_{2n+2} + H$$

were believed to be responsible for formation of saturated products.

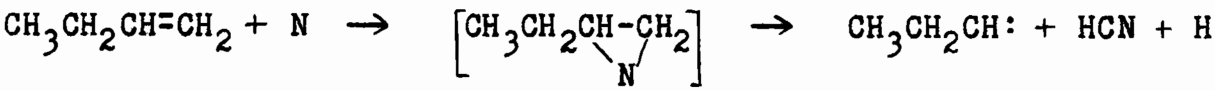
The activation energy for the over-all reactions was taken as less than 6 kcal. and probably less than 4 kcal. by comparison with the ethylene reaction. Since the combination of reactions (1) and (2) is endothermic by about 27 kcal. (Appendix A), it appears that this mechanism is inadequate.

Butenes

The reactions of active nitrogen with butene-1, cis-butene-2, and isobutene at 88° and 240°C were found to produce hydrogen cyanide, propylene, and ethylene mainly (166). Smaller quantities of butane, propane, ethane, methane, and hydrogen were also obtained, together with trace amounts of acetylene and hydrocarbons higher than C_4 at high butene flow rates. The order of reactivity of the butenes studied was

butene-1 > cis-butene-2 > isobutene

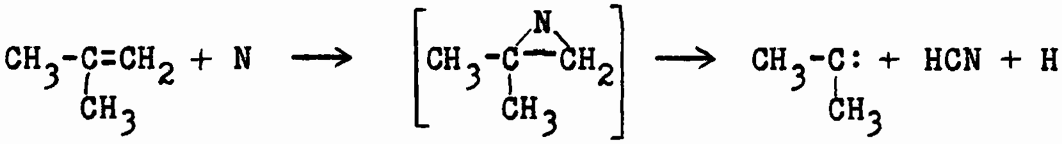
All the suggested mechanisms involved the formation of an activated complex and its decomposition in a manner similar to that postulated for the propylene reaction. For butene-1 the scheme was represented as



$$CH_3CH_2CH{=}CH_2 + N \rightarrow \left[\underset{\diagdown N \diagup}{CH_3CH_2CH-CH_2}\right] \rightarrow CH_3CH_2CH: + HCN + H \quad (1)$$

$$CH_3CH_2CH: \longrightarrow CH_3CH{=}CH_2 \quad (2)$$

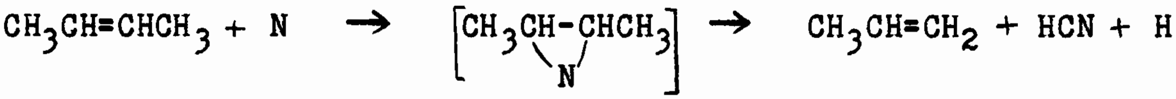
Similarly for isobutene,



$$CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2 + N \longrightarrow \left[CH_3-\overset{N}{\underset{\underset{CH_3}{|}}{C}}-CH_2\right] \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}: + HCN + H \quad (3)$$

$$CH_3-\dot{\underset{\cdot}{C}}-CH_3 \longrightarrow CH_3CH{=}CH_2 \quad (4)$$

Since propylene was also recovered as a primary product of the cis-butene-2 reaction, it was necessary to postulate a rearrangement within the complex such that its subsequent dissociation gave propylene.



$$CH_3CH{=}CHCH_3 + N \rightarrow \left[\underset{\diagdown N \diagup}{CH_3CH-CHCH_3}\right] \rightarrow CH_3CH{=}CH_2 + HCN + H \quad (5)$$

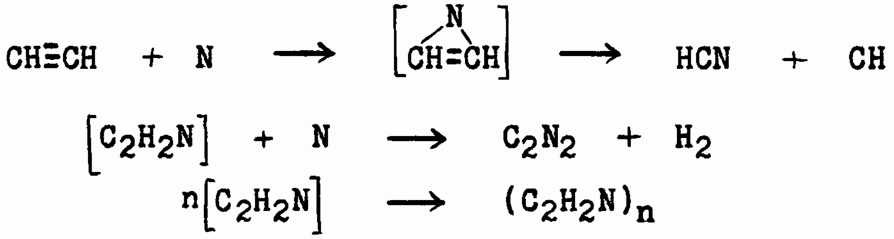
The propylene formed in all three reactions was assumed to react further as described previously.

The saturated products were believed to result from hydrogen atom reactions.

However, reactions (1) and (3) again involve the production of a biradical and are endothermic by about 18 and 16 kcal. respectively (Appendix A, also cf. ethylene and propylene). Reaction (5) involves considerable shift in atom positions in the activated complex, but it is exothermic by about 28 kcal. and would probably occur more readily than reactions of type (1) and (3). It appears, therefore, that alkyl biradicals would not be formed in these reactions, but the direct decomposition of the activated complexes into olefins may be possible.

Acetylene

The products of the active nitrogen-acetylene reaction were hydrogen cyanide and a polymer (containing 32% nitrogen) with smaller amounts of cyanogen and methane (167). The mechanism postulated was



$$CH{\equiv}CH + N \longrightarrow \left[\overset{N}{CH{=}CH}\right] \longrightarrow HCN + CH$$

$$[C_2H_2N] + N \longrightarrow C_2N_2 + H_2$$

$$n[C_2H_2N] \longrightarrow (C_2H_2N)_n$$

The methane recovery was small and erratic and was thought to result from hydrogen abstraction from the polymer by the methyne radical.

Ethyl and Vinyl Chlorides

The reaction rates of ethyl chloride and vinyl chloride were comparable with those of ethylene and acetylene respectively (168). Hydrogen cyanide and hydrogen chloride were the main products of both reactions, and smaller amounts of acetylene, cyanogen and a brown polymer were also formed. Ethylene was a product of the ethyl chloride reaction, and relatively greater amounts of polymer and cyanogen were formed in the vinyl chloride reaction. The observed variation in the amounts of products formed at different reactant flow rates indicated the following mechanisms: (a) ethyl chloride:

$$CH_3CH_2Cl + N \longrightarrow \begin{array}{c}\text{collision}\\ \text{complex}\end{array} \longrightarrow HCl + [CH_3CHN]$$

$$[CH_3CHN] \longrightarrow HCN + CH_3$$

$$2[CH_3CHN] \longrightarrow N_2 + 2C_2H_4$$

$$N + [CH_3CHN] \longrightarrow C_2N_2 + 2H_2$$

with subsequent reaction of the methyl radicals with active nitrogen. (b) vinyl chloride: essentially similar to that for ethyl chloride.

n-Propyl and Isopropyl Chlorides

The products of the reactions of active nitrogen with n-propyl chloride and isopropyl chloride were similar and consisted of hydrogen cyanide and hydrogen chloride with smaller amounts of propylene, ethylene, acetylene and cyanogen and traces of ethane and propane (168). It appeared that the C_2 and C_3 hydrocarbons were produced in secondary reactions. The mechanisms suggested for both reactions were essentially the same, viz.

$$N + C_3H_7Cl \longrightarrow \begin{matrix}\text{collision}\\ \text{complex}\end{matrix} \longrightarrow HCl + \left[C_3H_6N\right] \tag{1}$$

$$\left[C_3H_6N\right] \longrightarrow HCN + C_2H_5 \tag{2}$$

$$2\left[C_3H_6N\right] \longrightarrow N_2 + 2CH_3CH{=}CH_2 \tag{3}$$

where C_3H_6 represents a n-propylidene radical in the n-propyl chloride reaction and an isopropylidene radical in the isopropyl chloride reaction. In the latter case, reaction (2) must involve a rearrangement within the complex to produce an ethyl radical and HCN. The ethyl radicals would subsequently react with active nitrogen. Various reactions which might generate the observed C_2 hydrocarbons were considered.

To sum up, the order of reactivity of the various organic compounds with active nitrogen appears to be

radicals $>$ unsaturates and halides $>$ saturates.

Regardless of the postulated mechanisms of the reactions, the nature of the products seem to indicate that the organic compounds are degraded stepwise in units containing one carbon atom. This suggests that active nitrogen reacts in units of one nitrogen atom. Thus if N_2^* or N_3 are reactive species, it appears that they dissociate upon reaction.

Products attributable to radical-hydrocarbon reactions or radical recombination are virtually absent.

No indication has ever been found of hydrogen abstraction by active nitrogen.

The higher reactivity of the olefins and halides over that of the paraffins seems to indicate that active nitrogen reactions are facilitated by a region of high electron density in the reactant molecule. The shielding effect of the hydrogen atoms may also contribute to the lower reactivity of the paraffins.

The Present Problem

The reactions of active nitrogen with a series of unsaturated hydrocarbons, open chain and cyclo-saturated hydrocarbons, and organic chlorides have been studied.

In the present work, the series was extended to include amino type compounds. The investigation began with ammonia, the simplest amine, and proceeded through hydrazine and methylamine.

EXPERIMENTAL

MATERIALS

Anhydrous ammonia (Canadian Industries Ltd.) and C.p. ethylene (Ohio Chemical Co.) were used after a single bulb-to-bulb distillation under vacuum during which only the middle fraction was retained.

Anhydrous hydrazine (99% pure) was very kindly contributed by the Mathieson Chemical Corp. It was used after removal of a first fraction (5 - 10%) by vacuum distillation at room temperature.

To obtain methylamine, equal volumes of 25% methylamine solution (C.p., Fisher Scientific Co.) and 50% sodium hydroxide solution were cooled to 10°C and mixed in a flask. Nitrogen was bubbled through the mixture, and the gas stream passed through a condenser cooled with Dry Ice into a similarly cooled receiver containing potassium hydroxide pellets. About 10% of the recovered methylamine was removed by distillation under vacuum and discarded. The residue was distilled twice, with rejection each time of the last 20% to remove traces of water. Infra-red analyses of the final distillate showed that it contained 98.7% methylamine and 1.3% ammonia.

Nitrogen, obtained from the Dominion Oxygen Co., and known by mass spectrometer analysis to contain 0.1% oxygen, was purified of oxygen by passing the gas through copper turnings ("Chore Girl") heated to 400° - 450°C. A trap immersed in liquid nitrogen placed immediately after the furnace removed water from the nitrogen.

Hydrogen, obtained from the Dominion Oxygen Co., was dried by passing it through a liquid nitrogen trap.

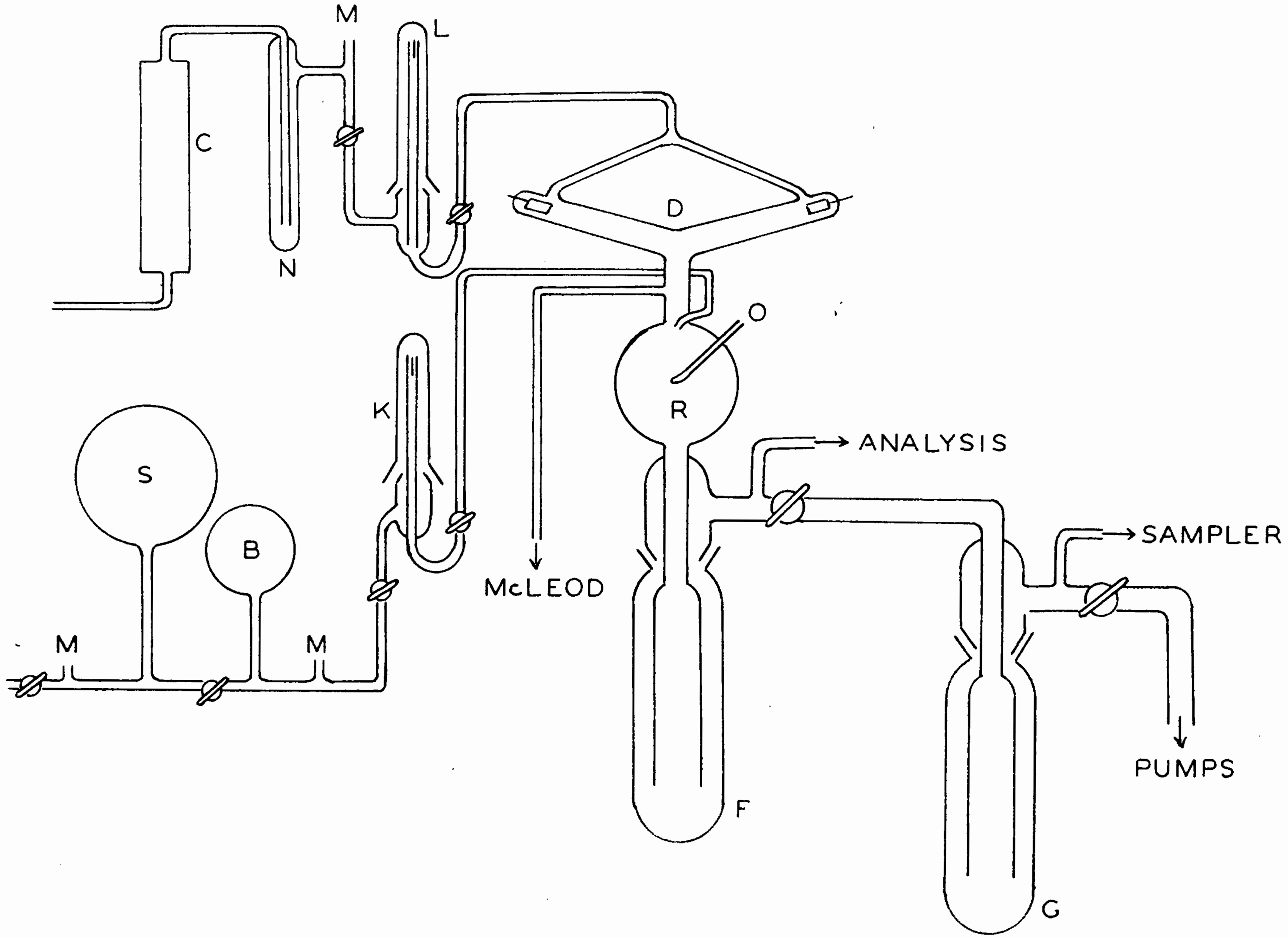
APPARATUS

The apparatus was a typical Wood-Bonhoeffer fast flow system constructed of Pyrex glass and is shown diagramatically in Figure 1.

Nitrogen was passed from a cylinder through a bubbler which could be adjusted to give a constant pressure head despite fluctuations in atmospheric pressure. Dibutyl phthalate was the liquid used in this simple manostat. From the manostat, the nitrogen passed through the hot copper turnings, C, and through the liquid nitrogen trap N. The purified nitrogen passed through a calibrated capillary flow meter, L, into both ends of a discharge tube, D. The activated nitrogen passed out the centre of the discharge tube, through 12 cm. of 18 mm. tubing,

FIGURE 1

DIAGRAM OF APPARATUS


M
L
C
N
D
O
R
K
S
B
M
M
→ ANALYSIS
→ SAMPLER
McLEOD
F
PUMPS
G

into the spherical reaction vessel, R. The dimensions of the connecting tube were such that the velocity of active nitrogen through it prevented the back diffusion of reaction gases into the discharge tube. The flow meter, L, was calibrated by measuring the rate of evacuation of a known volume.

The discharge tube, constructed from 25 mm. Pyrex glass tubing, was about 66 cm. in length and was bent in the middle to permit a solution of phosphoric acid to be drawn up into it without touching the electrodes. The electrodes were cylindrical pieces of aluminum attached to tungsten wires sealed into each end of the discharge tube.

Ammonia, ethylene and methylamine were stored as gases in a vessel of known volume, S. Because the pressure in the reactant reservoir, S, decreased with the time of flow, the gas was passed from the reservoir through a scratched stopcock into a ballast volume, B. Adjustment of the scratched stopcock made it possible to maintain a constant pressure in the ballast volume. The gas then passed through a capillary flow meter, K, and into the reaction vessel through a jet. This arrangement gave any desired reactant flow rate by choosing an appropriate ballast pressure. The amount of reactant used during an experiment was determined from the pressure change in the calibrated volume, S, read from the manometer M.

Since hydrazine is a liquid (boiling point 113°C) with a vapor pressure of 10 mm. at 20°C, it was not convenient to store it as a gas. It was stored as a liquid in a cylindrical bulb (cross sectional area=28 sq. cm.) which was connected to the vessel, S, through 8 mm. Pyrex tubing. The storage bulb was immersed in a thermostat regulated to 20.95±0.05°C. The scratched stopcock between S and B was always left open and the rate of flow of hydrazine into the reaction vessel was varied by placing jets of different sizes in the flow meter, K. The jets were calibrated by doing blank experiments in which the nitrogen was not activated.

The reaction vessel, R, was a 300 cc. spherical bulb. A copper-constantan thermocouple was placed in a well, O, in the centre of the reaction vessel to give an indication of the reaction temperature. Temperatures in the range 30° to 490°C were attained by an electrically heated furnace of asbestos molded around the reaction vessel. Low temperatures were attained by surrounding the reaction vessel with powdered Dry Ice.

All condensable products of the reaction were collected in two traps, F and G, cooled with liquid nitrogen. In this way all products except hydrogen, nitrogen and methane were removed quantitatively from the gas stream. Both traps were about 30 cm. long and of wider diameter than the remainder of the flow system to decrease the linear flow rate across the cold surface, thereby increasing the trapping efficiency.

Samples of the non condensable products were removed from the gas stream by a Toepler pump connected to the flow system after the second liquid nitrogen trap. These samples were compressed into bulbs for subsequent mass spectrometric analysis.

The walls of the discharge tube and reaction vessel were "poisoned" by drawing into these parts of the system a one per cent solution of phosphoric acid and allowing it to drain out slowly, leaving a thin film of phosphoric acid on the surface. Water was removed from the film by evacuating the system and pumping on it for several hours. The furnace on the reaction vessel was then turned on and heated to 450°C. and the pumping was continued for several more hours. The remaining film was probably dehydrated nearly to metaphosphoric acid.

The pumping system consisted of two rotary oil pumps (a Cenco Megavac and a Welsh Duoseal) operating in parallel. These gave an ultimate vacuum of 5×10^{-3} mm. Hg. A molecular nitrogen flow rate of 9.2×10^{-5}

mole/sec. through the flow meter was used in all experiments and this gave a pressure of 1.43 mm. Hg. in the reaction vessel.

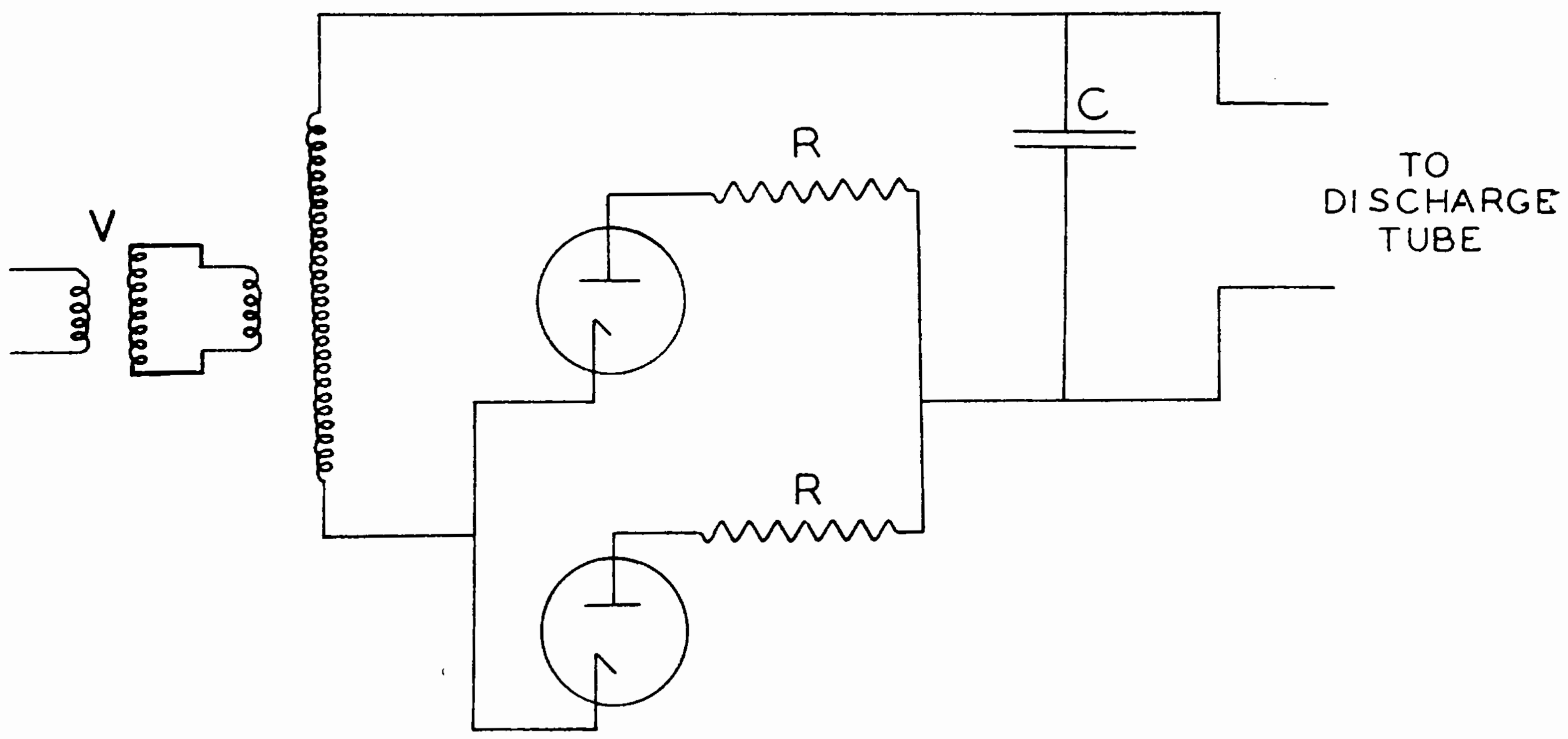
The electrical circuit used to generate the condensed discharge is represented in Figure 2. A 115 volt AC current was passed through a Variac, V, to the primary of a 3000 volt Hammond transformer. The current was rectified by two half-wave rectifier tubes (866-A) connected in parallel. The pulsating direct current from these tubes charged a 4 microfarad condenser, C, through 3000 ohm resistors, R. When a critical potential was reached, the condenser discharged through the discharge tube. The critical potential was dependent upon the distance between the electrodes and upon the nitrogen pressure in the discharge tube. With 45 volts across the primary of the transformer and 1.43 mm. Hg. pressure of nitrogen in the discharge tube, the discharge frequency was about 10 per sec.

PROCEDURE FOR A TYPICAL EXPERIMENT

The system was kept under vacuum at all times except when it was necessary to clean and repoison the reaction vessel or regrease stopcocks.

FIGURE 2

ELECTRICAL CIRCUIT


V
R
R
C
TO
DISCHARGE
TUBE

To prepare for an experiment, the furnace on the copper deoxygenating column and the one surrounding the reaction vessel were turned on several hours in advance to allow temperature equilibrium to be established. The pressure on the nitrogen flow meter was adjusted to 770±1 mm. Hg.

Before each series of experiments, active nitrogen and the reactant were allowed to react in the reaction vessel for several minutes to condition the walls.

At the beginning of each individual experiment, a trap containing a suitable reagent solution was connected to the tube marked 'analysis' by a ground glass joint. This trap was partially evacuated, immersed in liquid nitrogen to freeze the reagent solution, then completely evacuated. The nitrogen flow and the pulsating discharge were then turned on for five minutes to allow steady flow conditions to be established. The traps, F and G, were immersed in liquid nitrogen to a level which was kept constant from experiment to experiment. This ensured a constant interval between mixing the reactants and trapping the products. The temperature and pressure within the system were recorded.

The reaction was started by opening the stopcock between the reactant flow meter, K, and the reaction vessel. The pressure differential across the flow meter was maintained constant as described previously. After a few minutes, the temperature and pressure in the flow system were recorded again. The duration of an experiment, accurately measured with a stop watch, was governed by the time required to introduce sufficient reactant to be measured accurately or to obtain sufficient products for precise analysis. It varied from 2 to 50 minutes.

The reaction was stopped by turning off the reactant flow, the discharge and the nitrogen flow, in that order. The system was evacuated to 5×10^{-3} mm. Hg. to remove non-condensables. The trapping system was then isolated from the pumps and opened to the analysis trap which contained the frozen reagent solution. The Dewars containing the liquid nitrogen surrounding the product traps, G and F, were removed. If hydrogen cyanide was a product, the first trap, which contained essentially all the condensable products, was immediately immersed in carbon tetrachloride for about 10 seconds. The layer of carbon tetrachloride frozen on the outside of the trap in this manner prevented the liquefaction, and subsequent polymerization, of the hydrogen cyanide during the distillation. The final pressure after a one hour period was usually in the neighborhood of 10^{-2} mm. Hg. The residual pressure might have been due to small amounts of nitrogen or hydrogen which had been occluded on the trapped products.

The analysis trap, closed with a stopcock, was then separated from the system and warmed to room temperature.

ANALYTICAL PROCEDURE

Reaction with Ammonia

To analyse for ammonia, the analysis trap contained 10 ml. of 0.2N standard sulphuric acid. The amount of ammonia passed into the reaction vessel was estimated from the change in pressure in the reservoir, S, while the amount remaining unreacted was determined by titration to methyl red end point of the excess acid in the analysis trap. The amount of ammonia consumed was then given by the difference between these quantities. The presence of hydrogen cyanide did not affect the titration.

To test for hydrazine, the analysis trap contained 3 ml. conc. hydrochloric acid. To the warmed trap, 15 ml. distilled water and one ml. carbon tetrachloride were added, followed by 0.01N potassium iodate added dropwise to the continuously shaken mixture. Blank experiments indicated that the iodine liberated by 0.05 mgm. hydrazine imparted sufficient color to the carbon tetrachloride to permit its detection.

Reaction with Ethylene

Hydrogen cyanide was collected in the analysis trap containing 10 ml. of 1N sodium hydroxide. The trap was removed from the liquid nitrogen and the bottom end carefully immersed in hot water. This allowed some of the sodium hydroxide to melt without liquefaction of the hydrogen cyanide. By a rapid swirling motion, the hydrogen cyanide was dissolved in the hydroxide solution before polymerization could occur. The amount of cyanide present was then determined by making the solution ammoniacal and titrating it with 0.05N silver nitrate, using potassium iodide as the indicator (Liebig-Dénigès method (169)).

Reaction with Hydrazine

The condensable reaction products were collected in the analysis trap containing standard sulphuric acid. The total amount of base in the products was determined by titration to methyl red end point. The hydrazine content of the solution was then determined by adding an equal volume of concentrated hydrochloric acid and 3 ml. carbon tetrachloride and titrating the vigorously shaken mixture with 0.1N potassium iodate until iodine was no longer visible in the carbon tetrachloride (170). The difference between the amounts of total base and hydrazine gave the amount of ammonia. The amount of hydrazine initially passed into the reaction vessel was obtained by multiplying the reaction time by the known flow rate of hydrazine through the calibrated jet.

Reaction with Methylamine

The amount of methylamine passed into the reaction vessel was estimated from the change in pressure in the reservoir, S. Condensable products were collected in the analysis trap containing 10 ml. standard 0.2N sulphuric acid and their base content was determined by titration of the excess acid to methyl red end point. The presence of hydrogen cyanide did not affect the titration.

Ammonia was determined by infra-red analysis. The condensable reaction products were collected in an evacuated bulb immersed in liquid nitrogen, then distilled into an evacuated 10 cm. absorption cell with sodium chloride end windows. The wave numbers of the absorption peaks used were 968 $cm.^{-1}$ for ammonia and 2930 $cm.^{-1}$ for methylamine.

The hydrogen cyanide content of the condensable products was determined by the Liebig-Dénigès method (169).

In some experiments these products were also analysed for cyanogen. To do this, the condensable products were collected in the analysis trap containing 20 ml. of 0.5N silver nitrate solution and 0.5 ml. 6N nitric acid. The cyanogen was flushed out of the solution with nitrogen (1 hour), and the cyanogen removed from the nitrogen stream by bubbling it through potassium hydroxide solution. The cyanogen was immediately hydrolyzed by the hydroxide according to the equation

$$C_2N_2 + 2KOH \longrightarrow KCN + KCNO + H_2O$$

and was determined by a Liebig-Dénigès titration of the cyanide.

The total C_2 hydrocarbon fraction in the products was estimated with a LeRoy still, and its composition was determined with a mass spectrometer. The non-condensable products were similarly analysed for methane and hydrogen.

TEMPERATURE MEASUREMENT

The temperatures recorded might not have been the true temperatures of the reaction gases. If any reaction occurred on the surface of the thermocouple well, the temperature recorded by the thermocouple would be too high. The recorded temperatures may therefore be accepted only as an indication of the approximate reaction temperature.

Considerable temperature gradients probably existed in the reaction vessel. These would be greatest at low temperatures, due to heat loss through the walls, and at high reactant flow rates, due to a more localized zone of reaction under these conditions.

RESULTS

The temperature in the reaction vessel increased from room temperature to about $65^{\circ} \pm 10^{\circ}C$ when active nitrogen streamed through it. When the reactant was introduced, the temperature increased further, depending upon the rate and exothermicity of the reaction. In experiments at higher temperatures, during which the reaction vessel was heated with the furnace, the flow of active nitrogen alone raised the temperature by a smaller amount the higher was the furnace temperature (about 10° at $450^{\circ}C$). The increase in temperature due to the introduction of reactant also decreased as the furnace temperature increased. Since the temperature varied somewhat during any given experiment, only the maximum temperature reached was recorded.

The production of HCN from the ethylene-active nitrogen system was used to estimate the total active nitrogen concentration under conditions similar to those used to study the reactions with ammonia, hydrazine and methylamine. This method of estimation was used since hydrogen cyanide production from other hydrocarbons studied thus far has never been found to exceed that from ethylene.

Reaction of Active Nitrogen with Ammonia

During these experiments the molecular nitrogen flow rate was 9.2 x 10^{-5} mole/sec., which gave a pressure of 1.43 mm. in the reaction system. No detectable increase in pressure occurred during the active nitrogen-ammonia reaction. The Variac in the electrical circuit was set at 45 volts, which gave a discharge rate of about 9 to 10 per sec.

The reaction of ammonia with active nitrogen produced no visible reaction flame and the yellow afterglow of active nitrogen was not quenched completely even at the highest ammonia flow rate used.

A bluish-green glow appeared in the cold trap, F, during the reaction at all flow rates. This glow could also be produced by condensing some ammonia in the inner tube of the trap and passing active nitrogen over it.

No hydrazine was detected as a product from the active nitrogen-ammonia reaction over the temperature range -5°C to 440°C. The reaction products may therefore be assumed to be hydrogen and nitrogen only.

The relations between ammonia flow rate and the amount destroyed at different temperatures are shown in Table I and plotted in Figure 3A. The initial slope in Figure 3A is essentially the same at all temperatures over the range studied and corresponds to nearly complete destruction of ammonia. The rate of ammonia destruction at 69°C with flow rates greater than 2×10^{-6} mole/sec. remained constant at 1.77×10^{-6} mole/sec. The increased amounts of ammonia consumed at the low and high temperatures, relative to the value at 69°C, were suspected to be due to secondary hydrogen atom attack. The hydrogen atom-ammonia reaction was therefore studied over the temperature range -67° to 442°C, and the results are listed in Table II and plotted in Figure 3B. Ammonia decomposition occurred at -67° and 442°C but none was detected at 31°C.

During the hydrogen atom reactions the molecular hydrogen flow rate was 6.9×10^{-5} mole/sec., which gave an operating pressure of 0.85 mm. Hg. A Variac setting of 36 volts gave a continuous, bright red discharge.

No hydrazine was detected in the products of the hydrogen atom reaction at any temperature.

The low temperatures during the reactions of ammonia with active nitrogen (-5°C) and hydrogen atoms (-67°C) were attained by surrounding the reaction vessel with powdered Dry Ice. Dry Ice was carefully repacked around the vessel immediately before each experiment to ensure good contact between the coolant and the vessel wall.

TABLE I

Reaction of Ammonia with Active Nitrogen at Various Temperatures

T(°C)	NH_3 flow	NH_3 destroyed	T(°C)	NH_3 flow	NH_3 destroyed
	mole/sec. x 10^6			mole/sec. x 10^6	
-5±3	0.42	0.42	283±1	1.37	1.18
	0.96	0.93		2.92	1.83
	1.98	1.84		3.85	1.86
	2.91	2.30		9.07	1.93
	6.17	3.58			
	9.02	4.92			
	9.18	5.28	357±3	0.88	0.81
	13.28	7.18		3.13	1.66
				9.02	1.89
				12.81	2.37
69±7	0.40	0.38			
	0.67	0.63			
	2.91	1.74	442±1	2.88	1.77
	5.51	1.81		7.92	2.59
	9.03	1.77		10.80	3.79
	9.07	1.86		13.41	4.14
	9.16	1.70			
	13.38	1.75			
	13.52	1.77			

TABLE II

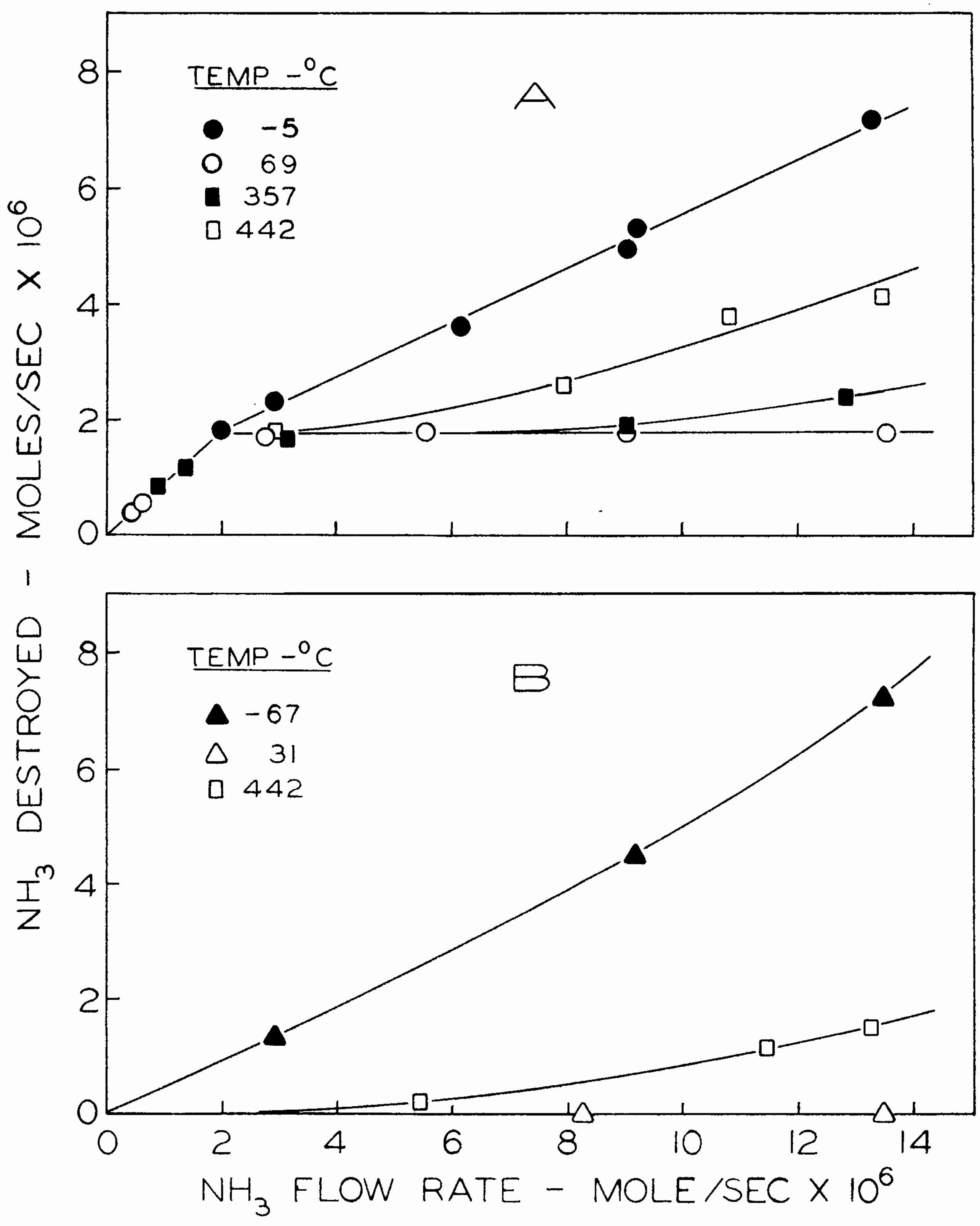
Reaction of Ammonia with Hydrogen Atoms at Various Temperatures

T(°C)	NH_3 flow	NH_3 destroyed
	mole/sec. x 10^6	
-67±1	2.96	1.33
	9.19	4.49
	13.49	7.21
31±1	8.25	0.00
	13.50	0.00
442±6	5.44	0.20
	11.47	1.11
	13.26	1.48

FIGURE 3

Fig. 3A - AMMONIA DESTRUCTION IN ACTIVE NITROGEN-AMMONIA REACTION AT DIFFERENT TEMPERATURES

Fig. 3B - AMMONIA DESTRUCTION IN HYDROGEN ATOM-AMMONIA REACTION AT DIFFERENT TEMPERATURES

A
TEMP -°C
● -5
○ 69
■ 357
□ 442
B
TEMP -°C
▲ -67
△ 31
□ 442
0
2
4
6
8
0
2
4
6
8
0
2
4
6
8
10
12
14
NH3 DESTROYED - MOLES/SEC X 10^6
NH3 FLOW RATE - MOLE/SEC X 10^6

Since most of the experiments were of short duration, and the low pressure reactants had low heat capacities, it is reasonable to assume that the temperature of the vessel walls was of the order of -70°C in both types of reaction, although the temperatures of the reaction gases, as recorded by the thermocouple, were quite different.

Ethylene and mixtures of ethylene and ammonia were also subjected to attack by active nitrogen, and the results are given in Table III and plotted in Figure 4. The furnace around the reaction vessel was not turned on for these experiments and the increase in temperature above room temperature was due to the heat of reaction.

Hydrogen cyanide production from pure ethylene at about 125°C reached a constant value of $10.0 \pm 0.2 \times 10^{-6}$ mole/sec. with ethylene flow rates greater than about 9×10^{-6} mole/sec. In both mixtures, with ammonia:ethylene ratios of 4.1 and 14.1, as the ammonia flow rate was increased, the rate of ammonia destruction appeared to level off at the same constant value as that found for pure ammonia (1.77×10^{-6} mole/sec.), whereas hydrogen cyanide production continued to increase rapidly as the ethylene flow rate increased.

A series of experiments was made in which the rate of production of base (probably ammonia) in the active

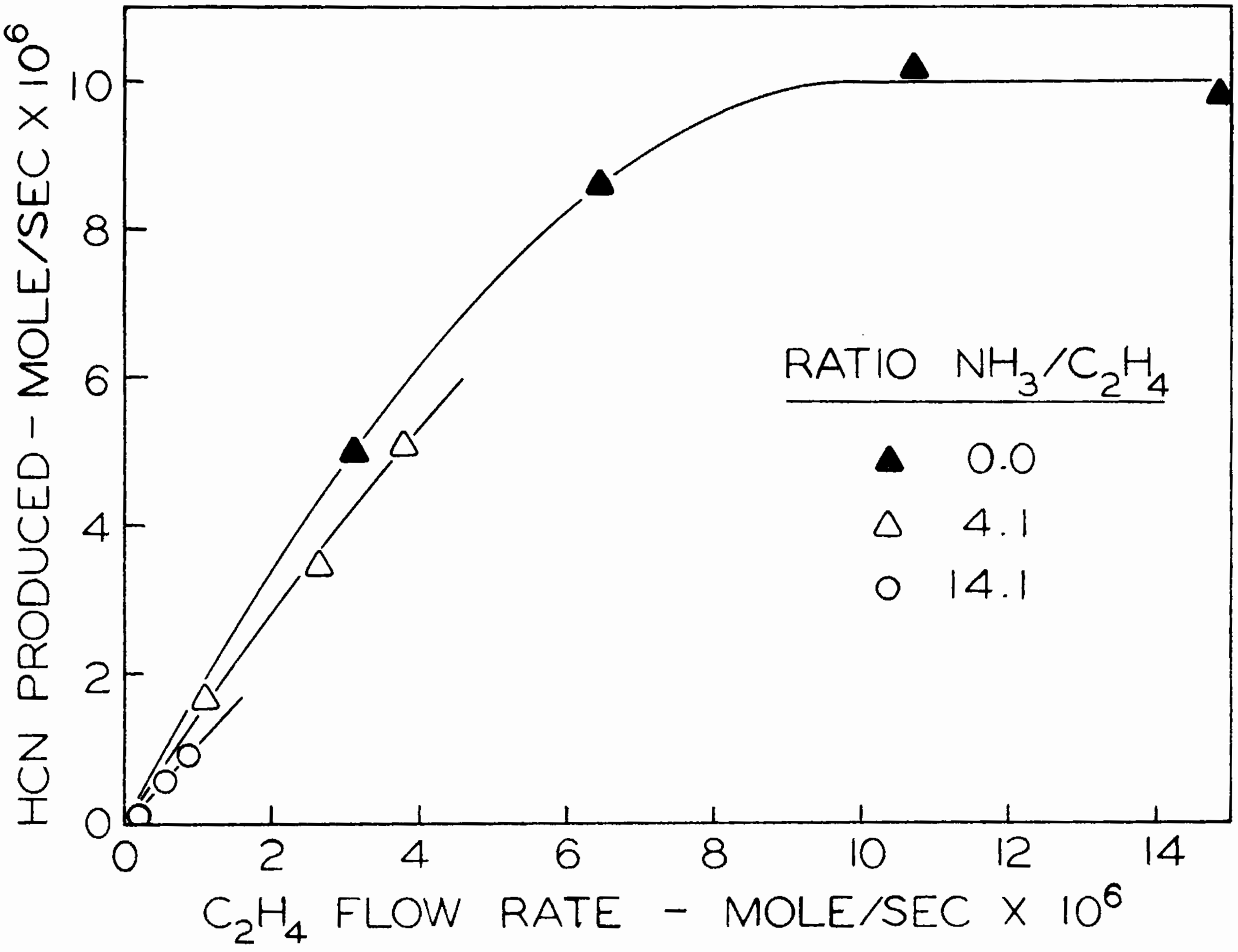
TABLE III

Reaction of Active Nitrogen with Ethylene-Ammonia Mixtures

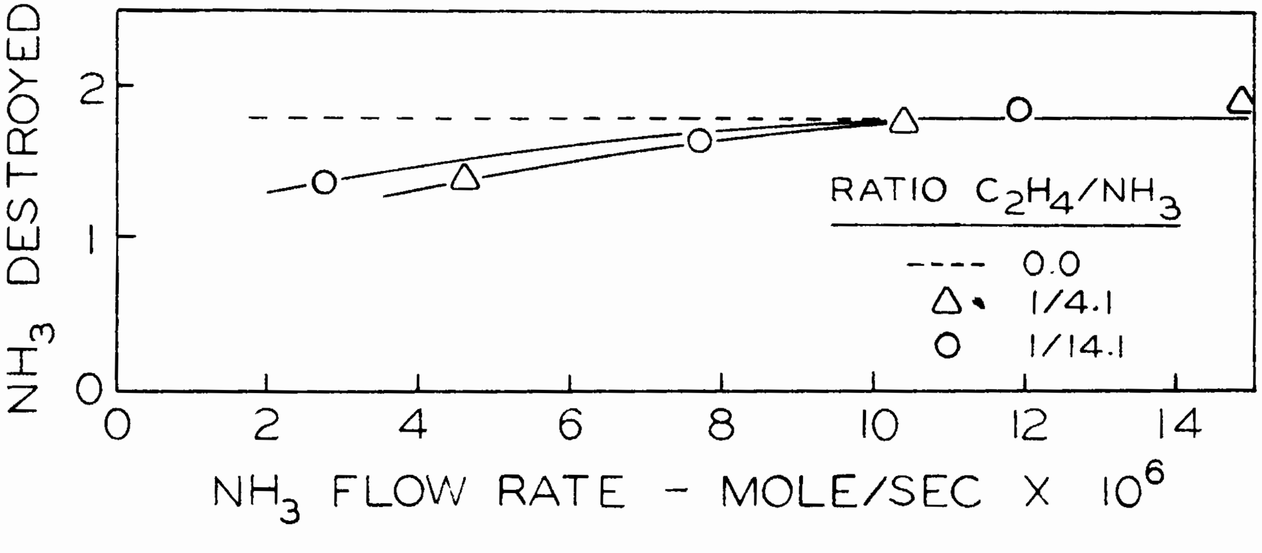
NH_3/C_2H_4	NH_3 flow	NH_3 destroyed	C_2H_4 flow	HCN produced	T(°C)
		mole/sec. x 10^6			
0	-	-	3.12	4.98	70
	-	-	6.48	8.60	120
	-	-	10.76	10.20	124
	-	-	15.17	9.85	127
4.13	4.63	1.36	1.10	1.62	86
	10.42	1.73	2.65	3.44	80
	15.53	1.91	3.77	5.09	95
14.1	2.78	1.36	0.19	0.06	73
	7.76	1.62	0.54	0.50	70
	11.93	1.85	0.87	0.88	71

FIGURE 4

HYDROGEN CYANIDE PRODUCTION AND
AMMONIA DESTRUCTION IN
ACTIVE NITROGEN REACTION WITH
AMMONIA-ETHYLENE MIXTURES



HCN PRODUCED - MOLE/SEC X 10^6
0
2
4
6
8
10
0
2
4
6
8
10
12
14
C2H4 FLOW RATE - MOLE/SEC X 10^6
RATIO NH3/C2H4
▲ 0.0
△ 4.1
○ 14.1



NH3 DESTROYED
0
1
2
0
2
4
6
8
10
12
14
NH3 FLOW RATE - MOLE/SEC X 10^6
RATIO C2H4/NH3
---- 0.0
△ 1/4.1
○ 1/14.1

nitrogen-ethylene system was measured. A blank was first done to check whether any base was formed due to an impurity in the nitrogen or in the reaction system. Active nitrogen was streamed through the two traps, F and G, surrounded by liquid nitrogen, for 46 minutes. After evacuation of the system, the liquid nitrogen was removed from the traps and any products were distilled into the analysis trap containing distilled water and methyl red indicator, immersed in liquid nitrogen. Since the indicator was the same color before and after the experiment it was concluded that no base was formed. With the ethylene experiments, which varied in duration from 1000 to 125 sec. as the ethylene flow rate increased from 1.19 to 31.85 x 10^{-6} mole/sec., the reaction products were similarly distilled into the analysis trap containing about 2ml. standard sulphuric acid, 7 ml. distilled water and 3 drops methyl red indicator. The amount of base in the resulting solution was determined by back titration with standard base. The amount of base formed decreased from 4.8% to 2.1% of the amount of hydrogen cyanide formed as the ethylene flow rate increased from 1.19 to 31.85 x 10^{-6} mole/sec.

Introduction of ethylene into the active nitrogen stream increased the gas temperature by about 50° (i.e., from about 70° to 120°), whereas the introduction of ammonia increased the temperature by only 2°.

Reaction of Active Nitrogen with Hydrazine

The active nitrogen-hydrazine reaction generated no visible reaction flame. The products of the active nitrogen-hydrazine reaction were nitrogen, hydrogen and ammonia. The relations between the hydrazine flow rate, the amount of hydrazine destroyed, and the corresponding amount of ammonia produced are shown in Table IV and plotted in Figure 5 for different temperatures. At both 150° and 480°C hydrazine was completely destroyed up to a flow rate of about 22×10^{-6} mole/sec. The maximum rate of destruction at 150°C was about 25×10^{-6} mole/sec. and increased by about 14% when the temperature was increased from 150° to 480°C.

Blank experiments, in which the nitrogen was not activated, were made at 450°C to measure the extent of thermal decomposition of hydrazine at this temperature. No thermal decomposition could be detected.

Ammonia production was small at hydrazine flow rates below about 14×10^{-6} mole/sec., but increased quite rapidly above this flow rate and leveled off again for hydrazine flow rates above about 24×10^{-6} mole/sec. The amount of ammonia produced at 480°C was smaller than

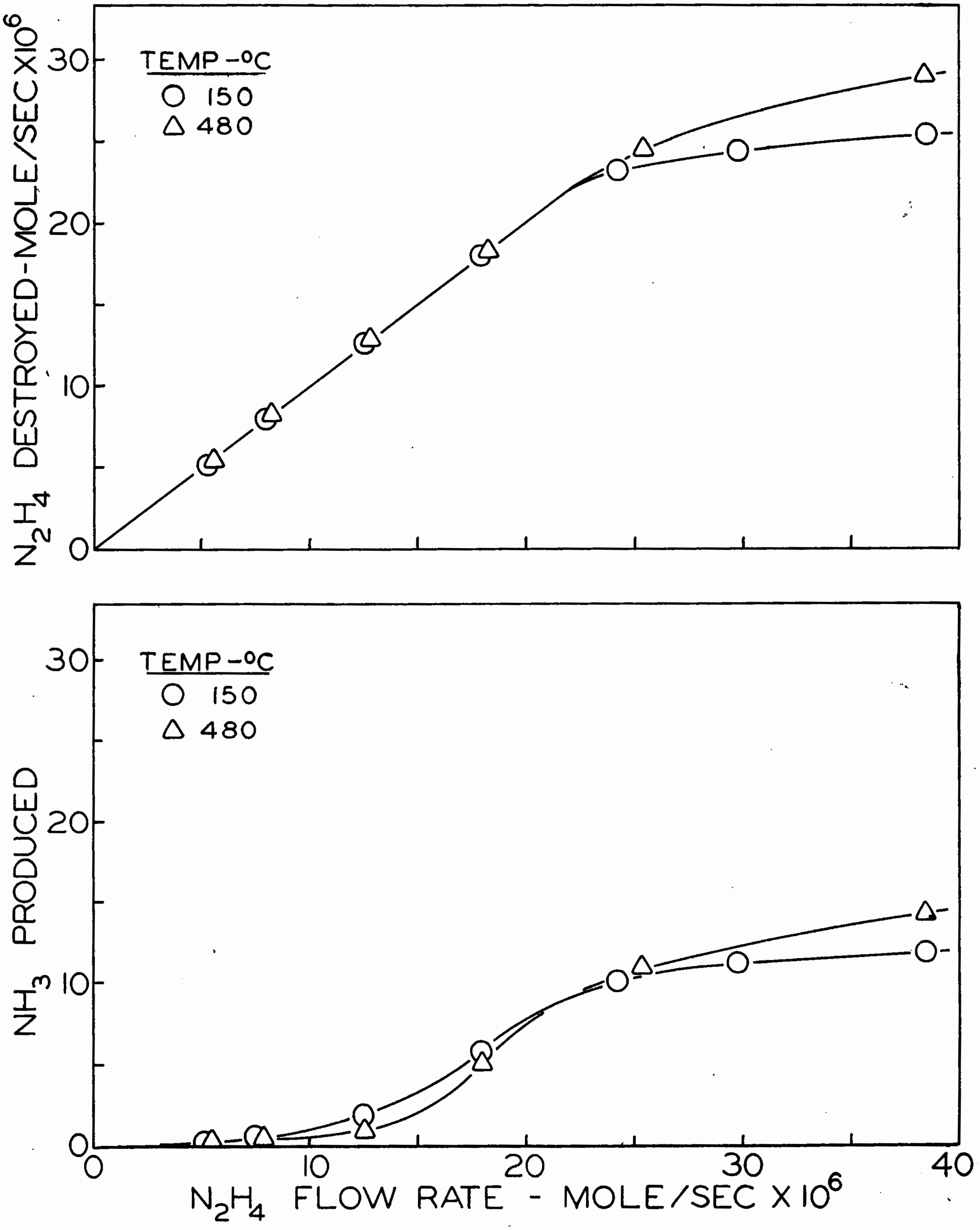
TABLE IV

Reaction of Active Nitrogen with
Hydrazine at Various Temperatures

T(°C)	N_2H_4 flow	N_2H_4 destroyed	NH_3 produced
		mole/sec. x 10^6	
150±6	5.3	5.3	0.31
	7.7	7.7	0.65
	12.6	12.6	1.90
	18.0	18.0	5.59
	24.3	23.3	10.0
	29.8	24.3	11.1
	38.5	25.4	11.9
480±5	5.3	5.3	0.35
	7.9	7.9	0.51
	12.6	12.6	0.93
	18.0	18.0	5.04
	25.4	24.4	10.74
	38.5	28.8	14.5

FIGURE 5

HYDRAZINE DESTRUCTION AND AMMONIA PRODUCTION
IN ACTIVE NITROGEN-HYDRAZINE REACTION
AT DIFFERENT TEMPERATURES


N_2H_4 DESTROYED-MOLE/SEC X 10^6
TEMP -°C
○ 150
△ 480
0
10
20
30
NH_3 PRODUCED
TEMP -°C
○ 150
△ 480
0
10
20
30
0
10
20
30
40
N_2H_4 FLOW RATE - MOLE/SEC X 10^6

the amount produced at 150°C in the range of lower flow rates, but the reverse was true at the higher flow rates (above about 20 x 10^{-6} mole/sec.).

The over-all reaction was extremely exothermic, because introduction of hydrazine into the active nitrogen stream increased the gas temperature from about 70° to about 150°C, i.e., an increase of about 80°.

When nitrogen alone was flowing through the system at a rate of 9.2 x 10^{-5} mole/sec., which gave an operating pressure of 1.43 mm. Hg., a Variac setting of 45 volts in the electrical circuit gave a discharge rate of between 7 and 10 per sec. However, as hydrazine was introduced into the system at increasing flow rates, the pressure increase due to the large amounts of non condensable products formed was so great that the Variac setting had to be increased to maintain a discharge rate of 7 per sec., and a setting of 52 volts was required for hydrazine flow rates above 24 x 10^{-6} mole/sec. (The pressure in the system under these conditions was 2.1 mm. Hg.). Increasing the Variac voltage increases the power of the discharge, thereby increasing the amount of active nitrogen produced. The active nitrogen concentration was therefore estimated under similar conditions with the ethylene system at 451°C and was found to be $19.0 \pm 0.4 \times 10^{-6}$ mole/sec.

In the hydrazine-active nitrogen system the yellow afterglow of active nitrogen was observable in the tube leading from the reaction vessel to the cold trap at all hydrazine flow rates until that corresponding to the maximum rate of decomposition of hydrazine was approached (up to about 20×10^{-6} mole/sec.). In the ethylene-active nitrogen reaction, the yellow afterglow was gradually replaced by the cyanogen flame; at 420°C, no nitrogen afterglow could be observed at flow rates of ethylene above about 1×10^{-6} mole/sec. However, at this temperature the cyanogen flame was observable in the tube leading from the reaction vessel to the cold trap at all ethylene flow rates until that corresponding to the maximum rate of production of hydrogen cyanide was approached (up to about 13×10^{-6} mole/sec.).

There was a possibility that hydrogen atoms might be formed from the attack of active nitrogen on hydrazine. Although the hydrogen atom-hydrazine reaction has been studied (54, 73), some experiments were made in the present apparatus to permit a more direct estimate of the extent to which hydrogen atom reactions might contribute to the over-all active nitrogen-hydrazine reaction. During these experiments the molecular hydrogen flow rate was 8.0×10^{-5} mole/sec., which gave an operating pressure of 1.0 mm. Hg. A Variac setting of 36 volts gave a continuous, bright red discharge.

The hydrazine-hydrogen atom reaction was studied at 48° and 458°C., and the results are listed in Table V and plotted in Figure 6. At 48°C., approximately one mole of ammonia was produced for each mole of hydrazine destroyed. At 458°C., (1-x) mole of ammonia was formed for each mole of hydrazine destroyed, where $0<x<1$. The value of x decreased, i.e., ammonia production increased, as the hydrazine flow rate was increased.

A small amount of product which decomposed to form non condensable gases on warming was trapped out of the reaction gases at very high hydrazine flow rates (greater than 24×10^{-6} mole/sec.) in the active nitrogen reaction, and at all hydrazine flow rates in the hydrogen atom reaction. The amount formed was determined only approximately by measuring the residual pressure in the reaction system after the products had been allowed to distil into the analysis trap for two to three hours. This residual pressure was then multiplied by the approximate volume of the reaction system. The amount of decomposable product collected increased with increasing hydrazine flow rate and increasing temperature, and was roughly parallel to the ammonia formation. The maximum amount of gas collected under any conditions, however, corresponded to only about 3% of the amount of ammonia on a molar basis.

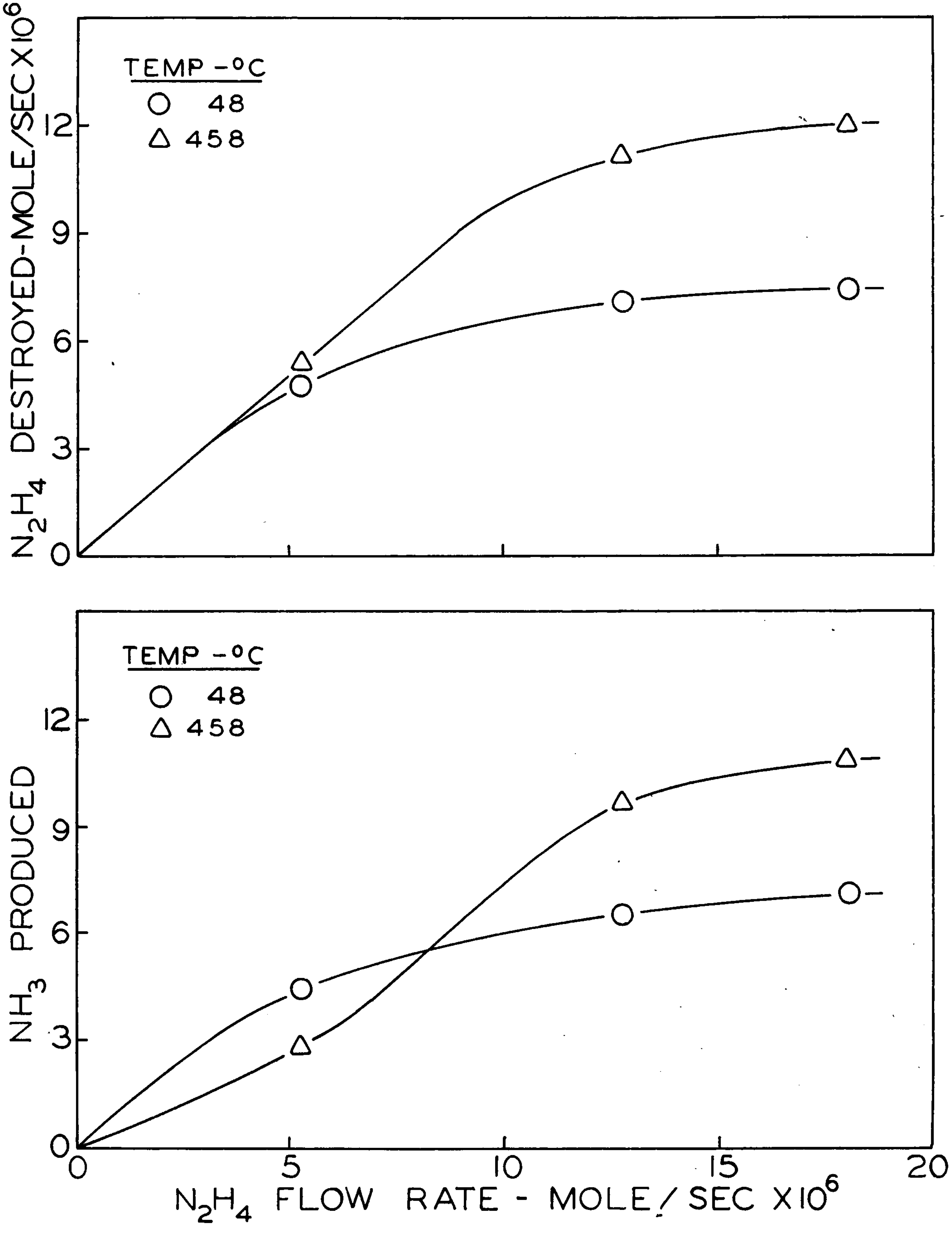
TABLE V

The Reaction of Hydrogen Atoms with Hydrazine at Various Temperatures

T(°C)	N_2H_4 flow	N_2H_4 destroyed	NH_3 produced
		mole/sec. x 10^6	
48±1	5.30	4.69	4.38
	12.8	7.03	6.46
	18.3	7.4	7.05
458±1	5.30	5.30	2.75
	12.8	11.1	9.57
	18.3	12.0	10.80

FIGURE 6

HYDRAZINE DESTRUCTION AND AMMONIA PRODUCTION IN HYDROGEN ATOM-HYDRAZINE REACTION AT DIFFERENT TEMPERATURES



TEMP -°C
○ 48
△ 458
N$_2$H$_4$ DESTROYED-MOLE/SEC X10^6
0
3
6
9
12
TEMP -°C
○ 48
△ 458
NH$_3$ PRODUCED
0
3
6
9
12
0
5
10
15
20
N$_2$H$_4$ FLOW RATE - MOLE/SEC X10^6

Mass spectrometric analysis of a sample of the gas showed that it contained 14% hydrogen and 86% nitrogen.

Reaction of Active Nitrogen with Methylamine

The reactions of active nitrogen with all hydrocarbons and organo-halides studied thus far have been accompanied by the cyanogen flame. The relative intensities of the various bands in the cyanogen flame varies as the type of compound varies, and the color varies from lilac to a bright peach. The flame is, obviously, associated with the carbon-nitrogen bonds but it is not known definitely whether the flame is excited during the formation of the bonds or whether the cyano group is excited subsequently by energy transfer from active nitrogen, or both.

The active nitrogen-methylamine reaction generated a bright peach-colored flame at low methylamine flow rates which decreased in intensity as the methylamine flow rate was increased. At the highest flow rates, the flame was quite dull and seemed to be localized near the vessel walls. Curiously enough, at extremely low flow rates (below 0.9×10^{-6} mole/sec.) the flame was not steady but occurred in brilliant flashes with a frequency of about two per second. The flash started at the bottom of the reaction vessel and passed upwards, against the direction of gas flow, to fill the lower half of the reaction vessel. As the methylamine flow rate was decreased further, the flashes increased in frequency and volume and decreased in intensity until only a flicker in the flame, which then filled the entire reaction vessel, could be noticed. As the methylamine flow rate was increased, the transition from pulsing to steady reaction flame was quite sharp and occurred at a flow rate of about 0.9×10^{-6} mole/sec. above which flow rate the flame again occupied the entire reaction vessel. Although this strange behavior would seem to indicate a chain reaction, no explanation can be offered as yet.

The molecular nitrogen flow rate during these experiments was 9.2×10^{-5} mole/sec., which gave a pressure of 1.43 mm. Hg. in the reaction system. The pressure during the reaction increased gradually as the methylamine flow rate and temperature were increased, and reached a maximum of 1.6 mm. with methylamine flow rates above about 9×10^{-6} mole/sec. at 477°C. A Variac setting of 46 volts gave a discharge rate of about 7 per sec. under these conditions.

Introduction of methylamine into the active nitrogen stream increased the gas temperature from about 70° to about 100°C, i.e., a temperature increase of about 30°.

The products of the reaction between active nitrogen and methylamine were found to be hydrogen cyanide and hydrogen, with smaller amounts of ammonia and a polymer, and traces of cyanogen, methane, ethane, ethylene and acetylene. The results are shown in Tables VI to IX and plotted in Figures 7 and 8.

In Figure 7 the flow rate of methylamine is plotted for different temperatures against (i) a quantity, $\triangle$(Base), defined as the flow rate of methylamine introduced minus the flow rate of total base found in the condensable products (i.e. residual methylamine plus ammonia produced) - see also Table VI - and (ii) the flow rate of ammonia produced - see Table VII. Obviously, (i) plus (ii) gives the rate of destruction of methylamine. The relations at different temperatures between the methylamine flow rate, the rate of destruction of methylamine, and the rate of production of hydrogen cyanide are shown graphically in Figure 8 and listed in Tables VIII and VI respectively. The rates of production of hydrogen, methane, cyanogen, ethane, ethylene and acetylene are shown in Table IX. The C_2 hydrocarbons were approximately 20% ethane, 30% ethylene, and 50% acetylene.

The rate of methylamine destruction increased rapidly with increasing temperature in the range -7° to 263°C,

TABLE VI

Hydrogen Cyanide Production and Δ(Base)* in the Active Nitrogen-Methylamine Reaction at Different Temperatures

(all units except temperature are mole x 10^{-6}/sec.)

T(°C)	CH_3NH_2 flow	HCN produced	Δ(Base)	T(°C)	CH_3NH_2 flow	HCN produced	Δ(Base)
477±5	0.58	0.25	0.58	263±1	6.04	5.65	5.65
	1.63	1.28	1.55		10.22	7.51	7.74
	5.62	5.07	5.29		12.69	7.16	7.36
	7.87	7.24	7.36		15.83	8.24	8.45
	9.43	8.44	8.36				
	12.21	9.29	9.21				
	13.17	8.62	8.22	99±5	0.55	0.38	0.53
	15.16	8.46	8.54		1.69	1.26	1.43
	16.67	7.40	7.50		2.82	1.95	2.25
	16.94	8.64	8.55		4.66	2.57	2.75
					7.06	3.09	3.65
					9.32	3.47	3.91
387±2	3.60	3.30	3.24		12.13	4.57	5.10
	7.05	6.56	6.35		14.59	4.64	5.00
	10.31	8.00	7.94		15.70	4.77	5.10
	12.92	8.40	8.40				
	14.91	8.94	9.05				
	16.82	8.72	8.79	-7±4	1.01	0.10	0.78
	17.00	7.80	8.00		1.18	0.13	0.78
					2.80	0.26	1.55
					6.56	0.13	1.74
					9.66	0.24	2.06
					14.23	0.18	1.62

* Δ(Base)= flow rate of methylamine introduced minus the flow rate of total base found in the condensable products (i.e., residual methylamine plus ammonia produced).

TABLE VII

Ammonia Production in the Active Nitrogen-Methylamine Reaction at Different Temperatures

(all units except temperature are mole x 10^{-6}/sec.)

T(°C)	CH_3NH_2 flow	NH_3 produced
477±5	2.21	0.27
	7.38	0.76
	8.92	0.88
	11.11	1.79
	13.54	1.98
	15.43	2.19
84±8	2.06	0.28
	7.35	1.25
	11.83	1.00
-4±3	2.24	0.29
	7.39	0.84
	11.14	1.22

TABLE VIII

Methylamine Destruction by Active Nitrogen at Different Temperatures

(all units except temperature are mole x 10^{-6}/sec.)

T(°C)	CH_3NH_2 flow	CH_3NH_2* destroyed
477	3.0	3.2
	6.0	6.3
	8.0	8.3
	9.0	9.2
	10.0	9.8
	12.0	10.3
	14.0	10.6
	16.0	10.7
99	2.0	2.0
	3.0	2.7
	5.0	3.5
	8.0	4.6
	12.0	5.8
	15.0	6.3
-7	1.0	0.9
	2.0	1.6
	3.0	2.0
	5.0	2.4
	8.0	2.6
	12.0	2.9
	15.0	3.0

* CH_3NH_2 destroyed = Δ(Base) + NH_3 produced.

TABLE IX

Production of H_2, CH_4, C_2N_2, and C_2 Hydrocarbons in the Active Nitrogen-Methylamine Reaction at Different Temperatures

(all units except temperature are mole x 10^{-6}/sec.)

T(°C)	CH_3NH_2 flow	H_2	CH_4	C_2N_2	C_2 total	C_2H_6	C_2H_4	C_2H_2
477±4	7.01	13.7	0.00	0.010	0.010	0.001	0.002	0.007
	10.4	17.7	0.18	0.003	0.092	0.055	0.015	0.022
	10.4				0.118			
103±4	0.56			0.015				
	1.57			0.010				
	7.11		0.00	0.003	0.041	0.001	0.026	0.014
	7.23				0.031			
	10.29	9.2	0.11	0.000	0.095	0.015	0.033	0.047
	12.47			0.000				
-2±2	0.96	1.88	0.00					
	1.68				0.02	0.000	0.004	0.016
	7.10	3.04	0.00					
	7.55				0.065			

FIGURE 7

ACTIVE NITROGEN-METHYLAMINE REACTION
AT DIFFERENT TEMPERATURES

Δ(BASE), DEFINED AS FLOW RATE OF METHYLAMINE INTRODUCED MINUS THE FLOW RATE OF TOTAL BASE FOUND IN THE PRODUCTS (I.E. RESIDUAL METHYLAMINE PLUS AMMONIA PRODUCED)

AMMONIA PRODUCTION

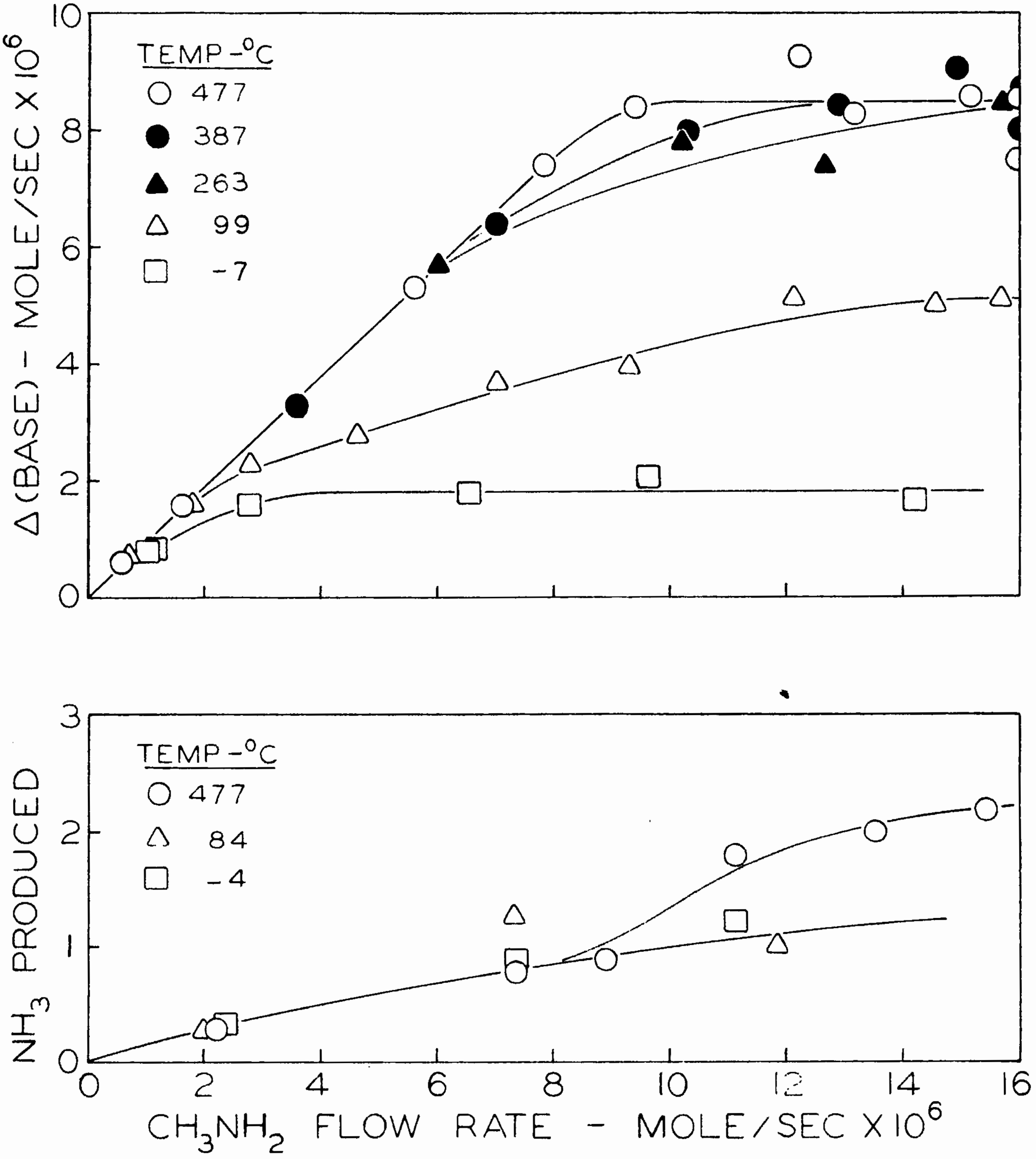
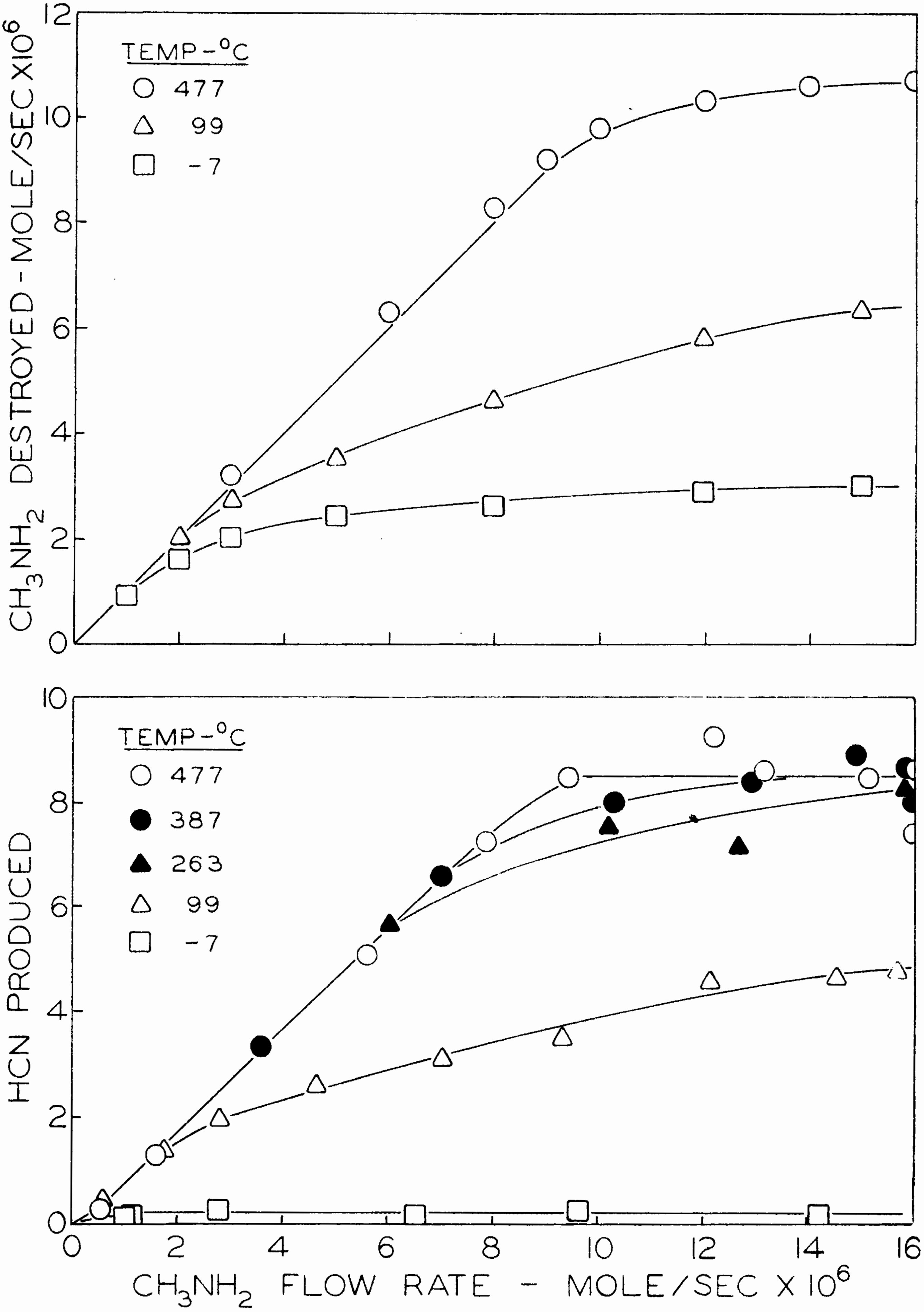

TEMP - °C
○ 477
● 387
▲ 263
△ 99
□ -7
Δ (BASE) - MOLE/SEC X 10^6
0
2
4
6
8
10
TEMP - °C
○ 477
△ 84
□ -4
NH3 PRODUCED
0
1
2
3
0
2
4
6
8
10
12
14
16
CH3NH2 FLOW RATE - MOLE/SEC X 10^6

FIGURE 8

ACTIVE NITROGEN-METHYLAMINE REACTION AT DIFFERENT TEMPERATURES

METHYLAMINE DESTRUCTION

HYDROGEN CYANIDE PRODUCTION



CH_3NH_2 DESTROYED - MOLE/SEC X10^6
TEMP - °C
○ 477
△ 99
□ -7
0
2
4
6
8
10
12
HCN PRODUCED
TEMP - °C
○ 477
● 387
▲ 263
△ 99
□ -7
0
2
4
6
8
10
0
2
4
6
8
10
12
14
16
CH_3NH_2 FLOW RATE - MOLE/SEC X 10^6

and then more slowly until, at 477°C, methylamine was completely destroyed at all flow rates up to that corresponding to complete consumption of active nitrogen. This can be seen most easily from the Δ(Base) curves in Figure 7 because, although ammonia production was measured at only three temperatures, similar amounts were produced at each. Thus all the Δ(Base) curves would be shifted up by similar amounts to form methylamine destruction curves.

Nearly two moles of hydrogen were produced for each mole of methylamine destroyed. Methane was not produced at methylamine flow rates below about 8×10^{-6} mole/sec., and the amount produced above that flow rate increased with increasing temperature. Cyanogen production decreased with increasing methylamine flow rate and increased with increasing temperature. The amount of C_2 hydrocarbons produced at methylamine flow rates below about 8×10^{-6} mole/sec. increased with decreasing temperature.

The amount of hydrogen cyanide produced and the quantity Δ(Base) corresponded very closely at 477°C. In other words, the difference between the amount of methylamine destroyed and the amount of hydrogen cyanide produced corresponded closely to the amount of ammonia produced at this temperature. The amount of carbon in this difference is much more than that contained in the methane, cyanogen and C_2 hydrocarbons. As the temperature was decreased, the amount of carbon which was measured in the products decreased progressively, and at Dry Ice temperature (gas phase temperature about -5°C) it corresponded to only about 10% of the amount of methylamine destroyed. However, at this low temperature, the walls of the reaction vessel became coated with a solid white polymer which melted upon warming to room temperature. The liquid turned light yellow upon standing. During the course of several experiments in the uncleaned reaction vessel, the polymer turned into a light brown solid, which did not melt at room temperature. It was assumed that, at all temperatures, the polymer accounted for the carbon which was not measured in the products.

As in the ammonia experiments, it seems reasonable to assume that, when the reaction vessel was surrounded with powdered Dry Ice, the wall temperature was of the order of -70°C although the reaction gases were at about -5°C. The Dry Ice was removed before the reaction products were distilled into the analysis trap.

Infra-red analysis of the products of a blank experiment at 470°C, in which the nitrogen was not activated, showed 1.9% ammonia in the methylamine. Since only 1.3%

ammonia was found in blanks done at room temperature, a small amount of thermal decomposition might have taken place at 470°C.

DISCUSSION

REACTIONS OF AMMONIA WITH ACTIVE NITROGEN AND HYDROGEN ATOMS

For conciseness, a brief discussion of the ammonia-hydrogen atom reaction will be given before the reaction of ammonia with active nitrogen is discussed.

Although no reaction was observed between ammonia and hydrogen atoms at 31°C, there was considerable reaction at both -67° and 442°C. The amount of ammonia decomposed at -67°C was about five times the amount destroyed at 442°C (Figure 3B), but part of this difference was probably due to a lower hydrogen atom concentration at the higher temperature.

The fact that reaction occurs at very high and very low temperatures but not at intermediate temperatures indicates that a change of mechanism in the reaction probably occurs with change of temperature. By analogy with hydrogen atom-hydrocarbon reactions, the mechanism at high temperatures is probably

$$H + NH_3 \longrightarrow NH_2 + H_2 \qquad \Delta H = 3 \text{ kcal.}^{*} \qquad (1)$$

---

[*] The method of, and material for calculating the heats of the reactions in the 'Discussion' of this thesis are also given in Appendix A.

followed by recombination of the NH_2 radicals to form nitrogen, hydrogen and possibly hydrazine, although none was detected in the reaction products. If hydrazine were formed, it would be subsequently decomposed by reaction with hydrogen atoms to produce ammonia, nitrogen and hydrogen (48, 67) which would decrease the over-all efficiency of the reaction. The recombination of NH_2 radicals with H atoms would also decrease the over-all efficiency of the reaction.

The reaction at low temperatures is more difficult to explain. The fact that the reaction rate increases rapidly with decreasing temperature probably indicates that it occurs on the walls of the reaction vessel, since it is very difficult to conceive a gas phase reaction between hydrogen atoms and ammonia that would have a large negative temperature coefficient. The decomposition might therefore proceed through a reaction such as

$$NH_3 + H \longrightarrow NH_4 \tag{2}$$

which might occur either in the gas phase or on the walls, followed by decomposition of the NH_4 radicals on the walls. Although this particular mechanism is sheer speculation, it might be pointed out that reaction (2) was one of the many different reactions which have been postulated to explain the low hydrogen atom concentration present during the photolysis of ammonia at room temperature (56).

Comparison of the curves for destruction of ammonia by active nitrogen and hydrogen atom reactions at different temperatures (Figures 3A, 3B) shows that the increased amounts of ammonia destroyed in the active nitrogen reaction at low and high temperatures, relative to the optimal value at 69°C, were due to secondary hydrogen atom attack. It may therefore be concluded that the reaction between active nitrogen and ammonia is unaffected by temperature over the range -5° to 442°C. It follows, therefore, that the constant amount (1.77×10^{-6} mole/sec.) of ammonia destroyed at 69°C, for ammonia flow rates above 2×10^{-6} mole/sec., corresponds to complete consumption of the active nitrogen with which ammonia is capable of reacting.

The reaction of ethylene with active nitrogen under similar conditions at 120°C produced a maximum of 10.0×10^{-6} mole/sec. of hydrogen cyanide (Figure 4), and it was later found that raising the temperature to about 350°C increased this amount by about 20%. A further increase in temperature did not increase hydrogen cyanide production appreciably. Thus the total flow rate of active nitrogen which is capable of producing hydrogen cyanide from ethylene under these conditions may be taken as 12 x 10^{-6} mole/sec. It is apparent, then, that active nitrogen produced under similar conditions was capable of producing hydrogen cyanide at a rate nearly 7 times greater than it was capable of destroying ammonia. Having regard particularly for the negligible influence of temperature on the ammonia reaction, the difference in behavior of ammonia and ethylene is difficult, if not impossible, to explain by any reasonable scheme based on a single reactive species in active nitrogen such as, for example, partial deactivation by ammonia without decomposition.

On the other hand, it is readily explained if two reactive species are assumed to be present, one of which is capable of reacting with ammonia while the other, or both, may react with ethylene.[*]

Further evidence for the presence of two reactive species was obtained by reacting ammonia-ethylene mixtures with active nitrogen. Although the rate of ammonia destruction in both mixtures levelled off at a value

---

[*] Although the present results do not preclude the possibility that more than two reactive species are present in active nitrogen (for example, different excited states of atoms and/or molecules), it seems reasonable as a working hypothesis to limit consideration to two until such time as further investigation might require recognition of more than this number.

essentially the same as that for pure ammonia, hydrogen cyanide production continued to increase rapidly (Figure 4). In other words, in the same gas mixture, the component which was capable of ammonia destruction was completely consumed whereas that which produced hydrogen cyanide from ethylene was not. If a correction were applied to the curves for ammonia destruction to take account of the amount of base formed during the ethylene reaction, the curves would be raised slightly. The maximum correction would have been within experimental error of the curves (0.1×10^{-6} mole/sec.), and could not be intelligently applied in any case, since it is not known which active species led to formation of a basic product from ethylene.

The yellow afterglow of active nitrogen in the hydrazine system, and the cyanogen flame in the ethylene system persisted into the tube leading from the reaction vessel to the cold trap only for reactant flow rates below that corresponding to the maximum amount of reaction. The yellow afterglow persisted in the ammonia reaction up to flow rates much higher than that corresponding to the maximum rate of destruction of ammonia. This may be taken as a further indication of the presence of two reactive species in active nitrogen. The persistence of the yellow afterglow implies the persistence of nitrogen which contains at least 170 kcals. of energy, i.e., a species with sufficient energy to generate nitrogen molecules in the $B^3\Pi_g$ state.

The possible identities of the two reactive species are a matter of conjecture. However, since there appears to be no evidence for the presence of significant quantities of ions, and there is considerable evidence for the presence of at least some atoms, it seems reasonable to suggest that the two species are atoms and either excited molecules or N_3. It also seems reasonable to assume that nitrogen atoms, rather than excited molecules or N_3, might attack the ammonia molecule at the site of its free pair of electrons to cause the high rate of destruction observed experimentally. The present results also indicate that a facile equilibrium does not exist between the two species, whatever their identities.

Thus the over-all reaction mechanism suggested for the ammonia-active nitrogen system is

$$N + NH_3 \longrightarrow N_2 + H_2 + H \qquad \Delta H = -50 \text{ kcal.} \quad (3)$$

followed by hydrogen atom attack on ammonia, which differs at different temperatures.

The energy required to dissociate an N_3 or an excited N_2 molecule should make the reaction of these particles with ethylene slower, and of higher activation energy, than the reaction of nitrogen atoms. However, if excited molecules are assumed to be the second reactive species, the relatively high rate of the active nitrogen-ethylene reaction might be explained by assuming a chain reaction initiated by atomic nitrogen, for example

$$
\begin{array}{lclcr}
 & & & \underline{\Delta H\ (\text{kcal.})} & \\
N + C_2H_4 & \longrightarrow & HCN + CH_3 & -59 & (4) \\
CH_3 + N_2^* & \longrightarrow & HCN + H_2 + N & -(112-E) & (5)
\end{array}
$$

where E is the energy required to dissociate N_2^*. Some hydrogen cyanide might also form by

$$
\begin{array}{lclcr}
 & & & \underline{\Delta H\ (\text{kcal.})} & \\
C_2H_4 + N_2^* & \longrightarrow & HCN + CH_3 \quad N & -(59-E) & (6) \\
 & \longrightarrow & 2HCN + 2H & -(68-E) & (7)
\end{array}
$$

If N_3 were the other reactive species, the reactions would be essentially the same as those of N (with the additional production of N_2), and a chain reaction might involve hydrogen atoms as chain carriers, for example, reaction (4) followed by

$$
\begin{array}{lclcr}
 & & & \underline{\Delta H\ (\text{kcal.})} & \\
N + CH_3 & \longrightarrow & HCN + 2H & -10.7 & (8) \\
H + C_2H_4 & \longrightarrow & C_2H_5 & -32 & (9) \\
C_2H_5 + N_3 & \longrightarrow & HCN + CH_3 + H + N_2 & -(26-E) & (10)
\end{array}
$$

where E is the dissociation energy of the N_2-N bond in

N_3. Some formation of hydrogen cyanide might also occur by

$$C_2H_4 + N_3 \longrightarrow HCN + CH_3 + N_2 \qquad \Delta H = -(57.5 - E)\text{kcal.} \qquad (11)$$

It might be suggested that if reaction (6) occurred, the destruction of ammonia should be greater in the presence of appropriate amounts of ethylene than in pure ammonia. However, a nitrogen atom formed in such a reaction would be available for attacking ammonia in an ammonia-ethylene mixture only if it were not rapidly consumed by the CH_3 radical formed simultaneously with it.

Walsh (193) has suggested that it is important to consider the spins of the reactants and products of any reaction step since any process which involves a change of spin is improbable. Spin would be conserved in reactions (1), (2), (8) and (9) (3/8 of the collisions in reaction (8) would be effective on a spin basis). However, if the nitrogen atoms are in their ground state (^4S) spin would not be conserved in reactions (3) and (4), although spin might be conserved in reaction (4) if the hydrogen cyanide molecule has a triplet level with less than 59 kcal. excitation energy. Reactions (3) and (4) would conserve spin if the atoms were in a doublet state (^2P or ^2D), but all attempts, by various methods, to detect excited atoms in active nitrogen have failed. It seems reasonable to assume, therefore, that atoms in a doublet state were not present in sufficient quantity to produce the observed amount of destruction of ammonia. There has been no evidence for hydrogen atom abstraction in any of the active nitrogen reactions studied thus far; indeed it is difficult to devise a mechanism based on hydrogen abstraction which will explain the results of any of the active nitrogen reactions. Thus it appears reasonable to assume that, although hydrogen abstraction would conserve spin, it does not occur in the active nitrogen-ammonia reaction. In any case, for the ammonia reaction it would be endothermic by about 20 kcal., and therefore is highly improbable. Reaction (3) would also conserve spin if the generated nitrogen molecules were in a triplet state, but the lowest lying triplet state ($A^3\Sigma$) contains about 140 kcal. excitation energy, which would make this reaction about 90 kcal. endothermic. Reaction on a quartet surface to produce ground state nitrogen molecules plus three hydrogen atoms would also be endothermic by about 53 kcal. Other things being equal, a reaction in which spin is conserved is much more probable than one in which spin is not conserved, but it seems clear that the highly endothermic character of the reactions mentioned above must rule them out despite the favourable spin conservation.

If the ground state nitrogen atom were not in a pure quartet state, i.e., if the wave function describing the atom contained a small amount of a doublet wave function in addition to the quartet wave function

$$\psi = a\,\psi_q + b\,\psi_d$$

where ψ_q = quartet wave function, ψ_d = doublet wave function, and a, b are the respective fractions of quartet and doublet wave functions in the total wave function ψ, then there would be a finite probability that a collision between a ground state nitrogen atom and a reactant in a singlet state (ammonia, ethylene, etc., in their ground states) would form a collision complex on a doublet surface. This probability would be given by

$$p = \frac{(ab)^2}{(a)^2 + (b)^2}$$

Due to the interaction between the spin magnetic moment and the orbital magnetic moment of an electron in an atom, there is a certain amount of admixture of states, although in the light elements the amount of admixture is small. However, in conjunction with the very low activation energy of the active nitrogen-ammonia reaction (cf. temperature independence of initial slope and plateau of Figure 3A) a steric factor of 10^{-3} to 10^{-4}

would still allow the type of behavior observed. It is possible to calculate an upper limit for the steric factor which would be allowed on a spin basis in the ammonia-active nitrogen reaction if decomposition occurred only when an activated complex formed on a doublet surface. This upper limit is given by the probability factor, p, defined above. Thus if b were greater than 10^{-2}, this mechanism might be possible.

Calculation of an upper limit for b:

The Hamiltonian, H, of an atom may be written as

$$H = H_o + H'$$

where H_o is the Hamiltonian of the atom in the absence of perturbation and H' is the perturbation Hamiltonian, or in other words, H_o gives the energy of the atom in the absence of perturbation and H' gives the energy of perturbation. For the case under consideration, H' represents the energy of interaction between the spin and orbital magnetic moments, and is small compared to H_o. If ψ_i are the eigenfunctions of H_o, then the relative amplitude of ψ_n admixed with ψ_m due to H' is given by the expression

$$\frac{\int \psi_n^* H' \psi_m \, d\tau}{E_n - E_m}$$

In the case under consideration $\psi_n = \psi_d$ and $\psi_m = \psi_q$, $(E_n - E_m)$ is the energy difference between the doublet and quartet states, and H' is given by

$$H' = \frac{1}{2m^2c^2} \cdot \frac{1}{r} \cdot \frac{dV}{dr} (\bar{L} \cdot \bar{S})$$

where m = electron mass, c = speed of light, r = radius of orbit, V = potential experienced by electron, $\bar{L}$ = orbital angular momentum of electron = $\hbar = \frac{h}{2\pi}$, $\bar{S}$ = spin angular momentum of electron = $\hbar/2$. If we make the crude approximations

$$V = \frac{-Z^{*} e^2}{r},$$

where Z^{*} = effective atomic number $\approx$ 3 for 2p electron in nitrogen atom and $r \approx 0.5A$,* then

$$H' = \frac{1}{2m^2c^2} \frac{Z^{*} e^2}{r^3} \frac{\hbar^2}{2} \approx 1 \times 10^{-3} \text{ ev.}$$

The lowest lying doublet state in the nitrogen atom is the ^2D state which contains 2.37 ev. excitation energy. Since this level involves 2p orbitals only, we may get an

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* This is a reasonable estimate for the average radius of a 2p electron orbit in a nitrogen atom, since p orbits penetrate and the atomic nitrogen single covalent bond radius is 0.7A (194).

upper limit of b by assuming $\psi_q = \psi_d$. Therefore

$$b < \frac{\int \psi_d^* H' \psi_q \, d\tau}{E_d - E_q} \approx \frac{10^{-3}}{2.4} \approx 4 \times 10^{-4}$$

and $\quad p < 1.6 \times 10^{-7}$

It is thus evident that direct formation of collision complexes in a doublet state from ammonia molecules and ground state nitrogen atoms would be much too improbable to explain the observed rate of reaction.

There is a possibility that a collision complex formed on a quartet surface would undergo a transition to a doublet surface, with subsequent decomposition into products in a doublet state. According to quantum-theory, such transitions can only occur between energy levels that are closely matched. These transitions would also be due to spin-orbit interaction, and the order of magnitude of the probability of a transition in a collision complex can be calculated from time dependent perturbation theory. The Hamiltonian can be written

$$H = H_o + H'$$

where H_o is the Hamiltonian without spin-orbit interaction and H' is the small spin-orbit interaction perturbation. H_o depends on the time, t, through the position of the particles (i.e., the reactants), since the particles are in motion. Neglecting H', the possible electron wave functions ψ_n satisfy the Schroedinger equation

$$i\hbar \frac{\partial \psi_n}{\partial t} = H_o \psi_n \qquad \text{(i)}$$

If equation (i) is multiplied by ψ_m^* and integrated over all space

$$i\hbar \int \psi_m^* \frac{\partial}{\partial t} \psi_n \, d\tau = \int \psi_m^* H_o \psi_n \, d\tau \qquad \text{(ii)}$$

and the complex conjugate of equation (ii) with m and n interchanged is subtracted from equation (ii), the result is

$$2i\hbar \frac{\partial}{\partial t} \int \psi_m^* \psi_n \, d\tau = 0$$

Thus since the ψ's were orthogonal and normalized when the molecules were far apart, they will remain orthogonal and normalized. We have to solve

$$i\hbar \frac{\partial \psi}{\partial t} = (H_o + H')\psi$$

Assume the total wave function, ψ, to be a linear combination of wave functions, ψ_n.

$$\psi = \sum A_n \psi_n$$

where the A_n are constants. Then

$$i\hbar \sum A_n \frac{\partial \psi_n}{\partial t} + i\hbar \sum \dot{A}_n \psi_n = \sum H_o A_n \psi_n + \sum A_n H' \psi_n \qquad \text{(iii)}$$

The first term on the left hand side of equation (iii) is equal to the first term on the right hand side (cf. equation (i)), so

$$i\hbar \sum \dot{A}_n \psi_n = \sum A_n H' \psi_n \qquad \text{(iv)}$$

Multiply equation (iv) by ψ_m^* and integrate

$$i\hbar \sum \dot{A}_n \int \psi_m^* \psi_n \, d\tau = \sum A_n \int \psi_m^* H' \psi_n \, d\tau$$

Therefore $$\dot{A}_m = \frac{1}{i\hbar} \sum A_n H'_{mn}$$

where $$H'_{mn} = \int \psi_m^* H' \psi_n \, d\tau \qquad \text{(v)}$$

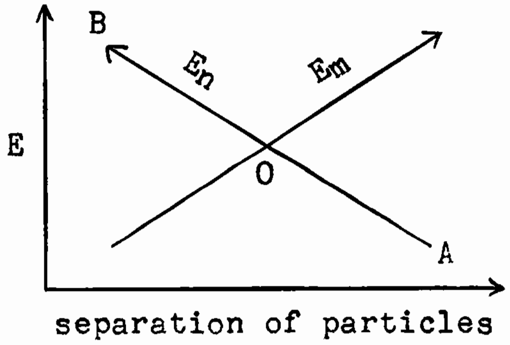
To first order in H', $A_n = \delta_{no}$, i.e., all the A_n are zero except the first, which is equal to unity.

$$\dot{A}_m = \frac{1}{i\hbar} H'_{mn}$$

Since H_o varies only slowly with time (due to the motion of the molecules), the wave functions ψ_r can be written

$$\psi_r = \chi_r e^{iE_r t/h} \qquad \text{(vi)}$$

where the wave function χ_r and the energy E_r vary slowly with time. Since we are interested in the transition from a quartet reaction surface to a doublet reaction surface while the reactants are together in a collision complex, and since these surfaces cross (the quartet state of the reactants has the lowest energy, while the doublet state of the products has the lowest energy), the case we must consider is the one in which E_m crosses E_n, where E_m = energy in final state and E_n = energy in initial state. To first order, in the region near the intersection of the two potential surfaces, the energy difference, E_m-E_n, is proportional to the time that the reacting bodies have been moving away from the point of intersection of the surfaces. In other words, in a small region near the intersection, O, the potential surfaces may be assumed to be approximately linear.



As the reactants approach each other along E_n (from A), $\Delta E = |E_m - E_n|$ will decrease as point O is approached, become zero at point O, and increase on the other side of O (towards B). If no transition to the surface represented by E_m occurs as point O is passed, the reactants will pass back along E_n from B to A, and as they pass O transition to E_m will have another opportunity. If time is measured from point O, the energy difference, ΔE, will obviously be roughly proportional to the time during which the particles have been moving away from O.

$$\Delta E = bt$$

where b is the rate of change of ΔE with time during a collision or during a vibration in the collision complex. Therefore, substituting the ψ's according to equation (vi) into equation (v) we get

$$H'_{mn} = H'_{(mn)}\, e^{-ibt^2/\hbar}$$

where $$H'_{(mn)} = \int \chi_m^* H' \chi_n \, d\tau$$

and since the χ's vary only slowly, $H'_{(mn)}$ is practically constant. Hence,

$$A_m = \frac{H'(mn)}{i\hbar} \int_{-\infty}^{\infty} e^{-ibt^2/\hbar}\, dt$$

$$= \frac{2H'(mn)}{2i\hbar} \int_0^{\infty} e^{-ibx/\hbar}\, x^{-\frac{1}{2}}\, dx$$

$$= \frac{H'(mn)\sqrt{\pi}}{i\hbar} \left(\frac{\hbar}{ib}\right)^{\frac{1}{2}}$$

The probability that a transition from surface n to surface m will occur during one pass across 0 is given by the square of A_m,

$$|A_m|^2 = \frac{\pi}{\hbar} \frac{|H'(mn)|^2}{b}$$

Since the point 0 is passed twice during each vibration, the transition probability will be $2|A_m|^2$. If the collision complex has a finite life time, such that w vibrations may occur before the complex dissociates, the transition probability, p, will be given by

$$p = \frac{2w}{\hbar} \frac{|H'(mn)|^2}{b} \qquad \text{(vii)}$$

The order of magnitude of p may be calculated by substituting approximate values for $H'_{(mn)}$ and b into equation (vii). $H'_{(mn)}$ will be the same order of magnitude as the H' calculated previously for the spin-orbit interaction of the 2p electrons of atomic nitrogen, i.e., about 10^{-3} ev. The potential gradient near 0 will be of the order of an electron volt per angstrom (this figure would be given from the slopes of the potential surfaces at the intersection, and while 10 ev. per angstrom seems too high, 1 or possibly even 0.1 ev. per angstrom appear to be reasonable estimates for this type of system). The particle velocities near 0 will be thermal, or less due to the repulsive forces. Thus for a nitrogen atom and an ammonia molecule, thermal velocity would be about 5×10^4 cm./sec., and b would be about 5×10^{12} ev./sec. These values yield

$$p \approx 2 \times 10^{-3} w$$

It might be well to emphasize that the various numerical values used to calculate this probability factor were the ones that were considered to be the most reasonable within an order of magnitude or less, and that the final result is only an order of magnitude. If the collision complex had a finite life time, say 10^{-10} sec., this probability factor could increase to the order of 0.1. It thus becomes evident that, although changes of spin cause marked reductions in the rates of reactions compared to those which require no change of spin (other things being equal), the probability for a spin change to occur in the collision complex can be large enough to explain the observed rate of the active nitrogen-ammonia reaction, and similarly the observed rates of the active nitrogen-hydrocarbon reactions. The longer the life of the activated complex the greater will be the spin transition probability, and consequently the faster will be the reaction. Kinetic considerations also seem to indicate that the faster active nitrogen-hydrocarbon reactions form the more stable collision complexes. For example, the active nitrogen-acetylene reaction is faster than the corresponding ethylene reaction and about five times as much cyanogen was produced in the acetylene as in the ethylene reaction (10% and 2% of the amount of hydrogen cyanide respectively). The mechanisms postulated for cyanogen formation were

$$[C_2H_2N] + N \longrightarrow C_2N_2 + H_2$$
$$[C_2H_4N] + N \longrightarrow C_2N_2 + 2H_2$$

i.e., the activated complexes were assumed to have a long enough life to undergo collisions with more active nitrogen. The increased amount of cyanogen produced in the acetylene reaction might be partly due to the longer life of the $[C_2H_2N]$ complex, thereby allowing a larger number of collisions with active nitrogen.

The cis-trans isomerizations of dimethyl maleic ester and butene-2 involve transitions between singlet and triplet states. An attempt to introduce quantum restrictions into the calculation of the frequency factors of these reactions yielded results which were too low by a factor of 10 to 100 (195).

The only alternative to a reaction between active nitrogen and ammonia which involves a change of spin seems to be that ground state nitrogen atoms are not the species that react with ammonia. There is strong evidence that ground state atoms are present in active nitrogen and it does not seem reasonable to suggest that they would be inert towards ammonia. Reactions that conserve spin can be written if they involve two nitrogen atoms, eg.

$$2N(^4S) + NH_3 \longrightarrow N_2 + H_2 + H + N(^4S)$$

but these would involve termolecular collisions and would therefore not be rapid enough to explain the observed rate of ammonia decomposition.

Nothing can be said about the conservation of spin in the reactions involving N_2^* or N_3 since it is not certain what spin state they might be in.

To sum up, it has been shown that although it is exceedingly improbable that collision complexes between ground state nitrogen atoms and ammonia form directly in the doublet state, the probability for spin transitions to occur from the quartet to the doublet state in the collision complex can be large enough to explain the observed rate of ammonia decomposition, even if the collision complex lasts for only one vibration. The transition probability increases linearly with the number of vibrations and therefore with the life time of the collision complex. It is therefore suggested that reaction (3), and similarly reaction (4), occurs. By analogy with these reactions, and since the steric factors of most of the other active nitrogen-hydrocarbon reactions are of the order of 10^{-2} to 10^{-4}, it is also suggested that the other active nitrogen-hydrocarbon reactions involve spin transitions if the corresponding spin-allowed reaction is highly unfavorable energetically.

REACTION OF HYDRAZINE WITH ACTIVE NITROGEN

If the extent of reaction is used as a basis for comparison, hydrazine is more similar to ethylene than to ammonia in its reaction with active nitrogen.

From the shape of the ammonia production curves (Figure 5) it appears that ammonia is formed only by reaction of hydrazine with a product of the hydrazine-active nitrogen reaction. The smaller amount of ammonia produced at 480°C than at 150°C in the lower range of hydrazine flow rates, while the reverse was true at the higher flow rates (above about 20×10^{-6} mole/sec.) was probably due to a greater increase in the rate of the active nitrogen-hydrazine reaction than in the rates of the secondary reactions. Thus there would be less hydrazine available for secondary reactions until all the active nitrogen was consumed. The possibility that ammonia was produced in the initial reaction, and destroyed by subsequent reaction with excess active nitrogen is ruled out because the maximum rate of destruction of ammonia by active nitrogen in the absence of any other reactant would be about 3×10^{-6} mole/sec. (15% of 19.0×10^{-6} mole/sec. HCN produced from ethylene) under similar conditions. It is probable, also, that the component in active nitrogen capable of reacting with ammonia would be rapidly removed by reaction with hydrazine.

There was a possibility that hydrogen atoms might be formed from the attack of active nitrogen on hydrazine, and thus might be responsible for the secondary reactions in the active nitrogen-hydrazine system. The hydrogen atom-hydrazine reaction will therefore be discussed briefly before proceeding with the discussion of the active nitrogen-hydrazine reaction.

At 48°C, one mole of ammonia was produced for each mole of hydrazine destroyed (Figure 6). At 458°C, $(1-x)$ mole of ammonia was formed for each mole of hydrazine destroyed, where $0 < x < 1$. The decrease in x with increasing hydrazine flow rate probably paralleled a decrease in hydrogen atom concentration available for secondary reactions (due to direct reaction between hydrogen atoms and hydrazine). This implies that the decrease in yield of ammonia with increase of temperature was due to attack of hydrogen atoms on ammonia, or on an intermediate from which ammonia might be derived. The reaction

$$H + N_2H_4 \longrightarrow NH_3 + NH_2 \quad \Delta H=-40 \text{ kcal.} \qquad (1)$$

probably does not occur, to an appreciable extent, since in addition to the reasons given in the 'Introduction' to this thesis(analogy with H + C_2H_6; ratio NH_3 produced to N_2H_4 destroyed usually less than one prohibits $2NH_2 \longrightarrow N_2H_4$), the large value of x at 458°C and low hydrazine flow rates means that a large proportion of the ammonia formed by reaction (1) would have to be subsequently destroyed by hydrogen atoms. This would seem to require that the ammonia so formed be excited, since the rate of destruction previously observed with hydrogen atoms at 440°C (see Figure 3B) was much too small to explain the large value of x found at 458°C and low hydrazine flow rates. Reaction (1) would also prohibit the reaction

$$NH_2 + N_2H_4 \longrightarrow NH_3 + N_2H_3 \quad \Delta H=-(12 \text{ to } 17) \text{ kcal.} \qquad (2)$$

since ammonia production never exceeded hydrazine consumption on a molar basis.

The results of the hydrogen atom reaction with hydrazine can be explained by the following reactions:

	ΔH (kcal.)	
$H + N_2H_4 \longrightarrow H_2 + N_2H_3$	- (8 to 13)	(3)
$2N_2H_3 \longrightarrow N_2 + 2NH_3$	-(144 to 154)	(4)
$H + NH_3 \longrightarrow H_2 + NH_2$	+4	(5)
$NH_2 + N_2H_3 \longrightarrow N_2 + H_2 + NH_3$	-(117 to 122)	(6)
$2NH_2 \longrightarrow N_2 + 2H_2$	-89	(7a)
$2NH_2 + M \longrightarrow N_2H_4 + M$	-66	(7b)
$2H + M \longrightarrow H_2 + M$	-103	(8)
$H + N_2H_3 + M \longrightarrow N_2H_4 + M$	-(90 to 95)	(9a)
$H + N_2H_3 \longrightarrow N_2 + 2H_2$	-(113 to 118)	(9b)

The high value of x at 458°C and low hydrazine flow rates is explained readily by the combined effects of reactions (5) and (9b). It is also possible that some N_2H_3 radicals are destroyed on the walls at high temperatures to yield nitrogen and hydrogen but no ammonia. Although the NH_2 radicals might have a significant concentration at high temperatures and low hydrazine flow rates (due to reaction (5)), the hydrazine concentration should be very low (because of reaction (3)); hence reaction (2) should not occur to an appreciable extent.

Spin is conserved in all the reactions in the above mechanism.

There are two possible exothermic reactions between nitrogen atoms and hydrazine,

$$\begin{array}{lcllr}
 & & & \underline{\Delta H \text{ (kcal.)}} & \\
N + N_2H_4 & \longrightarrow & N_2 + H_2 + NH_2 & -91 & (10a) \\
 & \longrightarrow & N_2 + H_2 + NH + H & -1 & (10b)
\end{array}$$

If N_3 were an active species, it would react in the same manner as N, but the corresponding reactions would be less exothermic by the amount of the N_2-N bond energy in N_3. Since hydrazine reacts rapidly with both active species in active nitrogen, the most probable mechanism for the reaction, if N and N_3 are assumed to the reactive species, would seem to be:

$$\begin{array}{rcllr}
 & & & \underline{\Delta H \text{ (kcal.)}} & \\
N + N_2H_4 & \longrightarrow & N_2 + H_2 + NH_2 & -91 & (10a) \\
NH_2 + N_2H_4 & \longrightarrow & NH_3 + N_2H_3 & -(12 \text{ to } 17) & (2) \\
2N_2H_3 & \longrightarrow & N_2 + 2NH_3 & -(144 \text{ to } 154) & (4) \\
NH_2 + N_2H_3 & \longrightarrow & N_2 + H_2 + NH_3 & -(117 \text{ to } 122) & (6) \\
2NH_2 & \longrightarrow & N_2 + 2H_2 & -89 & (7a) \\
2NH_2 + M & \longrightarrow & N_2H_4 + M & -66 & (7b)
\end{array}$$

Since spin is conserved in reaction (10b) and not in (10a), reaction (10b) might occur to a certain extent. However, the analogous reaction with N_3 would be endothermic and probably would not occur to an appreciable extent. If it is assumed that atoms are the species which react with ammonia, then N_3 would be present in much larger concentration than N, and reaction according to (10a) would be the predominant initial process. The same type of argument concerning spin conservation in the ammonia-active nitrogen reaction applies to reaction (10a).

If N_2^* is assumed to be a reactive species, several exothermic reactions may be written, a priori, which would result in the direct or indirect decomposition of hydrazine. N_2^* might react directly with hydrazine

$$N_2^* + N_2H_4 \longrightarrow N_2H_4^* + N_2 \longrightarrow N_2H_3 + H + N_2 \qquad (11a)$$

$$\longrightarrow 2NH_2 + N_2 \qquad (11b)$$

or it might react in a secondary reaction with N_2H_3 radicals derived from a previous reaction (presumably initiated by N atoms)

$$N_2^* + N_2H_3 \longrightarrow N_2H_3^* + N_2 \longrightarrow NH_2 + NH + N_2 \qquad (12a)$$

$$\longrightarrow 2NH + H + N_2 \qquad (12b)$$

$$\longrightarrow NH_3 + N_2 + N \qquad (12c)$$

or it might react with hydrogen atoms derived from a previous reaction

$$N_2^* + H \longrightarrow NH + N \qquad (13)$$

Reaction (13) is immediately ruled out because, if this reaction occurred to any appreciable extent, ammonia should have been destroyed to a much greater extent in the ammonia-active nitrogen system than was observed experimentally. Reaction (11a) is also ruled out because N_2H_3 radicals decompose to form ammonia, which would make ammonia a primary product of the reaction and this was not observed. Reactions (12a), (12b) and (12c) would lead indirectly to the decomposition of hydrazine because the atoms and radicals produced in these reactions would react further with hydrazine. However NH_2 radicals would produce ammonia according to reaction (2), H atoms would react according to reaction (3), and NH radicals would probably react according to

$$NH + N_2H_4 \longrightarrow NH_3 + N_2 + H_2 \qquad \Delta H \approx -116 \text{ kcal.} \quad (14)$$

Reaction (12c) generates one ammonia molecule for each N_2^* that reacts. Thus reactions (12a), (12b) and (12c) would lead to the production of ammonia as essentially a primary product, and since this was not observed experimentally, these reactions are ruled out. Thus only reaction (11b) is allowed, and each N_2^* would result in the decomposition of only one hydrazine molecule.

Since ammonia is a product of secondary reactions only it is possible to separate the effect of the secondary reactions from that of the total reaction. Hydrogen cyanide production from the ethylene-active nitrogen reaction at 451°C indicated that the total active nitrogen concentration was 19.0±0.4 x 10^{-6} mole/sec. It may be assumed that if N_3 were a reactive species, each N_3 would yield one molecule of hydrogen cyanide, and if N_2^* were a reactive species, each N_2^* would yield two molecules of hydrogen cyanide. Therefore, if N_3 and N were the reactive species, the maximum amount of hydrazine decomposed without the production of ammonia should be approximately equal to the maximum amount of hydrogen cyanide produced from ethylene. If, however, N_2^* makes a predominant contribution to the activity of active nitrogen, the maximum amount of hydrazine decomposed without the production of ammonia should be much smaller than the maximum amount of hydrogen cyanide produced from ethylene.

Essentially the only product of the active nitrogen-hydrazine reactions considered above which could react further with hydrazine is the NH_2 radical. Therefore, each hydrazine molecule decomposed in a secondary reaction (reaction (2), followed by reactions (4) and (6)) would yield two molecules of ammonia. Since, in the hydrogen atom-hydrazine reaction at low temperature little, if any, N_2H_3 was destroyed without production of ammonia, it is reasonable to assume that the same is true for the active nitrogen reaction at 150°C. Therefore, by subtracting one half of the amount of ammonia formed at 150°C from the total amount of hydrazine destroyed at this temperature, for hydrazine flow rates of 24×10^{-6} mole/sec. and higher, it was estimated that 18.8×10^{-6} mole/sec. of hydrazine was destroyed by direct reaction with active nitrogen. This estimate must be increased by an amount corresponding to the amount of hydrazine generated by reaction (7b). It was not possible to calculate from the present results the extent to which reaction (7b) occurred under the conditions of the reaction reported in this thesis. Therefore, it may be concluded only that the maximum rate of destruction of hydrazine by active nitrogen was approximately 18.8×10^{-6} mole/sec. The close agreement of this figure with that for hydrogen cyanide production in the ethylene-active nitrogen reaction indicates that N_2^* makes, at best, only a small contribution to the chemical reactivity of active nitrogen, and therefore, that reaction (11b) only occurs to a small extent or not at all.

It might be pointed out that, if nitrogen molecules were present in another excited state (i.e., a third reactive species) such that they could decompose hydrazine but could not produce hydrogen cyanide from ethylene, the above conclusion could not be drawn. However, as indicated earlier, the persistence of the yellow afterglow of active nitrogen at all hydrazine flow rates until that corresponding to the maximum amount of reaction is approached, indicates the persistence of a species of nitrogen that can generate N_2 $B^3\Pi$ molecules, and must therefore contain at least 170 kcal. excitation energy. Since such a molecule should have enough energy to react with ethylene as well as hydrazine, it does not seem reasonable to postulate the existence of a third reactive species.

To summarize, the most probable reaction mechanism for the reaction of active nitrogen with hydrazine appears to involve N and N_3 which react according to reaction (10a), followed by reactions (2), (4), (6), (7a) and (7b).

The increase in the maximum amount of hydrazine destroyed when the temperature was increased from 150° to 480°C was presumably due to an increased rate of decomposition of hydrazine in reaction (2).

The long "induction period" in the ammonia production curves (Figure 5) indicates that reaction (10a) is much faster than reaction (2), which would be expected.

The curves for ammonia production tend to level off at a value corresponding to only about 35% of the NH_2 radicals reacting according to reaction (2). This indicates that the NH_2 radicals are removed quite rapidly by the combined effects of reactions (6), (7a) and (7b).

REACTION OF METHYLAMINE WITH ACTIVE NITROGEN

For the discussion of this reaction it will be assumed that N and N_3 are the reactive species in active nitrogen, because the study of the hydrazine-active nitrogen reaction seemed to indicate that excited nitrogen molecules do not make a significant contribution to the chemical reactivity.

Methylamine contains both an amino and an alkyl group and might be expected to undergo both ammonia and hydrocarbon type reactions. Since the reaction

$$CH_3NH_2 + N \longrightarrow N_2 + H_2 + CH_3 \qquad \Delta H = -78 \text{ kcal.} \qquad (1)$$

obviously would not produce hydrogen cyanide, the maximum amount of hydrogen cyanide produced in the active nitrogen-methylamine reaction would be expected to be less than the maximum amount produced in the active nitrogen-ethylene reaction. This was, in fact, observed (8.5 ± 0.3 and $12.3 \pm 0.4 \times 10^{-6}$ mole/sec. respectively). Further evidence for the occurrence of reaction (1) is the observation of methane and C_2 hydrocarbons in the reaction products. The methyl radicals would be rapidly consumed by further reaction with active nitrogen,

$$N_3 + CH_3 \longrightarrow HCN + H_2 + N_2 \qquad \Delta H = -(113 - E) \text{ kcal.} \qquad (2)$$

where E is the dissociation energy of the $N-N_2$ bond in N_3. Thus methane was not produced at low methylamine flow rates (below about 8×10^{-6} mole/sec.), and the small amounts of C_2 hydrocarbons observed in this flow rate range decreased with increasing temperature.

The experimental results can be explained by the following type of mechanism:

	ΔH (kcal.)	
$CH_3NH_2 + N \longrightarrow CH_3 + N_2 + H_2$	-78	(1)
$CH_3 + N_3 \longrightarrow HCN + H_2 + N_2$	-(113-E)	(2)
$CH_3NH_2 + N_3 \longrightarrow HCN + H_2 + NH_2 + N_2$	-(35-E)	(3)
$CH_3NH_2 + NH_2 \longrightarrow NH_3 + CH_3NH$	-12	(4a)
$\longrightarrow NH_3 + CH_2NH_2$	-12	(4b)
$CH_3 + CH_3NH_2 \longrightarrow CH_4 + CH_3NH$	-6	(5a)
$\longrightarrow CH_4 + CH_2NH_2$	-6	(5b)
$\begin{matrix} CH_3NH \\ CH_2NH_2 \end{matrix}$ (+ possibly CH_3NH_2) $\longrightarrow$ polymer (+ possibly $H_2 + NH_3$)		(6)
$2NH_2 \longrightarrow N_2 + 2H_2$	-89	(7)
$2CH_3 \longrightarrow C_2$ hydrocarbons		(8)

Reactions (6) and (8) will be discussed in more detail later.

At high methylamine flow rates, the N_3 concentration would be depleted by reaction (3), thus allowing reactions (5a), (5b) and (8) to compete to a certain extent with reaction (2) for methyl radicals.

The production of ammonia in the region of low methylamine flow rates (below about 8 x 10^{-6} mole/sec.) was essentially independent of temperature. This could be explained by certain compensating effects: the rate constants of reactions (4a) and/or (4b) would increase with increasing temperature, but the amount of methylamine available for these reactions would decrease owing to an increase in the rate of reaction (3); the amount of reaction (6) decreases with increasing temperature, possibly due to removal of some of the CH_3NH (or CH_2NH_2) radicals by reaction with active nitrogen; although the NH_2 radical concentration would increase with increasing rate of reaction (3), they are removed by reaction (7) as well as by reaction (4a, b), and reaction (7) varies as the square of the NH_2 radical concentration.

Since nearly two molecules of hydrogen were produced for each molecule of methylamine destroyed, the polymer must have contained a low percentage of hydrogen. The apparent formation of some polymer at high temperatures in the presence of excess active nitrogen indicates that polymerization occurs quite rapidly.

The products from the photochemical (direct or mercury-sensitized) decomposition of methylamine have been found to be one mole of hydrogen, 0.5 mole of ammonia, 0.02-0.04 mole of methane, and a polymer, for each mole of methylamine decomposed (69 to 71). The mechanism of the over-all photochemical reaction has not been definitely established, but the initial process must be either

$$CH_3NH_2 + h\nu \longrightarrow CH_3NH + H$$

$$\text{or} \qquad \longrightarrow CH_2NH_2 + H$$

The fate of the CH_3NH (or CH_2NH_2) radicals is probably similar in both the photochemical and active nitrogen reactions, since in both cases they appear to form a similar polymer with a low hydrogen content. The various mechanisms that have been proposed for the photodecomposition involve interaction of the radicals with themselves, or rapid decomposition of the radicals to methylenimine and hydrogen atoms followed by reaction of the methylenimine with methylamine.

When the reaction vessel was surrounded by Dry Ice the value of Δ(Base) was the same as the amount of ammonia destroyed in the active nitrogen-ammonia reaction (1.8×10^{-6} mole/sec.). However, the maximum rate of destruction of methylamine was 3.0×10^{-6} mole/sec., with production of only 0.2×10^{-6} mole/sec. of hydrogen cyanide. These facts can be explained if it is assumed that reaction (3) does not occur appreciably at this temperature, and that the collision complex formed in reaction (2) (i.e., $\left[CH_3N\right]$)

reacts with methylamine and itself to form a polymer, hydrogen and ammonia. Thus at -7°C, reaction (1) would destroy 1.8×10^{-6} mole/sec. of methylamine and a corresponding amount of $[CH_3N]$ complexes would be formed by reaction (2). If it is assumed that reaction of $[CH_3N]$ with itself would produce polymer but no ammonia, and that reaction of $[CH_3N]$ with methylamine would produce both polymer and ammonia,

$$2\ [CH_3N] \longrightarrow \text{polymer} \qquad (9)$$

$$[CH_3N] + CH_3NH_2 \longrightarrow \text{polymer} + NH_3 \qquad (10)$$

(the $[CH_3N]$ might (172) or might not rearrange to $CH_2{=}NH$ before reacting further)

then one mole of ammonia would be produced for each mole of methylamine destroyed in excess of 1.8×10^{-6} mole/sec. This is, in fact, observed (see Table X).

Similarly, at 477°C, if the CH_3NH (or CH_2NH_2) radicals produced in reaction (4a, b) reacted further with methylamine to produce polymer and ammonia

$$NH_2 + CH_3NH_2 \longrightarrow NH_3 + CH_3NH \qquad (4a)$$

$$CH_3NH + CH_3NH_2 \longrightarrow \text{polymer} + NH_3 \qquad (6a)$$

(the CH_3NH or CH_2NH_2 radicals might (69, 70) or might not undergo a rearrangement before reacting further)

then approximately one mole of ammonia would be produced

TABLE X

Comparison of Amount of Ammonia Produced with Amount of Polymer formed directly from Methylamine

(all units except temperature are mole x 10^{-6}/ sec.)

T(°C)	CH_3NH_2 flow	CH_3NH_2 destroyed -1.8	NH_3 produced
-7	3.0	0.2	0.4
	5.0	0.6	0.6
	8.0	0.8	0.8
	11.0	1.0	1.0

T(°C)	CH_3NH_2 flow	CH_3NH_2 destroyed minus HCN produced	NH_3 produced
477	3.0	0.4	0.4
	5.0	0.4	0.6
	8.0	0.6	0.8
	11.0	1.6	1.6
	15.0	2.1	2.2

for each mole of methylamine that was decomposed but did not react to form hydrogen cyanide. This, also, was observed (see Table X).

The above mechanisms would imply that a negligible amount of CH_3NH radicals are formed at the low temperature and that essentially all the $[CH_3N]$ complexes decompose to form hydrogen cyanide and hydrogen at the high temperature. This does not seem unreasonable.

Hydrogen would also have to be generated in, or subsequent to reactions (9), (10) and (6a) to account for the large amount of hydrogen observed in the non-condensable reaction products.

Although these mechanisms are only speculative, they account reasonably well for the ammonia formation. If different mechanisms do occur at low and high temperatures, the transition between them must take place below room temperature, because hydrogen cyanide production was abnormally low only when the reaction vessel was surrounded with Dry Ice. Reactions of type (9) and (10) might take place on the cold vessel wall (cf. $H + NH_3$).

Since methylamine contains only one carbon atom, the C_2 hydrocarbons observed in the products of the reaction with active nitrogen must have been formed by the recombination of radicals produced in a reaction such as (1). However, the C_2 hydrocarbons produced in this reaction were highly unsaturated (approximately 50% acetylene, 30% ethylene, and 20% ethane). Ordinarily, methyl radical recombination yields ethane only. It does not seem reasonable to suggest that the acetylene and ethylene produced in the present reaction were formed by successive dehydrogenation of ethane. They must, therefore, have been produced directly from the recombination of radicals. Since reaction (1) is exothermic by 78 kcal. and $D(CH_2\text{-}H)$ is approximately 87 kcal. (173), CH_2 radicals probably would not be produced in a variation of reaction (1). Nor does it seem likely that CH_2 radicals were produced by the reaction

$$2CH_3 \longrightarrow CH_4 + CH_2 \tag{12}$$

because, at low methylamine flow rates, ethylene but no methane was produced. However, it is possible that part of the heat of reaction (1) remained as vibrational energy in the methyl radicals, in which case the "hot" methyl radicals might react according to

$$\begin{array}{lllll} & & & \underline{\Delta H\ (\text{kcal.})} & \\ 2CH_3^{*} & \longrightarrow & C_2H_4 + H_2 & -(2E+56) & (8a) \\ & \longrightarrow & C_2H_2 + 2H_2 & -(2E+7) & (8b) \end{array}$$

where E is the excitation energy of the methyl radicals. Stabilization of the products by collision with a third body, which is necessary in the ordinary recombination of methyl radicals to ethane (174, 175), might not be necessary in reactions (8a) and (8b) because part of the energy of the reaction could be carried off by the hydrogen molecules.

Another reaction which might produce ethylene and acetylene is

$$2\ [CH_3N] \longrightarrow C_2H_4 + H_2 + N_2 \qquad (13a)$$

$$\longrightarrow C_2H_2 + 2H_2 + N_2 \qquad (13b)$$

The only essential difference between these reactions and (8a,b) is that the methyl radicals produced in reaction (1) would not have to be in an excited state, since the $[CH_3N]$ complexes would presumably be highly energetic. Both sets of reactions would lead to a similar variation of C_2 hydrocarbon production with methylamine flow rate and with temperature. Reactions (8a,b) would require that the rate of reaction of methyl radicals with active nitrogen increase with temperature, and reactions (13a,b) would require that the rate of decomposition of $[CH_3N]$ complexes into hydrogen cyanide and hydrogen should increase with temperature. Both of these assumptions are reasonable. Thus, no choice can be made between the two possibilities.

The small amounts of cyanogen formed decreased with increasing methylamine flow rate and increased with increasing temperature. One possible explanation for this behavior might be

$$HCN + 2\,N_x \longrightarrow H + CN + x\,N_2 \tag{14a}$$

$$2\,CN \longrightarrow C_2N_2 \tag{14b}$$

where N_x might be either N or N_3. Reaction (14a) might occur in steps. Since hydrogen cyanide production increases in approximately linear manner with the decrease in active nitrogen concentration, and since reaction (14a) is first order with respect to hydrogen cyanide and second order with respect to active nitrogen, such a mechanism would yield a decreasing amount of cyanogen with increasing methylamine flow rate. Cyanogen production must obviously go through a maximum, although the experimental results indicate that this maximum must occur at a very low methylamine flow rate.

In summary, it seems probable that most of the methylamine-active nitrogen reaction occurs through reactions (1), (2) and (3), and that ammonia and polymer are produced in the same reactions (i.e., reactions (4a,b), (6a) and (10)). The small amounts of acetylene and ethylene are probably formed by the recombination of energy-rich methyl radicals or $[CH_3N]$ complexes. The traces of ethane are probably formed by recombination of methyl radicals in the usual manner.

RECONSIDERATION OF THE HYDROCARBON-ACTIVE NITROGEN REACTION MECHANISMS

It was pointed out in the 'Introduction' of this thesis that some of the processes that have been postulated in the mechanisms of certain hydrocarbon-active nitrogen reactions were highly endothermic and therefore improbable. It seems worth while to reconsider these reactions in an attempt to knit the various reaction mechanisms more firmly together.

Atomic nitrogen will again be considered as the only reactive species since, in addition to the reasons given in the 'Introduction', the present investigations with amino-type compounds also indicated that active nitrogen reacts in units of one nitrogen atom. If it is assumed that atomic nitrogen is the more energetic of the two reactive species that appear to be present in active nitrogen, the main difference between reactions involving the two species would probably be a difference in the heats of reactions. However, the spin state of the second reactive species (possibly N_3) is not known, and the possibility exists that some of its reactions might be more favored on a spin basis than those of atomic nitrogen. This would tend to diminish any difference in reaction probabilities due to the differences in energetics. For purposes of discussion, the degree of endothermicity will be taken as the main criterion by which the probability of a given reaction may be assessed, and it will be assumed that reactions which are not allowed on this basis for atomic nitrogen are also not allowed for the second active species.

Since products from radical-hydrocarbon reactions are almost entirely absent in the active nitrogen-hydrocarbon reactions that have been studied, the radicals must be attacked much faster by active nitrogen than the hydrocarbon itself. This might be expected since, in addition to more favorable energetics, the atomic nitrogen-radical reactions conserve spin whereas the hydrocarbon reactions do not (at least with ground state nitrogen atoms).

Two reactions have been proposed as possible primary steps in the ethylene-active nitrogen reaction,

$$\begin{array}{llll} \mathrm{C_2H_4} + \mathrm{N} & \longrightarrow \mathrm{CH_3} + \mathrm{HCN} & & (1) \\ & \longrightarrow \mathrm{CH_2} + [\mathrm{CH_2N}] & \longrightarrow \mathrm{CH_2} + \mathrm{HCN} + \mathrm{H} & (2) \end{array}$$

However, the series represented by reaction (2) is endothermic by about 28 kcal. and probably would not have an appreciable rate. Although reaction (1) involves the migration of a hydrogen atom, it is exothermic by about 59 kcal., and since it seems to be the only alternative to reaction (2), reaction (1) probably represents the primary step. The observation by Bawn and Milsted (74) that ethylene was the only product of the reaction between ethylidene bromide and sodium atoms, both in the presence and absence of hydrogen, led them to suggest that the reaction

$$CH_3CHBr_2 + 2\ Na \longrightarrow CH_2{=}CH_2 + 2\ NaBr$$

occurs directly, without the intermediate formation of ethylidene radicals. It is thus apparent that rearrangement reactions which involve the migration of a hydrogen atom to a neighboring carbon can be very rapid, and reactions of type (1) are not unfavorable on this basis.

By similar reasoning, it appears that the initial process in the propylene-active nitrogen would not be

$$CH_3CH{=}CH_2 + N \longrightarrow CH_3CH + [CH_2N] \longrightarrow CH_3CH + H + HCN \qquad (3)$$

but might be

$$CH_3CH{=}CH_2 + N \longrightarrow CH_2{=}CH_2 + HCN + H \qquad (4)$$

since reaction (3) is endothermic by about 27 kcal. while reaction (4) is exothermic by about 27 kcal.

Similarly, biradicals would probably not be formed in the initial attack of active nitrogen on butene-1 and isobutene because these reactions are endothermic by about 18 and 16 kcal. respectively. More probable initial steps for these reactions are

	ΔH (kcal.)	
$CH_3CH_2CH{=}CH_2 + N \longrightarrow CH_3CH{=}CH_2 + HCN + H$	-29	(5)
$(CH_3)_2C{=}CH_2 + N \longrightarrow CH_3CH{=}CH_2 + HCN + H$	-25	(6)

Since propylene was also a primary product of the cis-2-butene-active nitrogen reaction, it was necessary to postulate an apparently much more drastic rearrangement in the activated complex than those involved in the reactions discussed above, thus

$$CH_3CH{=}CHCH_2 + N \longrightarrow \left[CH_3\overset{N}{CH{=}CH}CH_3\right] \longrightarrow CH_3CH{=}CH_2 + HCN + H \qquad (7)$$

Nevertheless the reactivity of cis-2-butene was greater than that of isobutene, as indicated by the following order of relative reactivities (166).

butene-1 > cis-2-butene > isobutene

Reaction (7) is exothermic by about 28 kcal., which is comparable with the heats of reactions for (5) and (6) postulated above.

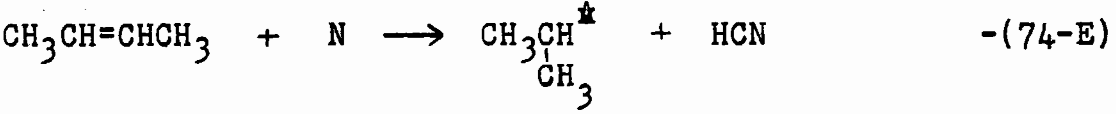
The analogy between reactions (1), (4), (5), (6) and (7) can be drawn more closely if it is assumed that reactions (4), (5), (6) and (7) take place in steps. As they are written, reaction (1) involves the migration of a hydrogen atom from the carbon atom attacked by active nitrogen to the adjacent carbon atom, while reactions (4), (5) and (6) involve migration of a hydrogen atom from the carbon atom three removed to that two removed from the point of attack; reaction (7) seems to involve a more complicated rearrangement. It is suggested that, by analogy with reaction (1), reactions (4), (5), (6) and (7) might all involve the migration of a group from the carbon atom attacked by nitrogen to an adjacent carbon, i.e., in reactions (4), (5) and (6) a hydrogen atom migrates and in reaction (7) a methyl group migrates.

$\underline{\Delta H\ (kcal.)}$

$$CH_3CH{=}CH_2 + N \longrightarrow CH_3CH_2^{*} + HCN \qquad -(63-E) \qquad (4a)$$

$$CH_3CH_2CH{=}CH_2 + N \longrightarrow CH_3CH_2CH_2^{*} + HCN \qquad -(69-E) \qquad (5a)$$

$$(CH_3)_2C{=}CH_2 + N \longrightarrow (CH_3)_2CH^{*} + HCN \qquad -(72-E) \qquad (6a)$$

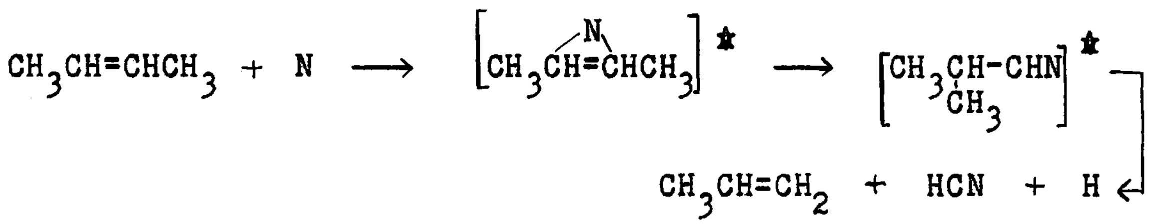


$$CH_3CH{=}CHCH_3 + N \longrightarrow CH_3\underset{\overset{|}{CH_3}}{CH^{*}} + HCN \qquad -(74-E) \qquad (7a)$$

where E is the energy of excitation of the radical produced. Since all these reactions are highly exothermic, the radicals could be formed in excited states (so-called "hot" radicals) and could subsequently decompose according to

$$\begin{array}{lllr} & & \underline{\Delta H \text{ (kcal.)}} & \\ CH_3CH_2^{\bigstar} \longrightarrow & CH_2{=}CH_2 + H & (37-E) & (4b) \\ CH_3CH_2CH_2^{\bigstar} \longrightarrow & CH_3CH{=}CH_2 + H & (40-E) & (5b) \\ (CH_3)_2CH^{\bigstar} \longrightarrow & CH_3CH{=}CH_2 + H & (46-E) & (6b,7b) \end{array}$$

Alternatively step (b) of reactions (4) to (7) might occur simultaneously with the decomposition of the activated complex formed in step (a), e.g.



$$CH_3CH{=}CHCH_3 + N \longrightarrow \left[CH_3\overset{N}{CH}{=}CHCH_3\right]^{\bigstar} \longrightarrow \left[CH_3\underset{CH_3}{CH}-CHN\right]^{\bigstar} \longrightarrow CH_3CH{=}CH_2 + HCN + H$$

This reaction is exothermic by 28 kcal. The C-H bond dissociation energy (e.g. $H-CH_2CH_2$) in an alkyl radical is considerably decreased from that in the hydrocarbon molecule, owing to extension of the C-H bond simultaneously with a coupling process in which the free electron of the radical couples with one of the electrons participating in the C-H bond (189). Thus rupture of the C-H bond to form an unsaturate occurs as the other half of the double bond is formed, and the energy liberated in completion of the double bond is, in effect, utilized in fission of the C-H bond. The activation energies of these reactions are therefore only slightly, if any, greater than the endothermic heats of reaction. Bywater and Steacie (192) found the activation energy of the reaction

$$CH_3CH_2 \longrightarrow CH_2{=}CH_2 + H$$

to be 39.5 kcal., and that of the reactions

$$CH_3CH_2CH_2 \longrightarrow CH_3CH{=}CH_2 + H$$

and $$(CH_3)_2CH \longrightarrow CH_3CH{=}CH_2 + H$$

to be about 38 kcal. This latter value was thought to be intermediate between the true activation energies of the last two reactions.

The formation of biradicals from the initial attack of active nitrogen on cycloparaffins is no more favorable energetically than from the corresponding attack on olefins. The cycloparaffin-active nitrogen reactions are energetically similar to the olefin-active nitrogen reactions, although the former are much slower than the latter. If olefins are postulated as primary products of the cycloparaffin-active nitrogen reactions, it is possible to calculate an approximate value for the ratio of the rate constants of the olefin and cycloparaffin reactions. For example, with cyclopropane

$$\text{cyclo-}C_3H_6 + N \longrightarrow C_2H_4 + HCN + H \quad , k_1 \qquad \text{(i)}$$
$$C_2H_4 + N \longrightarrow CH_3 + HCN \quad , k_2 \qquad \text{(ii)}$$
$$CH_3 + N \longrightarrow HCN + H_2 \quad , k_3 \qquad \text{(iii)}$$

$$k_3 \gg k_2 \gg k_1$$

If turbulent flow and steady state conditions are assumed, the ratio $k_1:k_2$ will be equal to the relative amounts of ethylene and cyclopropane, i.e., ratio $C_2:C_3$ hydrocarbons, found in the products. Since the flow of the reaction gases in the apparatus used in these experiments was probably not completely turbulent but partly streamlined, the concentration of N available for reaction (ii) would be smaller than that available for reaction (i) due to depletion by reaction (i), and the ratio $k_1:k_2$ would be smaller than the ratio $C_2:C_3$. At 150°C the ratio $C_2:C_3$ was approximately 1:400, hence $k_1:k_2$ would be something less than 1:400. At 50°C $k_1:k_2$ is of the order of 1:1000 (158, 163), which is in reasonable agreement with the value deduced from the ratio $C_2:C_3$. Since much less ethylene would be expected if it were produced only as a secondary product (i.e. $C_2:C_3 \ll k_1:k_2$), it is suggested that the active nitrogen-cyclopropane reaction occurs by reactions (i), (ii) and (iii).

A similar treatment of the active nitrogen-cyclobutane reaction would assume the mechanism

$$\text{cyclo-}C_4H_8 + N \longrightarrow C_3H_6 + HCN + H \quad , k_4 \qquad \text{(iv)}$$

$$C_3H_6 + N \longrightarrow C_2H_4 + HCN + H \quad , k_5 \qquad \text{(v)}$$

$$C_2H_4 + N \longrightarrow CH_3 + HCN \quad , k_2 \qquad \text{(ii)}$$

$$CH_3 + N \longrightarrow HCN + H_2 \quad , k_3 \qquad \text{(iii)}$$

and $$k_4 \ll k_2 \approx k_5 \ll k_3$$

This yields a ratio $k_4:k_5$ something smaller than about 1:150 at 60°C. The separately determined rate constants (158, 163) yield a ratio of the order of 1:300, which is in reasonable agreement with the value from the ratio $C_3:C_4$. With partially streamline flow, and since k_5 is approximately equal to k_2, more ethylene than propylene would be expected in the products because the concentration of N available for reaction (ii) would be smaller than that available for reaction (v). This was in fact observed.

Although the rate constants determined for the various hydrocarbon-active nitrogen reactions are only approximate, the experimental results obtained thus far are not inconsistent with the production of olefins as primary products of the cycloparaffin-active nitrogen reactions. The detailed mechanism could be very similar to that in the corresponding olefin reaction, i.e. an initial process which involves the migration of a hydrogen atom in the collision complex from the carbon that is attacked by active nitrogen to an adjacent carbon, with subsequent decomposition of the complex, either directly or indirectly, into hydrogen cyanide, an olefin and a hydrogen atom.

$$\mathrm{N} + \mathrm{cyclo}(\mathrm{CH_2})_n \longrightarrow \begin{array}{c}\text{collision}\\ \text{complex}\end{array} \longrightarrow \text{olefin} + \mathrm{H} + \mathrm{HCN} \qquad (8)$$

or

$$\longrightarrow \mathrm{CH_3(CH_2)}^{*}_{n-2} + \mathrm{HCN} \qquad (8a)$$

$$\mathrm{CH_3(CH_2)}^{*}_{n-2} \longrightarrow \text{olefin} + \mathrm{H} \qquad (8b)$$

Reactions (8), (8a) and (8b) are exothermic by about 28, (66-E) and (E-38) kcal. respectively, where E represents the excitation energy contained by the radicals. If this were the mechanism, the low rate constants for the cycloparaffin reactions compared with those for the olefin reactions would presumably be due to the difficulty in forming the collision complex in the former since cycloparaffins contain no region of relatively high electron density.

The ratio of the rate constant for the active nitrogen-propane reaction to that for the corresponding ethylene reaction at 50°C is of the order of 1:300 (158, 163) whereas the ratio of the amount of ethylene to the amount of propane, $C_2:C_3$, found in the products of the propane reaction at 63°C is about 1:70. It thus appears that ethylene is also a primary product of the active nitrogen-propane reaction, although the most energetically favorable reaction to produce ethylene

$$N + C_3H_8 \longrightarrow HCN + C_2H_4 + H + H_2 \quad , \quad k_9 \qquad (9)$$

is endothermic by about 6 kcal. Ethylene was previously recognized as a primary product (157, 158) but the reaction suggested involved the initial production of ethylidene radicals and was endothermic by about 59 kcal. Although it is surprising that ethyl radicals, rather than ethylene and hydrogen atoms, are not formed, reaction (9) seems to be the only one that gives a reasonable explanation of the experimental results (e.g., much more ethylene than ethane was recovered in the products).

A similar treatment of the n-butane and isobutane reactions, assuming the initial processes to be

$$\text{n-}C_4H_{10} + N \longrightarrow C_3H_6 + HCN + H_2 + H \quad , \quad k_{10} \qquad (10)$$
$$\text{iso-}C_4H_{10} + N \longrightarrow C_3H_6 + HCN + H_2 + H \quad , \quad k_{11} \qquad (11)$$

indicates that propylene is <u>not</u> a primary product of the isobutane reaction since the ratio $C_3:C_4$ is much smaller than the ratio $k_{11}:k_5$ (about 1:700 and 1:100 respectively). No conclusion seems to be possible concerning propylene production from n-butane; $C_3:C_4$ and $k_{10}:k_5$ are both approximately 1:200 at 250°C and if reaction (10) occurred to a large extent $C_3:C_4$ would be expected to be greater than $k_{10}:k_5$. Experimental error in the determination of the rate constants might mask the true relations. Ethylene does appear to be a primary product of the n-butane and isobutane reactions however, since the ratio $C_2:C_4$ in the products of these reactions is about 1:15 and 1:40 respectively. The mechanisms suggested previously for the butane reactions (159) appear to explain the experimental results adequately, although an alternative initial reaction might be suggested by analogy with reaction (9) and which would explain the results equally well, viz.

$$C_4H_{10} + N \longrightarrow HCN + C_2H_4 + CH_3 + H_2 \qquad (12)$$

Reaction (12) is exothermic by about 10 and 11 kcal. for n-butane and isobutane respectively. Bywater and Steacie found the activation energy for the decomposition of propyl radicals (probably a mixture of n-propyl and isopropyl) to ethylene and methyl radicals to be 20 kcal. Since the reaction suggested previously (159)

$$C_4H_{10} + N \longrightarrow HCN + C_3H_7 + H_2 \qquad (13)$$

would be exothermic by about 32 and 39 kcal. for n-butane and isobutane respectively, it is quite possible that part of the heat of reaction would remain as excitation energy in the propyl radicals and would cause them to decompose to ethylene and methyl radicals, or the collision complex might decompose directly according to reaction (12).

In the photosensitized decomposition of propane at high temperatures, Bywater and Steacie (192) found that the reaction

$$C_3H_7 \longrightarrow CH_3 + C_2H_4 \qquad (14)$$

became important at temperatures above 300°C and that the reaction

$$C_3H_7 \longrightarrow C_3H_6 + H \qquad (15)$$

became important at temperatures above 400°C. At 450°C reaction (15) seemed to occur to a greater extent than reaction (14), and since the activation energy of reaction (15) is nearly double that of reaction (14), the extent of the latter should eventually become small compared with the extent of the former as the temperature is increased. Since the reactions of active nitrogen with the butenes and cyclobutane were much more exothermic than the corresponding reactions with the butanes, the products of the former reactions could be generated with much higher vibrational temperatures than those of the latter. Thus, while the decomposition of the active nitrogen complexes with the butenes and cyclobutane might be expected to yield a certain amount of ethylene and methyl radicals, the larger part of the reaction might be expected to occur as indicated earlier in this discussion.

Small amounts of acetylene have been observed in the products of the reactions of active nitrogen with all the carbon-containing compounds studied thus far. Acetylene production usually appears to follow a trend similar to that of hydrogen cyanide production (with variation of reactant flow rate and temperature) and always corresponds to about 1% of the amount of hydrogen cyanide. The amount of acetylene collected in the products generally varies less with temperature than the amount of ethylene collected in the products. Acetylene is doubtless produced in secondary reactions because all the primary reactions which might generate it are highly endothermic. Since acetylene production shows the same general behavior whether the initial reactant is an olefin, a paraffin or a cycloparaffin, the suggestion that acetylene is formed by the dehydrogenation of ethylene by hydrogen atoms does not appear to be reasonable. Much more acetylene than ethane was collected in the products of the paraffin and cycloparaffin reactions and the reverse would be expected if acetylene were produced by the reaction of ethylene with hydrogen atoms. Although no definite mechanism may yet be assigned to acetylene production, it appears that the possibilities are confined to reactions of active nitrogen-hydrocarbon complexes or reactions of "hot" radicals, i.e. reactions that are analogous to thermal "cracking". These might be of the type mentioned in the discussion of the active nitrogen-methylamine reaction and might also include reactions such as

$$2\ [C_2H_4N] \longrightarrow 2\ C_2H_2 + 2\ H_2 + N_2$$

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The reactions of active nitrogen with ammonia, hydrazine and methylamine were studied over a range of temperatures in a fast flow apparatus. The flow of active nitrogen was maintained constant during the investigation of each reaction, while the flow rate of the reactant compound was varied over a wide range.

2. The active nitrogen-ammonia reaction was found to have the following properties:
   - (i) nitrogen and hydrogen were the only products over the temperature range -5° to 442°C
   - (ii) hydrogen atom reaction with ammonia accompanied the active nitrogen reaction at extremely low and high temperatures but not at intermediate temperatures
   - (iii) the active nitrogen reaction was fast and essentially independent of temperature over the range -5° to 442°C
   - (iv) decomposition of ammonia by active nitrogen occurred to a maximum extent which represented only about one-seventh of the total activity in the nitrogen as determined from its ability to form hydrogen cyanide with ethylene
   - (v) the yellow afterglow of active nitrogen was not completely quenched even at the highest ammonia

flow rates used

(vi) ammonia decomposition by active nitrogen occurred to the same maximum extent both in the presence and absence of significant amounts of ethylene, and large amounts of hydrogen cyanide were produced from ethylene even in the presence of a great excess of ammonia

3. The observations listed under 2. above were a strong indication that more than one chemically reactive species exists in active nitrogen. Consideration was limited to two reactive species, one of which reacts with ammonia while the other, or both, reacts with ethylene. The experimental results also indicated that a facile equilibrium does not exist between the reactive species.

4. The hydrogen atom-ammonia reaction was studied at -67°, 31° and 442°C. Although no reaction was observed at 31°C, there was considerable reaction at both -67° and 442°C. Nitrogen and hydrogen were the only products. The variation of the rate of reaction of hydrogen atoms with ammonia as the temperature is varied indicates that a change of mechanism in the reaction probably occurs as the temperature is increased from a very low to a very high value. The low temperature reaction is probably a surface reaction.

5. Small amounts of a basic product were formed in the active nitrogen-ethylene reaction. The amount of base produced decreased from 4.8% to 2.1% of the amount of hydrogen cyanide produced as the ethylene flow rate increased from 1.19 to 31.85 x 10^{-6} mole/sec.

6. The active nitrogen-hydrazine reaction was found to have the following properties:
   - (i) nitrogen and hydrogen were the primary products
   - (ii) ammonia was produced at high hydrazine flow rates, probably by reaction of NH_2 radicals with hydrazine
   - (iii) the active nitrogen reaction was very rapid and highly exothermic with both reactive species in active nitrogen at both 150° and 480°C
   - (iv) hydrazine decomposition by active nitrogen occurred to an extent which was similar to that of hydrogen cyanide production with ethylene
   - (v) the active nitrogen afterglow was completely quenched at a hydrazine flow rate just below that corresponding to the maximum amount of reaction

7. Comparison of the rate of hydrazine destruction with the rate of hydrogen cyanide production from ethylene in the active nitrogen reactions under similar conditions, indicates that excited nitrogen molecules do not make a large contribution to the chemical reactivity of active nitrogen.

8. The hydrogen atom-hydrazine reaction was briefly investigated at 48° and 458°C. Although approximately one mole of ammonia was formed for each mole of hydrazine destroyed at 48°C, considerably less than one mole of ammonia was produced for each mole of hydrazine decomposed at 458°C.

9. The active nitrogen-methylamine reaction had the following properties:
   (i) the products were hydrogen cyanide and hydrogen with smaller amounts of ammonia and a polymer and traces of acetylene, ethylene, ethane, methane and cyanogen
   (ii) the rate increased rapidly with increasing temperature and at 477°C methylamine was completely destroyed at all flow rates up to that corresponding to complete consumption of active nitrogen (both reactive species)
   (iii) less hydrogen cyanide was produced than in the ethylene-active nitrogen reaction under similar conditions
   (iv) the active nitrogen afterglow was completely quenched at all methylamine flow rates above about 1×10^{-6} mole/sec. and the reaction was accompanied by a peach colored cyanogen flame which decreased in intensity as the methylamine flow rate was increased

(v) ammonia and polymer appeared to be formed in the same secondary reactions

(vi) when the reaction vessel was surrounded with Dry Ice polymer was apparently a primary product. This polymer formation was probably a wall reaction

10. Mechanisms were proposed for the reactions of active nitrogen with ammonia, hydrazine and methylamine and of hydrogen atoms with ammonia. Evidence was given in favor of one and against the other of the two initial reactions that had been previously suggested as the initial step in the hydrogen atom-hydrazine reaction.

11. Although the identities of the reactive species in active nitrogen are still a matter of conjecture, it seems probable that one active species is ground state nitrogen atoms, while some other component such as N_3 might also contribute to the activity.

12. The conservation of spin in active nitrogen reactions was considered and probabilities for spin transitions were calculated (to an order of magnitude). Although it is exceedingly improbable that collision complexes between ground state nitrogen atoms and reactant molecules form directly in the doublet state, it appears that the probability for spin transitions to occur from the quartet to the doublet state in the collision complex is large enough to account for the observed rates

of the active nitrogen reactions studied thus far.

13. The mechanisms of the previously investigated active nitrogen-hydrocarbon reactions were reconsidered to present a more consistent picture of the series of reactions as a whole.

APPENDIX A

CALCULATION OF HEATS OF REACTIONS

All the heats of reactions given in this thesis have been calculated from the heats of formation of the reactants and products, i.e.

$$\Delta H_{reaction} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

The heat of formation of a substance, $H_f(\text{substance})$, is defined as the heat absorbed in the reaction when the substance is formed from its elements in their standard states.

The heats of formation of relevant compounds are listed in Table XI, those of relevant radicals in Table XII, and relevant bond dissociation energies in Table XIII. Two types of numbers are used in the columns under 'References'; numbers such as (172) refer to references in the bibliography of the thesis; numbers such as (ii) refer to footnotes which are given on the page following the table. Unless it is indicated otherwise, the heats of formation of the compounds and radicals are referred to 20°C. The heats of formation of most of the compounds were obtained from combustion data. Although the heats of formation of some radicals are listed by Szwarc (182), they are referred to 0°K. To get a self-consistent set of data, therefore, the heats of formation of the radicals at 20°C were calculated from the heats of formation of the parent compounds, the dissociation energies of the appropriate bonds, and the heats of formation of the simple groups split off (usually a hydrogen atom).

These data are not exact, but the reactions under consideration are either greatly exothermic or greatly endothermic, so relatively small inaccuracies in the data will not affect the conclusions drawn from any given calculated heat of reaction.

Sample Calculations

(a) Heat of formation of propane at 20°C

Heat of combustion of propane = -526.3 kcal. (1)
Heat of formation of 3 CO_2 + 4 H_2O = -556.6 kcal. (2)
Heat of formation of propane = (2) - (1)
= -30.3 kcal.

(b) Heat of formation of n-propyl radicals at 20°C

Heat of formation of propane = - 30.3 kcal. (1)
Heat of formation of H atoms = 51.5 kcal. (2)
$D(H\text{-}CH_2CH_2CH_3)$ = 95 kcal. (3)
Heat of formation of n-propyl radicals = (1) + (3) - (2)
= 13 kcal.

(c) Heat of reaction ($N + C_3H_8 \rightarrow HCN + C_2H_2 + 2\ H_2 + H$) at 20°C

$\Delta H_f(N) = 112.5$ kcal., $\Delta H_f(C_3H_8) = -30.3$ kcal.,

$\Delta H_f(HCN) = 30.1$ kcal., $\Delta H_f(C_2H_2) = 54.8$ kcal.,

$\Delta H_f(H_2) = 0$ kcal., $\Delta H_f(H) = 51.5$ kcal.

$$\Delta H_{reaction} = 30.1 + 54.8 + 51.5 - 112.5 + 30.3 \text{ kcal.}$$

$$= 54 \text{ kcal.}$$

This reaction is, therefore, 54 kcal. endothermic.

TABLE XI

Molar Heats of Formation of Selected Compounds in the Gaseous State at 20°C

Compound	ΔH_f(kcal.)	Reference
methane	-20.3	(i)
ethane	-25.5	(i)
ethylene	6.1	(i)
acetylene	54.8	(i)
propane	-30.3	(i)
cyclopropane	8.5	(i)
propylene	1.9	(i)
n-butane	-37	(ii)
isobutane	-36.0	(i)
cyclobutane	- 7	(iii)
1-butene	0	(iv)
cis-2-butene	- 1	(iv)
isobutene	- 3.8	(i)
ammonia	-10.9	(v)
hydrazine	22.7	(177)
hydrogen cyanide	30.1	(v)
methylamine	- 3.3	(vi)

Footnotes to Table XI

(i) Calculated from combustion data in reference (176).

(ii) Interpolated from heats of formation of ethane, propane and n-pentane, which were calculated as in (i).

(iii) Interpolated from cyclopropane, cyclopentane and cyclohexane, which were calculated as in (i).

(iv) Estimated from the heats of formation referred to 0°K, given in reference (15), by comparison with the heat of formation of isobutene referred to 0°K and 20°C.

(v) Listed in reference (176) referred to 18°C.

(vi) Estimated from the heat of combustion of gaseous methylamine at 25°C (178).

TABLE XII

Molar Heats of Formation of Selected Radicals
in the Gaseous State at 20°C

Radical	ΔH_f(kcal.)	Reference
H	51.5	(i)
N	112.5	(ii)
NH_2	44.6	(iii)
NH	83	(iii)
N_2H_3	61-66	(iii)
CN	93	(190)
CH_3	29.2	(iii)
CH_2	65	(iv)
CH	105	(iv)
CH_3CH_2	21	(iii)
CH_3CH	60	(iii)
CH_2CH	56	(iii)
$CH_3CH_2CH_2$	13	(iii)
$(CH_3)_2CH$	7	(iii)
$CH_2CH_2CH_2$	52	(iii)
CH_3CH_2CH	49	(iii)
$(CH_3)_2C$	43	(iii)
CH_3NH	40	(iii)
CH_2NH_2	40	(iii)

Footnotes to Table XII

(i) The values given in the literature for D(H-H) vary between 102 and 104 kcal., although 103 kcal. is favored.

(ii) Strong evidence has recently been obtained in favor of the value D(N-N) = 9.756 ev. = 225.0 kcal. (179 to 181), although some recent evidence has also been obtained in favor of D(N-N) = 7.373 ev. (182). The higher value was used in the present work.

(iii) Very recently, work has been published which supports the high value (170 kcal.) for the heat of sublimation of graphite (183, 184). However, the values $D(H\text{-}CH_3)$ = 101 kcal. and D(C-H) = 80 kcal. appear to be well established, and these values do not seem to be consistent with the high value for the heat of sublimation of graphite. The high value would mean that $D(H\text{-}CH_2) + D(H\text{-}CH) \approx 211$ kcal., which does not seem reasonable by comparison to $D(H\text{-}CH_3)$ = 101 kcal. The values for $D(H\text{-}CH_2)$ and D(H-CH) used in the present calculations were obtained from electron bombardment of methane, lead tetramethyl and diazomethane (173).

TABLE XIII

Selected Bond Dissociation Energies

Bond X-Y	D(X-Y)	References
H-H	103	(185,186)
N-N	225	(179 to 181)
$H-NH_2$	107	(188)
H-NH	90	(i)
H-N	81	(i)
$H-N_2H_3$	90-95	(ii)
H_2N-NH_2	66	(iii)
H_3C-NH_2	79	(187)
$H-CH_2NH_2$	95	(iv)
$H-NHCH_3$	95	(iv)
$H-CH_3$	101	(187)
$H-CH_2$	87	(173)
H-CH	92	(173)
$H-C_2H_5$	98	(187)
$H-CHCH_3$	90	(iv)
$H-CH_2CH_2$	38,39.5	(189),(192)
$H-CH_2CH_2CH_3$	95	(187)
$H-CH(CH_3)_2$	89	(187)
$H-CH_2CH_2CH_2$	90	(iv)
$H-CHCH_2CH_3$	87	(iv)
$H-C(CH_3)_2$	87	(iv)
$H-CHCH_2$	102	(191)

Footnotes to Table XIII

(i) Crude estimate from the total bond energy in NH_3 and $D(H-NH_2)$. Total bond energy in $NH_3 = 112.5 + 154.5 + 10.9 = 277.9$ kcal.

(ii) Estimated from the average N-H bond energy in N_2H_4. The total bond energy in hydrazine $= 225 + 206 - 22.7 = 408.3$ kcal. If it is assumed that the average H_2N-NH_2 bond energy $= 60$ kcal., then the average $H-N_2H_3$ bond energy $= 87$ kcal. It was therefore assumed that $D(H-N_2H_3) = 90$ to 95 kcal.

(iii) Estimated from the heats of formation of hydrazine, ammonia and hydrogen atoms, and $D(H-NH_2)$.

(iv) Crude estimate.

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