The Reaction of Nitrogen Atoms with Methane and Ethane

by

Herbert Blades, M.Sc.

Thesis submitted to the Faculty of Graduate
Studies and Research of McGill University
in partial fulfillment of requirements for
the Degree of Doctor of Philosophy.

From the
Physical Chemical Laboratory
McGill University
under the supervision of

Dr. C. A. Winkler

Sept. 1950

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the National Research Council for financial assistance in the form of a Studentship and to McGill University for a Demonstratorship.

TABLE OF CONTENTS

FREE ATOMS AND THEIR GAS REACTIONS

With the exception of the inert gases, the gaseous elements do not exist in the atomic state at ordinary temperatures. They combine with themselves to form stable molecules which will dissociate only at elevated temperatures. However, there are many chemical processes which involve these materials and which indicate that, at some time during the reaction, they exist as atoms. The combustion of hydrogen and oxygen, and the oxidation of nitrogen, are well known examples of such reactions:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$N_2 + O_2 \longrightarrow 2NO$$

Many of these reactions can be brought about by passing an electrical discharge through the reactants; from which observation early workers inferred that the gaseous elements might be dissociated into atoms in the electrical discharge.

With the development of spectroscopy it became possible to demonstrate the presence of atomic species in the electrical discharge. This conclusion has been amply verified by methods such as the Wrede gauge (1), which shows the presence of atoms by their high diffusion rates, and the Stern & Gerlach apparatus which shows the presence of atoms by their paramagnetic properties (2).

As indicated above, considerable chemical activity was expected of the gases in the atomic form, and this was demonstrated very early by such workers as Strutt (3), who described the activity of atomic nitrogen as it was produced in a condensed electric discharge, and by Wood (4), who studied the properties of atomic hydrogen produced in a continuous discharge. Subsequently the properties and reactions of all the gaseous elements in the atomic form have been studied to a widely varying degree. In addition to the discharge tube, photochemical procedures have been developed for dissociating the molecules into atoms.

Atomic Hydrogen

In 1922 Wood (4) first obtained and described the properties of atomic hydrogen which he produced in an electrical discharge tube. Hydrogen was pumped quickly through the discharge into a section of the tube unaffected by the electric current, where the atomic form became manifest by the increase in temperature of metal surfaces on which recombination of the atoms occurred.

It was shown (5) that atomic hydrogen was very active chemically, since it reduced the oxides of some of the metals and formed hydrides of some of the non-metals. It was found that when the apparatus was properly conditioned; i.e., when the walls were wet with phosphoric acid or water was present in the hydrogen, the half life of the atomic form was about 0.3 seconds. This was explained by the fact that a three body collision is necessary to allow the reaction:

$$H + H \longrightarrow H_2 ,$$

the third body being necessary to absorb the energy released, which is equal to the heat of dissociation of the molecule.

Such a long life made the study of atomic hydrogen reactions possible and in 1928 Bonhoeffer and Harteck (6) reported experiments on the reactions with hydrocarbons. They found that methane reacted scarcely at all, while ethane reacted slowly. Ethylene was very rapidly hydrogenated to form ethane.

Shortly after this, Paneth and Hofeditz (7) performed their classical experiment proving the existence of the methyl radical. This was followed by the free radical interpretation for the thermal decomposition of organic vapours by Rice (8) and his co-workers.

There developed rapidly a very extensive literature on free radical and atomic hydrogen reactions, an excellent review of which has been made by Steacie (9). It will be necessary here to discuss some of these reactions, but an effort will be made to confine these remarks to those which are directly relevant to the present problem.

Reactions of Atomic Hydrogen with Methane

When methane is mixed with atomic hydrogen or deuterium at temperatures of 300 to 500° C. the atom concentration drops sharply; with deuterium the resulting methane contains deuterium exchanged for hydrogen. There have been two mechanisms suggested for the reaction:

(1) Production of a methyl radical

$$D + CH_4 \longrightarrow CH_3 + DH$$

$$CH_3 + D \longrightarrow CH_3D$$

(2) Simple exchange

$$D + CH_4 \longrightarrow CH_3D + H$$

Sufficient evidence has not been obtained as yet to establish definitely which mechanism is correct. The activation energy calculated for the process is about 12,000 calories when the steric factor is taken as 0.1. The problem could presumably be settled if some material were found which was very reactive with methyl radicals, but relatively inactive with atomic hydrogen and methane at the experimental conditions used. No such material has been employed as yet, but the possibility of using atomic nitrogen will be discussed later.

Reaction of Atomic Hydrogen with Ethane

The reactions of atomic hydrogen and deuterium with ethane have been intensively studied and, like the reaction with methane, have not resulted in incontrovertible establishment of a single mechanism. Methane is formed and when deuterium is used at low temperatures the methane produced is deuterized but the ethane is not (10). This behaviour seems to be explained by the mechanism:

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

$$CH_3 + D \longrightarrow CH_3D \qquad (2)$$

However, this is contrary to a hypothesis of Rice (8) which is necessary, if his theory of the mechanism of the thermal decomposition of hydrocarbons is to be accepted. The assumption is that when a free radical reacts with a hydrocarbon, the reaction will be

$$R_1 + R_2H \longrightarrow R_1H + R_2$$

and not a rupture of the chain at a carbon carbon linkage. The theory of Rice is very successful in describing the course of hydrocarbon decomposition and largely on the strength of this, it was suggested (11) (12) that a more probable mechanism for the reaction of hydrogen atoms with ethane is

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5 \qquad (3)$$

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (4)$$

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

To date it has not been possible to establish directly the correctness of one or the other mechanism. As with methane, the problem might be settled if a detector for methyl radicals, unreactive with hydrogen atoms and ethane under the conditions where methane is formed, were available. The activation energy calculated for the hydrogen atom-ethane reaction is 6,700 ± 1,000 calories, again assuming a steric factor of 0.1.

Other Hydrocarbons

The reaction between hydrogen atoms and propane has been studied (13) and methane, ethane and ethylene have been found in the products. The reaction has the same velocity as the ethane hydrogen atom reaction and an activation energy of 8,600 calories is ascribed to it. The primary step here has been well established as dehydrogenation (14).

$$H + C_3H_8 \longrightarrow H_2 + C_3H_7 .$$

The higher saturated hydrocarbons react and are degraded to lower forms.

Unsaturated hydrocarbons may be hydrogenated to the saturated form or undergo polymerization. With hydrogen atoms acetylene appears unchanged but when reacted with atomic deuterium it is highly exchanged.

Inorganic Reactions of Hydrogen Atoms

As noted above, atomic hydrogen reacts with many elements and inorganic compounds. It reacts with the halogens very rapidly to form the hydrogen halide (15). With oxygen atomic hydrogen forms both hydrogen peroxide and water. With atomic nitrogen it forms ammonia.

Many other reactions have been noted but to the present they have not been investigated as extensively as have the hydrogen atom-hydrocarbon reactions.

Atomic Oxygen

Atomic oxygen was prepared by Harteck and Kopsch (16) in a discharge similar to that used for producing hydrogen atoms. Atomic oxygen reacts with molecular oxygen to form ozone but only in three body collisions. Thus at low pressures the atomic form is fairly stable at room temperature, although at liquid air temperatures it forms ozone. At atmospheric pressure the probability of three body collisions is much greater so that atomic oxygen quickly reacts with the molecular form.

Atomic oxygen has been found to react with materials (16) such as hydrogen, water, carbon monoxide, methane, methyl alcohol, benzene, hydrogen cyanide, ammonia and many others. Only a very few of these reactions have been studied intensively.

In the reaction between atomic oxygen and molecular hydrogen, water and not hydrogen peroxide is formed.

At normal temperatures atomic oxygen reacts slowly with methane with an activation energy of 8,000 calories. Steacie and Parlee (17) found carbon monoxide, carbon dioxide and water as products. However, other workers have found formaldehyde in the products (18) and the reaction is thought to be

$$O + CH_4 \longrightarrow H_2 + CH_2O$$

followed by the oxidation of the formaldehyde to water and the oxides of carbon.

The reaction between ethane and oxygen atoms was observed to have an activation energy of about 7,000 calories. Not enough work has been done to establish a mechanism for the reaction.

Atomic Chlorine and Bromine

It has been known that some reactions of chlorine are greatly accelerated by ultraviolet light. It was thought that chlorine was dissociated by the light into the atomic form which was very reactive and initiated chain reactions.

Atomic chlorine has been produced in the electric discharge in a similar manner to oxygen and hydrogen atoms. (19). It exhibits great chemical reactivity. With methane it reacts giving much heat and producing a mixture of chlorination products. With carbon monoxide it reacts to give phosgene.

Bromine atoms have been produced photochemically but they are not as reactive as atomic chlorine. This is explained by the fact that the reaction

$$RH + Br \longrightarrow HBr + R$$

is endothermic while the corresponding chlorine atom reaction is strongly exothermic.

The reaction of bromine atoms with methane (20) has been studied and an activation energy of about 18,000 calories determined for the process.

Atomic Nitrogen

When nitrogen is subjected to a condensed discharge, the gas continues to produce a yellow misty glow for some time after the discharge has been stopped. This behaviour was first observed by Lewis (21) but was not understood. Early in the century (1910) Strutt (3) became interested in the afterglow and by wetting the walls of a flask, connected to the discharge tube, with concentrated sulphuric or phosphoric acid, he was able to produce an afterglow which persisted for as long as six hours after the discharge was turned off. This extraordinary behaviour has intrigued investigators ever since that time.

There are now three procedures available for the production of the afterglow in nitrogen, the condensed discharge (1), high frequency electrodeless discharge (21) and under specific conditions the continuous discharge (22). In clean dry vessels and with very pure nitrogen, the duration of the afterglow is very short and it may not appear at all. However, if the walls of the vessel are poisoned either by admitting a small amount of foreign gas such as oxygen, water vapour, etc. with the nitrogen, or by conditioning with phosphoric acid, paraffin, etc. the glow will persist for a length of time which depends on the condition of the walls. For a time this phenomenon was not completely understood and there is considerable discussion in the early literature on the role played by oxygen, which is almost always present to some extent in the nitrogen.

The problem was solved by Strutt (3) who showed that traces of many gases enhance the afterglow, while their presence in greater amounts might either destroy or change it by chemical reaction with the glowing nitrogen.

It was early discovered that the glowing nitrogen was very reactive chemically. Strutt (3) investigated the effect of the gas on many gaseous compounds and solids. It was thought that the active ingredient in the glowing nitrogen was the atomic form, but this was not well established and for this reason the non-committal term "active nitrogen" was and still is used.

The apparatus used in this early work was not markedly different from that which was used later for atomic hydrogen work. Nitrogen was pumped rapidly at a controlled rate at about 1 mm. pressure through a discharge tube where it was activated and into a reaction chamber where it was allowed to react before passing through a liquid air trap into the pump. The experiments performed in this way were the first in the field of atomic gas reactions.

When some materials came into contact with the active nitrogen, they produced light of different wave length from that of the afterglow, and with gases the behaviour resembled a flame of burning material. A similar phenomenon has since been observed in other atomic reactions, the reaction between atomic hydrogen and ethylene being an example. In the early work a satisfactory analysis of all reaction products was not generally made, and the appearance of a flame was often the only criterion for stating that reaction did occur.

Materials which were observed to cause a flame were; phosphorous, iodine, sulphur, arsenic, sodium, various salts, nitric oxide, methane, pentane, ethylene, alcohol, ether, benzol, ethyl iodide, carbon disulphide, benzene, heptane, methyl bromide, ethyl chloride, ethyl iodide, chloroform, bromoform, ethylene dichloride, ethylidene dichloride and nitric oxide.

All compounds which reacted and contained carbon gave hydrogen cyanide as one end product. It was thought that those which contained halogens produced some cyanogen halide. No cyanogen was found in the end products of hydrocarbon reactions. Benzene was reported to give hydrogen cyanide and traces of C_6H_5CN and C_6H_5NC but these last two were identified only by smell.

The reaction of active nitrogen with methane and pentane was investigated by Koenig and Elöd (23). Methane was found to be unreactive only when carefully purified and like pentane it gave no flame. Pentane reacted to a small extent to form hydrogen cyanide and amylene, which was identified using mercuric acetate. It was concluded that the saturated hydrocarbons were relatively inactive and that methane did not react at all.

Strutt (3) then repeated his work on heptane, pentane and methane. He synthesized methane from sodium acetate and soda lime and also from aluminium carbide. With heptane he reported as products, hydrogen cyanide and some nitriles (identified by smell). With pentane he reported only hydrogen cyanide as product. With methane, Strutt reported less reaction than with pentane and heptane but, by carefully manipulating the flow rate of the methane, he could detect a faint flame. Hydrogen cyanide was the only product found. Strutt does not give complete numerical data but from his paper it may be inferred that about 0.3% of the methane which was passed into the apparatus appeared as hydrogen cyanide.

The latest reported work on methane was done by Baxter, Willey and Rideal (24)who found that carefully purified methane would not react with active nitrogen at room temperature.

The Nature of the Chemically Active Component of Active Nitrogen

Strutt has assumed in all his work that the active component in active nitrogen was atomic nitrogen. He noted that with certain metals, spectral lines could be excited for which only the atomic form could provide sufficient energy. This does not prove that the chemically active species is the atomic form and Strutt's hypothesis was later challenged by Baxter, Willey and Rideal (24).

These workers investigated the reactivity of a large number of compounds and classified them into two categories, those which reacted and those which did not react. They noted that the compounds which did not react were compounds which required energies of 55,000 calories or more for their dissociation, while all those compounds which did react required less than 55,000 calories.

Atomic nitrogen would be capable of providing energy considerably in excess of 55,000 calories but a metastable molecule of nitrogen might be expected to have a limit at about this value. Accordingly, a metastable molecule was postulated as being the chemically active component of active nitrogen.

However, it was fairly certain that atomic nitrogen was present and it was generally accepted that the afterglow was produced by the recombination of atomic nitrogen. Willey, therefore, attempted to show that chemical activity and the afterglow were not necessarily associated. His procedure was to destroy the afterglow by using an auxiliary high frequency discharge after the nitrogen had been activated with a condensed discharge. His early attempts served to indicate that chemical activity was not related to the afterglow (24) but later and more exact investigations made by him indicated the contrary. His attempts to show that chemically active nitrogen was different from nitrogen producing the afterglow must be regarded as unsuccessful.

Experiments performed since Willey's last publication on active nitrogen show that the chemically active species is related to the afterglow. Glowing active nitrogen will react with mercury, while nitrogen made glowless with an auxiliary discharge will not (25). Similarly, glowing nitrogen will heat thermocouples placed in the stream, but this is not observed if the glow is destroyed with the auxiliary discharge. Nitrogen which has been passed through ordinary continuous discharge contains metastable molecules but will not react with mercury (25). Thus the evidence suggested that the species producing the afterglow and the chemical activity are closely related.

Since Strutt's early experiments, considerable evidence has been obtained in support of his belief that atomic nitrogen, present in the afterglow, was responsible for its chemical activity.

It was shown by Wrede (1) that the concentration of atoms in a gas could be measured by the relative diffusion rates of the atoms and molecules. Experiments with a Wrede gauge indicated that active nitrogen, produced with a condensed discharge, contained up to 35% atomic nitrogen.

Atoms which have an unpaired electron can be detected in a Stern and Gerlach experiment by which their magnetic moment is measured. This experiment was performed on active nitrogen (2), using a metallic silver detector, and it was found that the only trace produced indicated atomic nitrogen. This has double significance since it at once indicates that atomic nitrogen is present and that only the atomic form reacts with the detector. If metastable molecules were present, they also would come into contact with the silver, but no trace indicating their reaction was observed.

It has been observed that when nitrogen is excited by an electrodeless discharge in a closed vessel, the pressure in the vessel almost doubles its previous value (26). This indicates almost complete dissociation into the atomic form.

The spectrum of atomic nitrogen was excited when glowing nitrogen produced in a condensed discharge was led through a high frequency discharge (27). The intensity of the lines were observed to be proportional to the concentration of atoms, and it was shown that an external discharge reduced the atom concentration when it removed the afterglow.

It has been found that the energy given up to a metal plate, when a stream of active nitrogen was passed over it, represented complete dissociation into the atomic form, plus excitation of the atoms (28).

Theoretical studies show that a mechanism involving atomic nitrogen can plausibly explain the afterglow phenomena and the large amount of heat generated at the surface of the metals. Debau (26) has presented such a mechanism involving atomic nitrogen in an excited state.

$$\mathrm{N} + \mathrm{N} \longrightarrow (\mathrm{NN})\ \text{complex}$$

$$(\mathrm{NN})\ \text{complex} \longrightarrow \mathrm{N} + \mathrm{N}$$

$$(\mathrm{NN})\ \text{complex} + \mathrm{M} \longrightarrow \mathrm{N}_2^{*}\ \text{(metastable molecule)}$$

$$\mathrm{N}_2^{*} \longrightarrow \mathrm{N}_2 + h\nu\ \text{(Afterglow)}$$

$$\mathrm{N}_2^{*} + \mathrm{M} \longrightarrow \mathrm{N}_2 + \mathrm{M}\ \text{(no afterglow)}$$

Thus it is fairly well established that active nitrogen does contain the atomic form, and more recent workers (29) (30) (31) have assumed that it is atomic nitrogen which is chemically active, although this fact has not been well established.

It has been shown, however, that some of the reactions of active nitrogen are fast (29), thus indicating that the chemically active species is present in high concentration. According to the Debau mechanism, the concentration of metastable molecules could not be large. Also, it has been shown that the reaction with ethylene goes at least partially to completion with respect to atomic nitrogen and that the extent of reaction is dependent on the atom concentration. Finally satisfactory mechanisms involving the atomic form have been worked out for three reactions (29) (30) (31).

While such arguments do not provide proof that the chemically active component of glowing nitrogen is the atomic form, it appears reasonable to assume that this is so.

The three reactions involving atomic nitrogen which have been studied with some degree of completeness are the reactions of atomic nitrogen with oxides of nitrogen; with molecular and atomic hydrogen; and with ethylene. Brief reviews of these are presented here.

Atomic Nitrogen - Oxides of Nitrogen (31)

If nitric oxide or nitrogen dioxide is added in small amounts to active nitrogen, the characteristic afterglow fades and only a faint bluish glow is observed. On adding larger quantities, the typical oxygen afterglow appears. A further increase in the amount of nitrogen dioxide will quench the afterglow but there is no change observed on further increasing the amount of nitric oxide. The reactions are strongly exothermic.

The reactions postulated are:

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

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

Reaction (1) effectively accounts for the appearance of the oxygen afterglow.

The reactions between atomic oxygen and nitric oxide and nitrogen dioxide were also studied. The reaction:

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

was slow and the oxygen afterglow persisted for all concentrations of nitric oxide.

The reaction :

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

was rapid and probably quantitative, so that with excess nitrogen dioxide the oxygen glow was quenched.

The behaviour with active nitrogen now becomes clear. In the reaction of nitric oxide with atomic nitrogen the following reactions would be expected:

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

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

Reaction (1) is fast, so that with excess nitric oxide it goes to completion. But (3) is slow and the atomic oxygen produced in (1) is not used and hence produces its characteristic afterglow.

In the reaction of active nitrogen with nitrogen dioxide the mechanism would be

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

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

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

All these reactions are rapid so that when atomic nitrogen is in excess atomic oxygen will be formed, even if reaction (4) does proceed and the oxygen afterglow will be produced. When nitrogen dioxide is in excess reaction (4) would remove atomic oxygen and the afterglow should be extinguished.

Nitrogen Atom - Hydrogen Systems

This system was first studied by Lewis (32) who showed that nitrogen atoms reacted with atomic hydrogen to form ammonia but no ammonia was formed from reaction with molecular hydrogen.

Steiner (30) discovered that atomic nitrogen did react with molecular hydrogen to form a small amount of hydrazine. With high nitrogen atom concentration both ammonia and hydrazine were formed when atomic hydrogen was used. At low concentrations of atomic nitrogen only ammonia was formed.

The mechanism proposed for ammonia formation was:

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

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

M being a third body.

The mechanism proposed for hydrazine formation was:

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

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

where M is again a third body.

To test the idea of triple collisions metals were placed in the path of the mixed atomic hydrogen and nitrogen stream. The yield of hydrazine dropped while the yield of ammonia increased. This confirms the proposed mechanism for ammonia production but suggests that hydrazine is formed in a homogeneous reaction which is slowed down by the decrease in atom concentrations in the region of the metal catalyst.

Atomic Nitrogen-Ethylene (29)

Atomic nitrogen produced in a condensed discharge was led into a reaction chamber where it was allowed to react with ethylene. Pressures of about 0.5 mm. and a flow rate of about 1.25 litres (S.T.P.) per hour were employed. Atom concentrations were measured with a Wrede gauge and ethylene to atomic nitrogen ratios were varied from about 0.3 to 1.5. The products of reaction were hydrogen cyanide, a polymerized material and some saturated hydrocarbon assumed to be ethane.

The reaction produced a flame and appeared to go to completion although a satisfactory accounting of neither the ethylene nor the atomic nitrogen was obtained.

The reaction mechanism suggested was:

$$C_2H_4 + N \longrightarrow HCN + CH_3 \qquad (1)$$

$$N + CH_3 \longrightarrow HCN + 2H \qquad (2)$$

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (3)$$

$$C_2H_5 + H \longrightarrow C_2H_6 \qquad (4)$$

Reaction (2) was written in preference to

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (5)$$

since it appeared that some source of hydrogen atoms was needed for the production of ethane.

The reaction of methyl radicals with ethylene

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

was ruled out on probability grounds since it must occur in a flame where presumably the concentration of ethylene is low. This argument might also be applied to (3) so that it is not a very convincing one.

It has been shown that methyl radicals react with ethylene to produce propane, butane and pentane (46). Hydrogen atoms react with ethylene to produce ethane (9). The solution to the question of whether reaction (3) or (5) takes place, obviously lies in a reliable identification of the saturated material produced the nitrogen atom ethylene reaction.

From collision yields an activation energy of 6,900 calories was calculated for the process assuming a steric factor of 0.1. However, the reaction takes place in a flame where there are undoubtedly large concentration gradients, so that the above figure represents only an upper limit.

Rate constants were also estimated using the diffusion flame technique. It was assumed that the visible flame marked the boundry of the reaction zone, and by adapting the technique of Polanyi (47), rate constants were determined for a series of temperatures.

In the temperature range studied the velocity constant did not vary beyond the experimental uncertainty of the measurements. This, however, permitted the calculation of an upper limit of 3,000 calories for the activation energy and a value of 10^{-2} for the steric factor.

The Reactions of Atomic Nitrogen with Methane and Ethane

The present investigation was concerned with the reactions of atomic nitrogen with methane and ethane, the main purpose being to extend the available information about nitrogen atom reactions. Such knowledge might, in turn, be of assistance in interpretation of other atomic reactions.

EXPERIMENTAL TECHNIQUE

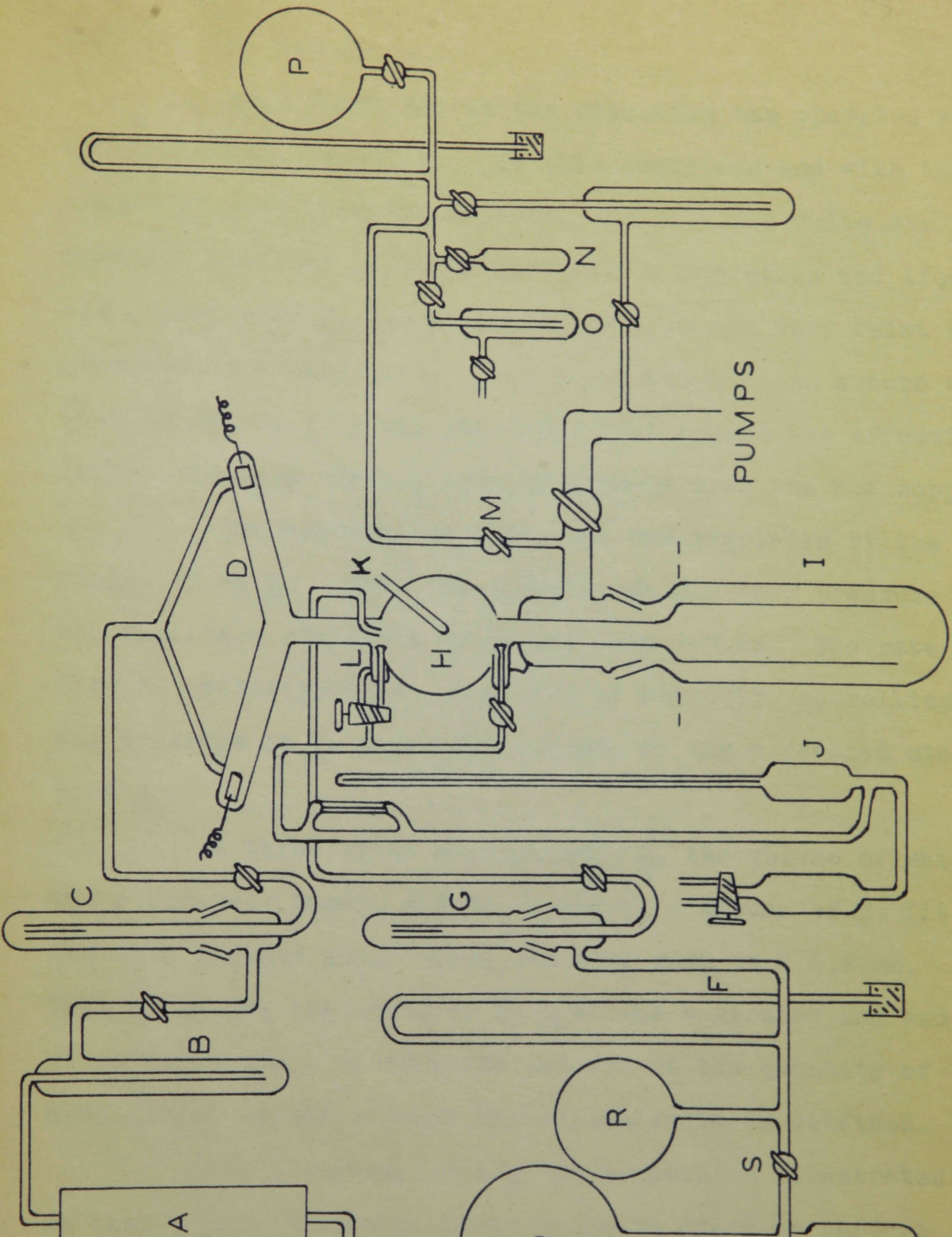
Apparatus

A condensed discharge was used to produce the active nitrogen since this method is reliable and effective over a considerable range of pressures. A flow system, similar to that used for hydrogen atom studies, was adopted. The apparatus is illustrated in figure 1 and the following description is made with reference to that figure.

The nitrogen was led from a commercial cylinder into a meteorological balloon for storage at essentially atmospheric pressure. From the balloon the nitrogen was taken through a tube, A, packed with copper shavings heated to about 500° C. to remove oxygen. From here it was passed through a liquid air trap, B, to remove water and CO_2. The rate of flow into the discharge tube was controlled by a capillary at C, As shown, this capillary was readily removed for changes or adjustment. From the capillary the nitrogen entered the discharge tube at each end, so that the incoming nitrogen would tend to sweep the activated form away from the metal electrodes.

The pressure exerted by a balloon when completely inflated was about 5 mm. higher than when it was only partially inflated. Thus it provided a supply of nitrogen at about one atmosphere with a pressure variation of around 0.2 per cent. The flow rate obtained with this sys-

<u>Figure I</u> Diagram of apparatus used for studying nitrogen atom reactions.


P
N
O
PUMPS
M
K
D
H
L
I
J
C
G
F
B
A
R
S
Q
E
STORAGE
TO BALLOON

tem was very steady.

When first set up the apparatus was operated without poisoning the walls. In this condition and with the copper in A at room temperature, the glow was quite strong. However, with the nitrogen purifier in operation and liquid air around trap B, the afterglow soon became very faint and practically disappeared. This observation is in accord with that of Strutt (2), and indicates that oxygen was effectively removed from the nitrogen by passage over the hot copper.

The hydrocarbon flow rate was regulated by the capillary at G. With the hydrocarbon the fore pressure on the capillary could not be higher than 500 mm. The rate of flow of hydrocarbon was regulated by manually controlling the pressure in R, a ballast volume, by the scratched stopcock S.

A three litre storage bulb Q, the volume of which was accurately known, was connected to a manometer E, fitted with a glass scale which could be read to ± 0.2 mm. Thus by noting the pressure in Q at the beginning and end of an experiment, an accurate measure of the quantity of hydrocarbon passed through the system could be obtained.

The discharge tube D was mounted as illustrated so that a wall poisoning fluid could be drawn up through the trap into H and D and then allowed to drain out completely.

The discharge tube was made of 2.5 cm. pyrex glass with the electrodes 54 cm. apart. The electrodes were aluminium attached to tungsten leads which were sealed into the glass. No experiments were made to determine the optimum size for the discharge tube, but several sizes were employed in the course of this work. The one used gave rather low concentrations of nitrogen atoms and probably does not represent the best size possible. Its performance, however, did prove adequate. During operation the tube was cooled by an air blast and it was surrounded by a cardboard shield which protected the operator's eyes from the bright flash of the intermittent discharge.

The discharge tube was connected to the reaction chamber by a tube 19 cm. long and 1.2 cm. in diameter. The critical factor in selection of this tube is that it must be of such dimensions that no appreciable quantity of gas can diffuse from the reaction chamber back to the discharge tube. The distance to which a gas will diffuse against a flow stream is given by (32)

$$\frac{N}{N_o} = e^{-vx/D}$$

where N_o is the concentration in the reaction chamber

N is the concentration at a distance X cm. up the connecting tube

D is the diffusion coefficient.

For most gases at 1 atmosphere D is approximately 0.7 (33). However, D is inversely proportional to the pressure so that at 1.5 mm D is approximately 400.

The linear velocity through this tube at 1.5 mm pressure was 12 meters per second.

For a value of 10^{-3} for $\frac{N}{N_0}$;

$$X = 0.22 \text{ cm.}$$

Thus, allowing for even a tenfold error in the diffusion coefficient, no significant quantity of hydrocarbon could diffuse back into the discharge tube.

The reaction chamber, H, was constructed from a 300 ml. flask and had one Wrede gauge installed at the entrance and one at the exit tube, as shown. With the two Wrede gauges so situated, it was possible to measure atom concentrations, both at the exit and the entrance to the reaction chamber.

These gauges were made from filter sticks of "fine" porosity which, according to the manufacturer, had a pore size of 5 microns which is smaller than the mean free path of nitrogen at 2 mm, pressure.

Pressures were measured with a McLeod gauge which had a very long capillary and was capable of measuring pressures up to 3 mm. with an uncertainty of 0.1 percent. In measuring atom concentrations this produces an uncertainty of about 5% due to the McLeod gauge alone.

A furnace containing a heating element of nichrome wire was moulded about the reaction chamber in at 1.5 mm D is approximately 400.

The linear velocity through this tube at 1.5 mm pressure was 12 meters per second.

For a value of 10^{-3} for $\frac{N}{N_0}$;

$$X = 0.22 \text{ cm}.$$

Thus, allowing for even a tenfold error in the diffusion coefficient, no significant quantity of hydrocarbon could diffuse back into the discharge tube.

The reaction chamber, H, was constructed from a 300 ml. flask and had one Wrede gauge installed at the entrance and one at the exit tube, as shown. With the two Wrede gauges so situated, it was possible to measure atom concentrations, both at the exit and the entrance to the reaction chamber.

These gauges were made from filter sticks of "fine" porosity which, according to the manufacturer, had a pore size of 5 microns which is smaller than the mean free path of nitrogen at 2 mm, pressure.

Pressures were measured with a McLeod gauge which had a very long capillary and was capable of measuring pressures up to 3 mm. with an uncertainty of 0.1 percent. In measuring atom concentrations this produces an uncertainty of about 5% due to the McLeod gauge alone.

A furnace containing a heating element of nichrome wire was moulded about the reaction chamber in two hemispheres. The heating element was wound evenly throughout the furnace to ensure uniform temperature. The reaction chamber was equipped with a thermocouple well, K, which permitted temperature measurements of the gas flowing through it. A second thermocouple was inserted between the wall of the chamber and the furnace and gave the temperature of the chamber wall.

The trap, I, used to collect the products is worthy of note here. As shown, it had an inner tube of large diameter, 2.6 cms, and an outside tube of 4.5 cms. The large diameter was found necessary because in smaller tubes the hydrogen cyanide produced by reaction quickly formed a plug of fine needle-like crystals which impeded the flow. With the large tube this did not occur.

The analysis system was connected to the main trap, I, by the stopcock M. It consisted simply of a train which had two traps, N and O, and a calibrated volume, P. Trap to trap distillation could be effected from N to O, and gas quantities could be measured by expansion into P. Trap N could be sealed off for weighing residues.

Power Supply

The circuit for the power supply is shown in figure II. A large transformer was not available so two neon sign transformers were connected in parallel, as shown. Their primary coils were also connected in parallel and to the secondary of a large "Variac". Thus the potential on the secondaries of the transformers could be varied at will from 0 to something in excess of 6,000 volts.

To rectify the current, two 866A mercury rectifier tubes were used in parallel. These were regulated with resistors R_1 and R_2 of 5,000 ohms each. The tubes were considerably overloaded beyond their rated capacity, but they held up well throughout the work. At around 6,000 volts sparks tended to jump between the prongs at their base and thus to spoil the insulation.

Various capacitances were used at C but, owing to difficulties in measuring atom concentrations, no satisfactory information was gained on the relation of atom concentration to condenser size. A bleeder resistance R_3 of 3 megohms was placed across C to discharge the condenser when not in use.

A spark gap, which consisted of two brass spheres, was placed in series with the discharge tube. This was not entirely satisfactory because the spheres became scored and covered with scale, so that the discharge rate fluctuated. This was remedied to some extent by scraping off the scale with a file. When lower concentrations of atoms were required, the discharge gap was shorted out.

The pumping system consisted of two large mechanical pumps connected in parallel and separated by a large bore stopcock. One was a Cenco Megavac in satisfactory running condition, the other was a Welch Duoseal with rather poor performance but it did contribute substantially to the pumping speed at pressures greater than 0.5 mms.

Operational Data

The pumping speed at 1.55 mm. was 6.63×10^{-3} moles per minute or 1.33 litres per second at 25° C. The volume of the reaction chamber was 318 ml. so that, on the average, an atom of nitrogen was in the chamber for 0.1 to 0.2 seconds.

Measurements of the atom concentration with the Wrede gauges were, at least initially, discouraging. To reduce pressure fluctuation in the system, a 12 litre flask was sealed to it. With this arrangement, the pressure could be held constant to one part in a thousand over a period of half an hour but still the atom concentration fluctuated widely.

Attempts made to determine the time necessary for the gauge to reach equilibrium indicated that it required about one minute, so that the lack of reproducibility could not be attributed to failure to attain steady state conditions across the gauge.

The final conclusion reached was that the atom concentration did vary by an amount greater than the uncertainty of the Wrede gauge. After the apparatus had been in operation for some time the fluctuations seemed to de-

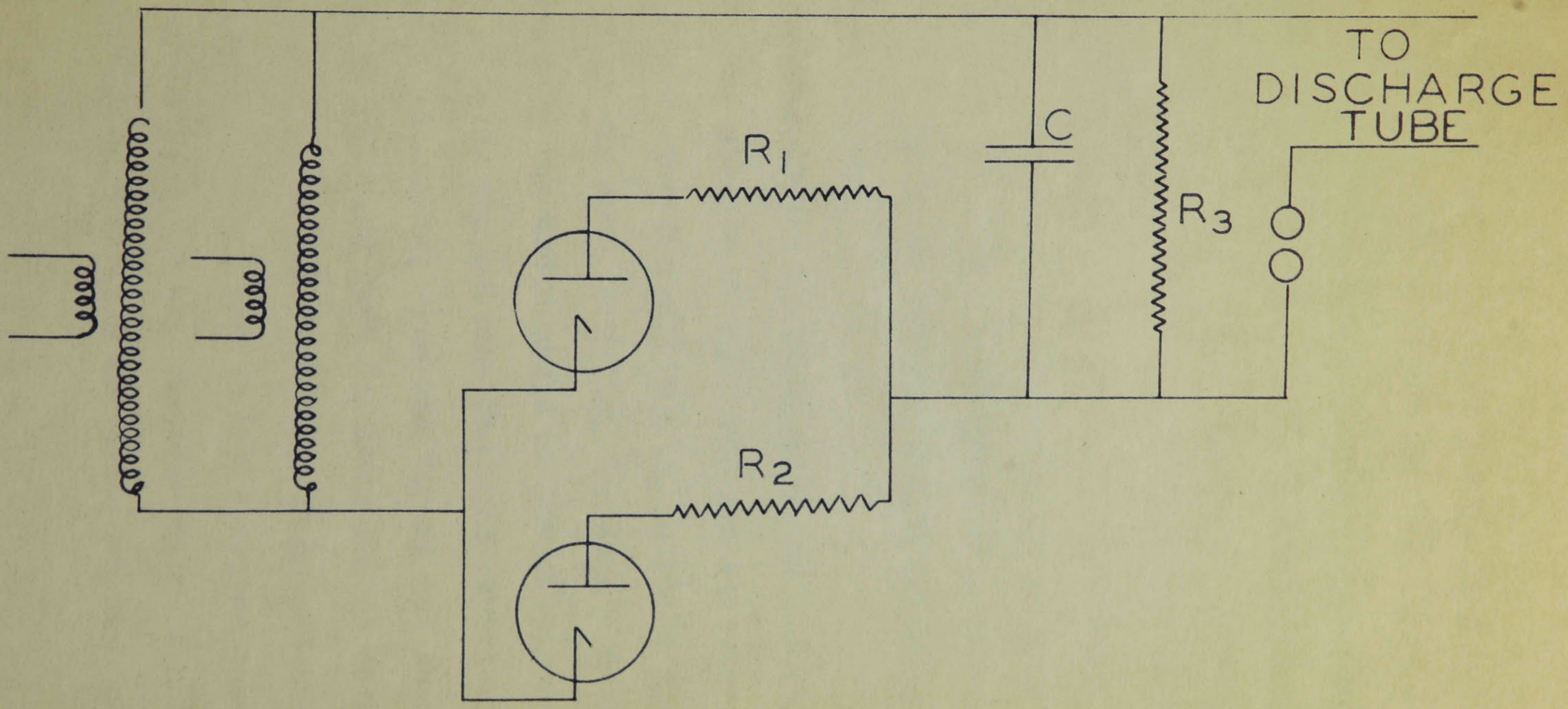


Figure II Circuit diagram for power supply.

crease somewhat, and reasonably satisfactory readings were then obtained.

A series of measurements of atom concentrations was made for three different conditions of the discharge. These values are given in Table I, along with a description of the discharge conditions. Each value recorded for the atom concentration is the mean of six consecutive readings. The figures listed under the heading "Variac" are the scale readings on the variac variable transformer and indicate roughly the potential applied to the primaries of the 6,000 volt transformers.

The effect of temperature on the atom concentration in the reaction chamber was investigated, with the walls of the reaction chamber, H, poisoned with phosphoric acid. This was done by noting the atom concentrations as registered by the Wrede gauge at the entrance and exit tubes. At room temperature the concentration decreased by about half in passing from the top of the chamber to the bottom. At 256° and 415° C. there was no detectable change in measured atom concentrations and the intensity of the glow in trap I and in the reaction chamber did not change detectably. Thus, the afterglow is not quenched up to 415° when the walls are poisoned with phosphoric acid.

Materials and Procedure

The experimental problems encountered in studying atomic nitrogen are essentially the same as those encountered in hydrogen atom work and many of the techniques used are adopted from that field.

The same flow rate of nitrogen, 6.63×10^{-3} moles per minute, was used throughout the project. The atom concentration was varied by changing the discharge conditions as described above.

The methane used was taken directly from a cylinder supplied by the Matheson Company and was guaranteed 99% methane. Ethane was obtained from Phillips Petroleum and was only 95% pure. It was purified by the method described by MacGillvray (34). It was bubbled twice through fuming sulphuric acid, then through a solution of 20% potassium hydroxide and finally through a tube containing potassium hydroxide pellets. The gas was then condensed in a trap, using liquid air, and distilled in a Podbielniak still. A middle cut was used, and the reflux temperature throughout the take-off did not vary detectably. After distillation, the gas was stored in a five litre bulb until needed.

The hydrocarbon flow rate was controlled by manipulating the scratched stopcock, S, to maintain the requisite pressure in R. The pressure in Q was noted both before and at the end of an experiment, to obtain a measure of the hydrocarbon used.

The reaction chamber was maintained at a steady temperature manually. The temperature of the flame, as

TABLE 1

Atom Concentrations measured with the Wrede Gauge under various discharge conditions.

Number of Exp't.	Condenser mfd	Variac Reading	Spark Gap	Discharge Potential Volts	Rate of Discharge Number per Second	Average Atom Concentration %	Average Deviation of % Atom Concentration
1	1	45	none	2750	10	8.9	1.5
2	2	85	none	3000	10	12.2	2.1
3	4	100	1.5 mm	3800	3-5	14.2	1.5

indicated by the thermocouple, K, fluctuated considerably but the temperature of the wall of the reaction vessel could be held quite steady. The average temperature indicated by the thermocouple, K, was taken as the reaction temperature.

The large trap I was immersed in liquid nitrogen to the dotted line, as shown in figure I. Ethane was trapped out quantitatively, and at no time did this trap plug up.

The length of time for an experiment was governed either by the time necessary to collect a significant quantity of product or that necessary for sufficient hydrocarbon to be used, so that the pressure change in Q could be accurately determined. The longest experiments required about one hour, and the shortest fifteen minutes.

When an experiment was complete, all stopcocks leading to the reaction chamber were turned off except that giving access to the pump. The system was evacuated using only the Megavac pump for several minutes. The system was then closed off and the analysis train evacuated. Stopcock M was then opened, trap N was immersed in liquid air, and the main trap, I, allowed to warm up to room temperature.

Condensed hydrocarbons melted and distilled over to trap N, but hydrogen cyanide did not melt and was sublimed. It was important that hydrogen cyanide be not allowed to melt in trap I, because whenever it did, it rapidly polymerized to a brown polymer (35, 36, 37). When polymerization was prevented, the total contents could be successfully transferred.

Stopcock <u>M</u> was then closed and trap <u>N</u> immersed in a mixture of ether and frozen ether (-116° C.) and material volatile at this temperature was collected in <u>O</u>, which was immersed in liquid air. In experiments with ethane, the unreacted portion was satisfactorily separated from the hydrogen cyanide in this way. The gas condensed in <u>O</u> was then estimated quantitatively by expanding it into <u>O</u> and <u>P</u>, and measuring the pressure exerted. This gas could then be recondensed and transferred to a Podbielniak still for analysis.

The residue left in trap <u>N</u> at -116° C. was weighed. This was done by sealing off trap <u>N</u>, allowing it to warm up to room temperature and weighing it. It was then broken open and the contents absorbed in 5% potassium hydroxide solution. The solution was titrated for hydrogen cyanide with the copper ammonium ion, as outlined in Scott (38).

The titration, when performed on experiments where polymerization had been avoided, could be compared with the weight of the residue. In this way it was possible to determine whether or not products other than hydrogen cyanide were present.

RESULTS AND DISCUSSION

Reaction of Nitrogen Atoms with Methane

In preliminary experiments an apparatus was used with a reaction chamber of about one half the volume of the one described above. With this apparatus no flame was observed when methane was brought into contact with the nitrogen atom stream. Hydrogen cyanide, corresponding to about 1% of the methane passed in, was collected in the trap. When the temperature of the reaction chamber was raised to 200° C. the yield of hydrogen cyanide did not increase detectably, and it was concluded that, at these temperatures, methane did not react and that the material collected in the liquid air trap was the result of reaction between atomic nitrogen and some small amount of impurity in the methane.

Experiments were then made in the apparatus described above, with the conditions indicated in Table II. At temperatures of 350 - 450° C., 7 to 20% of the methane passed reacted to form hydrogen cyanide.

If the products of reaction were allowed to melt in the main trap, they turned from white to yellow as melting proceeded, and the liquid solidified to a dark brown polymer if allowed to stand for a few hours.

It is known that hydrogen cyanide will polymerize and that to prevent this it must be stored in a pure form and must contain some inhibitor. In studying polymers

TABLE 11

Experimental and Calculated data on
the Methane-Atomic Nitrogen reaction.

Experiment Number	Ratio of Methane to Atomic Nitrogen	Temp. ^{o}C.	Flow Rate of Atomic Nitrogen moles/min.	Flow Rate of Methane moles/min.	Production Rate of HCN moles/min.	Pressure mm. Hg	Collision Yield	Log Collision Yield
1	0.282	416	$9.23x10^{-4}$	$2.60x10^{-4}$	$0.43x10^{-4}$	1.65	$1.79x10^{-6}$	-5.748
2	0.675	322	"	6.23	0.44	1.65	$4.71x10^{-7}$	-6.328
3	0.668	370	"	6.14	1.13	1.65	$1.37x10^{-6}$	-5.863
4	0.682	397	"	6.30	2.15	1.68	$2.74x10^{-6}$	-5.563
5	0.688	402	"	6.35	1.10	1.68	$1.37x10^{-6}$	-5.865
6	1.00	425	"	9.26	2.14	1.76	$1.88x10^{-6}$	-5.727
7	1.05	344	$6.45x10^{-4}$	6.77	0.54	1.68	$7.66x10^{-7}$	-6.117

TABLE 11 cont'd

Experimental and calculated data on
the Methane-Atomic Nitrogen reaction.

Experiment Number	Ratio of Methane to Atomic Nitrogen	Temp. °C.	Flow Rate of Atomic Nitrogen moles/min.	Flow Rate of Methane moles/min.	Production Rate of HCN moles/min.	Pressure mm. Hg	Collision Yield	Log Collision Yield
8	1.08	376	6.45×10^{-4}	6.95×10^{-4}	0.75×10^{-4}	1.68	1.13×10^{-6}	-5.947
9	1.08	389	"	6.98	0.74	1.71	1.15×10^{-6}	-5.940
10	1.04	401	"	6.70	1.42	1.70	2.62×10^{-6}	-5.582
11	1.08	435	"	6.95	1.21	1.68	2.24×10^{-6}	-5.648
12	2.17	377	9.23×10^{-4}	20.1×10^{-4}	3.22	1.93	1.25×10^{-6}	-5.903
13	"	424	"	19.9	5.71	1.93	2.46×10^{-6}	-5.611
14	"	446	"	20.0	5.28	1.93	2.38×10^{-6}	-5.623

of hydrogen cyanide the usual procedure is to polymerize a mass of the material by allowing it to stand with a polymerization initiator. Initiators used are; water (35), potassium cyanide (36), dimethyl aniline oxide (37), and presumably other materials would be effective too. The hydrogen cyanide in contact with an initiator polymerizes to a black or dark brown amorphous mass, which is then extracted with various solvents to separate the various polymers.

Polymers corresponding to $(HCN)_2$, $(HCN)_3$, and $(HCN)_4$ have been separated and identified, but the brown material is apparently more complex. It partially decomposes on heating into hydrogen cyanide and ammonia.

Hydrolysis of the trimer (39) gives carbon dioxide, ammonia and glycine. The polymer $(HCN)_4$ has been identified as 4, 5-dicyano 1, 2, 3-triazole (40).

A material which acts as an inhibitor to the polymerization of hydrogen cyanide is phosphoric acid (41). It is effective at concentrations of one half percent or less.

It was found that when trap I was conditioned by wetting the inside with a 5% solution of phosphoric acid and then drying by pumping the water off for about half an hour, hydrogen cyanide from an experiment could be distilled into trap N, and treated as outlined previously without polymerization, even when allowed to melt and warm up to room temperature. A trap prepared in this way retained its effectiveness for about six experiments. Phosphoric acid placed in N did not inhibit polymerization when trap I was not properly treated.

In early experiments it was noted that a ring of residue about half an inch wide formed on the inner tube of trap I. This residue remained behind after the hydrogen cyanide had sublimed and it did not melt at room temperature. If the trap was poisoned as described above, and the liquid air level held constant throughout the experiment, it was found possible to eliminate the residue completely. The most plausible explanation for the formation of this residue is that atomic nitrogen reacts with hydrogen cyanide at temperatures above that of liquid air. If the liquid air level is maintained constant, the condensed hydrogen cyanide cannot warm up and no polymerization occurs.

The procedure used for analysis of the products was that outlined above; i.e., the total contents of trap I were distilled to trap N, where a fraction volatile at -116° C. was separated. The vapour pressure of the residue from this fractionation was then measured and corresponded exactly with the vapour pressure of HCN.

Trap N was sealed off and weighed to determine the weight of the contents. The contents were then absorbed in a 5% solution of potassium hydroxide and titrated for hydrogen cyanide. This provided further confirmation that the product was hydrogen cyanide.

The volatile fraction separated at -116° C. was quite small. It was first cycled over ascarite where about half of it was absorbed, thus indicating either carbon dioxide or hydrogen cyanide. The remaining gas was mixed with oxygen and burned. The resulting gas was partially absorbed by anhydrone and the remainder with ascarite, thus indicating that the gas burned was a hydrocarbon.

The quantity of this hydrocarbon was very small and if assumed to be ethane, it would represent only 2% of the methane which had reacted and much less than 1% of the total methane passed. Its quantity did not vary significantly with the reaction conditions.

Since the volatile fraction at -116° C. was very small and since it was largely hydrogen cyanide or carbon dioxide, it was given no further consideration and has not been included in Table II.

The yields of hydrogen cyanide are recorded in Table II, and for the calculations which follow it has been assumed that the rate of production of hydrogen cyanide is a true measure of the rate of reaction.

Close examination shows that the rate of production of hydrogen cyanide was somewhat erratic, and the cause of this was not determined. However, considered as a whole, the data collected allow a reasonable estimation of of the activation energy of the process.

Collision yields were calculated for the process assuming that each hydrogen cyanide molecule represented a fruitful collision. The collision yield is defined as:

$$S = \frac{\text{number of fruitful collisions per second}}{\text{total number of collisions between reactants per second}}$$

The number of fruitful collisions is equal to the number of hydrogen cyanide molecules produced per second. The total number of collisions, Z, between reactants is given by:

$$Z = N_1 N_2 \sigma_{12}^2 \left\{ 8 \pi R \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}}$$

where: N_1 is the number of atoms of nitrogen per cm^3

N_2 " " " " molecules of methane per cm^3

σ_{12} " " mean collision diameter

M_1 " " atomic weight of nitrogen

M_2 " " molecular weight of methane

The collision diameter of methane was taken as 3.75 Å. The collision diameter for atomic nitrogen is not known with any certainty. Greenblatt (29) estimated it as about 3.0 Å, calculated from a value of the diffusion coefficient assumed by Strutt.

A value for the activation energy of a process may be calculated from the collision yield by the following relation:

$$S = Pe^{-E/RT}$$

where P is a steric factor. This factor is usually assumed to be 0.1, but there are indications that for some atomic and free radical reactions it is smaller than this (42). The average activation energy as determined, assuming $P = 0.1$, was 14,600 calories with an average deviation of 400 calories. This small average deviation indicates that the data obtained are more consistent than appears at first sight.

If logarithms are taken for both sides of the expression $S = Pe^{-E/RT}$ it reduces to the form:

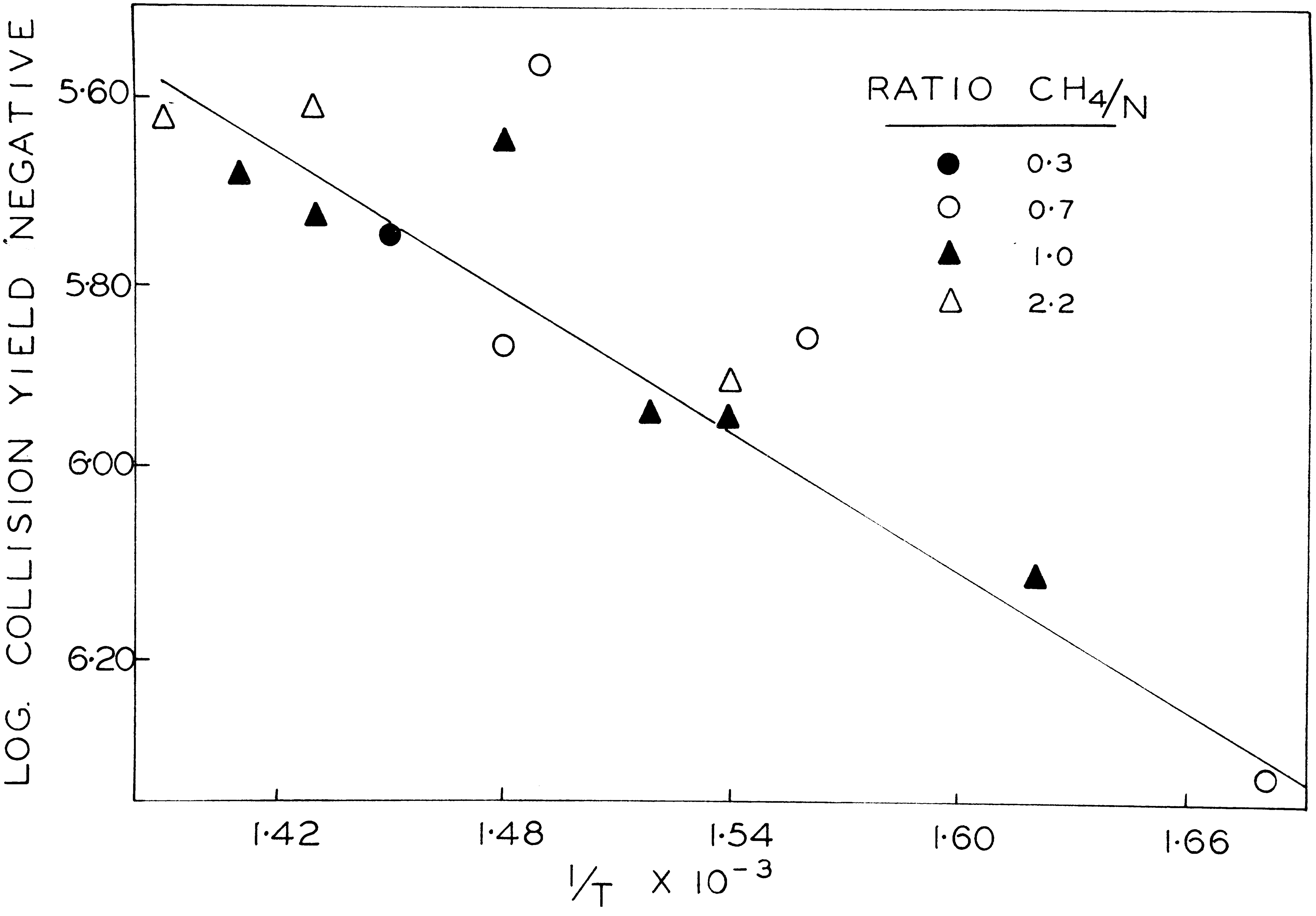
$$\log S = \frac{-E}{2.3R} \; 1/T + \log P$$

When log S and 1/T are taken as the variables, this becomes a linear relation. Thus if log S is plotted against 1/T, a straight line results, from which both E and P can be computed. Such a plot is shown in figure III, for different concentration ratios of methane to nitrogen atoms.

Inspection shows that there is no definite trend in the collision yield as the concentration is varied. The scattering of points must then be due to experimental uncertainties and not to changes in reaction mechanism arising from the variation of reaction conditions.

With the exception of three points, a straight line can be fitted to the data relatively well. From the straight

Figure III Plot of log collision yield versus I/T for the atomic nitrogen - methane reaction.


RATIO CH_4/N
0·3
0·7
1·0
2·2
LOG. COLLISION YIELD NEGATIVE
5·60
5·80
6·00
6·20
1·42
1·48
1·54
1·60
1·66
$1/T \times 10^{-3}$

line so drawn, values for the activation energy E and the steric factor P have been calculated. These values are:

$$E = 11,000 \text{ calories}$$

$$P = 5 \times 10^{-3}$$

The value for the probability factor is lower than is generally assumed for free radical and atomic reactions. It is, however, of the same order of magnitude as that estimated for the nitrogen atom-ethylene reaction (29), where a value of 10^{-2} or less was indicated. Presumably, a reaction with such a low steric factor does not involve a chain process.

Thus it appears that the reaction between methane and atomic nitrogen proceeds by a relatively simple mechanism:

$$N + CH_4 \longrightarrow HCN + H_2 + H \qquad (1)$$

In this mechanism, however, atomic hydrogen is formed and the consequences of this fact must be considered. It is known that at elevated temperatures the concentration of atomic hydrogen rapidly decreases, indicating the recombination reaction:

$$H + H \longrightarrow H_2 \qquad (2)$$

At 400° C. the reactions:

$$H + CH_4 \longrightarrow CH_3 + H_2 \qquad (3)$$

$$H + CH_4 \longrightarrow CH_4 + H \qquad (4)$$

may take place. If atomic hydrogen reacts by (4) with methane then no increase in the hydrogen cyanide yield could be expected due to the presence of atomic hydrogen. If atomic hydrogen reacts by (3), the reaction:

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (5)$$

would follow and the yield of hydrogen cyanide would be increased. According to the mechanism outlined for the reaction of atomic nitrogen with ethylene by Greenblatt and with ethane later in this paper, (5) is a rapid reaction and would go to completion.

Since the magnitude of the steric factor indicates that no chain process is involved, it seems likely that the yield of hydrogen cyanide is not increased by the hydrogen atoms produced by reaction (1). These hydrogen atoms must then either disappear by reaction (2) or react with methane according to reaction (4).

It would seem then, that the reaction between methane and atomic nitrogen can be adequately described by the mechanism:

$$N + CH_4 \longrightarrow HCN + H_2 + H \qquad (1)$$

$$H + H \longrightarrow H_2 \qquad (2)$$

where reaction (1) has an activation energy of 11,000 calories and a steric factor of 5×10^{-3}.

The Reaction of Ethane with Nitrogen Atoms

There is no reported work in the literature on the reaction of ethane with nitrogen atoms. Preliminary tests showed that it reacted at temperatures above 50° C. In this respect it is very similar to the reaction of hydrogen atoms with ethane (10). It is reported in the literature (23) that the saturated hydrocarbons are relatively unreactive and as the second member in the homologous series, ethane is of particular interest.

This system has an advantage over the methane-nitrogen atom system because any unreacted ethane may be easily trapped and estimated. Thus a material balance for the system before and after reaction may be sought without serious difficulty. Such a balance was possible in the present study with considerable precision; i.e., the ethane entering the reaction chamber would generally be accounted for within 2 - 3%.

The only products found in the trap after an experiment were ethane and hydrogen cyanide. These were separated as outlined above; i.e., the total contents of the main trap were sublimed to a smaller trap where the ethane and hydrogen cyanide were separated at -116° C.

The ethane was estimated quantitatively by expanding it into the calibrated volume and measuring the pressure exerted. The hydrogen cyanide was estimated both by weighing and by titration. When there was no polymerization these two determinations agreed well within the experimental uncertainty of the titration. As indicated above, these two fractions accounted for essentially all the ethane passed into the system.

The gas which was separated at -116°C. and designated here as ethane was characterized by distilling it in a Podbielniak still. No trace of any other material was indicated and the boiling point agreed exactly with the boiling point of the ethane fraction which was prepared for the reaction.

The vapour pressure of the fraction designated as hydrogen cyanide was measured and found to correspond to the vapour pressure of hydrogen cyanide. An approximate melting point was determined by surrounding the small trap with Dewars of successively higher temperatures until the white crystals in the trap melted. This melting point corresponded to that given for hydrogen cyanide.

When ethane reacted with atomic nitrogen, the violet flame, characteristic of all nitrogen atom-hydrocarbon reactions, was observed. The temperature of the flame, as indicated by the thermocouple K, in the well, was invariably higher than the temperature of the walls of the reaction vessel. This temperature difference was greater than the difference set up when only atomic nitrogen was passing through. Thus the reaction is strongly exothermic.

The temperature of the thermocouple at K was affected by small changes in atom concentration. This was noted when, during an experiment, the atom concentration was increased by increasing the discharge rate. This fact makes the control of the reaction difficult because, if during an experiment the concentration of atomic nitrogen fluctuates, the temperature of reaction fluctuates with it. The resulting fluctuation in reaction rate will then be much greater than the fluctuation in atom concentration.

In the work done on ethylene it was noted that the flame produced a sharp boundary which presumably marked the extent of the reaction zone. This made it very difficult to estimate the time of reaction. However, the flame produced by the ethane reaction is completely diffuse and fills the whole reaction chamber, indicating that reaction takes place throughout the whole time that the reactants are in the heated zone. This makes the estimate of the time of reaction reasonably accurate.

As with the methane reaction, it was found possible to handle the hydrogen cyanide produced without polymerization if the trap was poisoned with phosphoric acid. Experiments were made when about 0.1 gm. of hydrogen cyanide was produced and the residue remaining in the main trap after sublimation of the reaction products was scarcely visible.

The data collected on the reaction between ethane and atomic nitrogen are listed in Tables III and IV. Experiments where the ratio of ethane to atomic nitrogen was large are listed in Table III, while experiments where this ratio was small are listed in Table V.

It was found that, when the ethane to atomic nitrogen ratio was large, the reaction appeared to go to completion; i.e., to complete consumption of nitrogen atoms. In experiments 1 - 5 the ethane to atomic nitrogen ratio was held at a large and constant value, and the temperature of the furnace increased as indicated in the table. At a temperature of about 175° C. the rate of production of hydrogen cyanide became independent of temperature. This can only be interpreted as representing complete reaction of the nitrogen atoms. This conclusion was born out by the fact that no glow was observed in the liquid air trap in experiments 2 - 8, where atomic nitrogen was completely removed by reaction while in experiment 1, which represents a case where the atomic nitrogen did not all react, a faint glow was observed.

The fact that the ethane-nitrogen atom reaction can, under suitable conditions, be made to occur with complete consumption of the nitrogen atoms is of considerable interest, since it provides a chemical method of estimating the atom concentration for comparison with the value determined directly with the Wrede gauge measurements. Such a chemical determination of atom concentration requires that the reaction is not complicated by the presence of a large

TABLE III

Reaction of Ethane with Atomic Nitrogen when Ethane is in excess.

Experiment Number	Temperature Degrees C.	Average Mole Ratio of Ethane to Atomic Nitrogen	Flow Rate of Ethane Moles/min.	Production Rate of HCN Moles/min.	Discharge Condition *
1	93	2.7	1.74×10^{-3}	5.15×10^{-4}	2
2	176		1.71	6.91	2
3	194		1.73	6.43	2
4	208		1.74	6.56	2
5	285		1.72	6.36	2
6	260	3.4	1.72	5.11	1
7	250	2	1.70	9.59	3
8	285		1.77	8.86	3

---

* See Table 1

TABLE IV

Comparison of atomic nitrogen concentration as determined with ethane and a Wrede gauge.

Condition of Discharge ☆	Atom Concentration Determined using Wrede Gauge.		Atom Concentration from Ethane reaction at clean up conditions	Average Deviation
	Concentration	Deviation		
1	14.2 %	1.5 %	13.9 %	
2	12.2	2.1	9.9	0.3 %
3	8.9	1.5	7.7	

☆ See Table I

excess of reactant. This condition is satisfactorily met by ethane since in these experiments the ethane and hydrogen cyanide collected in the trap accounted for all the ethane passed into the system.

In experiments 2 - 8 the concentration of the chemically active species in active nitrogen was determined for the three discharge conditions listed in Table I. In Table IV, the concentration of atomic nitrogen determined by the Wrede gauge is compared with the concentration of the active species in active nitrogen determined from HCN production in the presence of excess ethane at high temperature.

The data indicate that, within the uncertainty of the measurements, the concentration of the chemically active species in active nitrogen is the same as the concentration of atomic nitrogen. This is probably the best evidence obtained to date that the chemical activity of active nitrogen arises only from the atomic nitrogen which it contains.

The average deviation cited in Table IV for the concentration of atomic nitrogen determined chemically is the average deviation from the mean value determined with reactions 2 - 5. This deviation is much smaller than the deviations indicated for the concentrations determined using the Wrede guage. Thus the chemical method of determining the concentration of atomic nitrogen is apparently more precise than the Wrede guage, and in subsequent calculations in this work the values obtained by this method were used.

Experiments 9 - 19 were made under conditions suitable for kinetic treatment of the data; i.e., the concentration of reactants and temperature of reaction were appropriately varied. The ratio of ethane to atomic nitrogen was about 1 to 4 in experiments 9 - 12, 1 to 2 in experiments 13 - 16 and 1 to 1 in experiments 17 - 19. For each concentration ratio a series of reaction temperatures was used. The discharge conditions were maintained at one of the conditions specified in Table I, so that in all experiments the atom concentration was known. The flow rate of molecular nitrogen was held constant at 6.63×10^{-3} moles per minute throughout the entire study.

TABLE V

Rate of Production of Hydrogen Cyanide from the Ethane-Nitrogen Atom Reaction under various reaction conditions.

Experiment Number	Ratio of Ethane to Atomic Nitrogen	Temp. °C.	Flow Rate of Atomic Nitrogen moles/min.	Flow Rate of Ethane moles/min.	Production Rate of HCN moles/min.	Pressure mm. Hg
9	0.256	127	9.23×10^{-4}	2.36×10^{-4}	1.36×10^{-4}	1.52
10	0.256	202	"	2.36	2.45	1.62
11	0.264	230	"	2.44	2.96	1.55
12	0.262	243	"	2.42	2.85	1.55
13	0.492	106	"	4.54×10^{-4}	1.65×10^{-4}	1.35
14	0.549	168	"	5.06	3.64	1.35
15	0.560	243	"	5.17	5.98	1.27
16	0.567	295	"	5.24	6.72	1.56
17	0.995	109	5.11×10^{-4}	5.09	0.975	1.25
18	1.01	192	"	5.14	2.36	1.35
19	0.985	264	"	5.04	3.32	1.26

TABLE VI

Calculated values of the second order rate constants for the Ethane-Nitrogen atom reaction

"integrated form" $k_1 = \frac{1}{(a-2b)t} \ln \frac{b(a-x)}{a(b-x/2)}$

"uniform concentration form" $k_2 = \frac{x}{(a-x)(b-x/2)t}$

Experiment Number	I/T	k_1	Log k_1	k_2	Log k_2
9	2.50×10^{-3}	3.09×10^{-5}	5.490	7.86×10^{-5}	5.895
10	2.11	8.85	5.947	30.1	6.479
11	1.99	14.5	6.161	57.0	6.756
12	1.94	14.4	6.156	54.6	6.737

TABLE VI cont'd

Experiment Number	I/T	k_1	Log k_1	k_2	Log k_2
13	$2.64\text{x}10^{-3}$	$2.48\text{x}10^{-5}$	5.394	$5.31\text{x}10^{-5}$	5.725
14	2.27	8.05	5.905	24.5	6.389
15	1.93	29.3	6.467	148	7.170
16	1.76	32.3	6.510	197	7.295
17	2.62	2.27	5.356	5.325	5.726
18	2.15	9.00	5.954	28.0	6.447
19	1.86	26.2	6.418	110	7.041

After each experiment the amount of hydrogen cyanide was measured and the rate of its production, which is recorded in Table V, was calculated by dividing the quantity produced by the length of time required for the experiment.

Thus, the rate of hydrogen cyanide production was investigated as a function of concentration of reactants and as a function of temperature, but its variation with time of reaction was not determined.

Discussion

Essentially, the only product formed in the reaction between ethane and nitrogen atoms was hydrogen cyanide, regardless of concentration conditions. This suggests that the mechanism of the process does not change over the range of reaction conditions encountered in this work. The stoichiometric equation for the process may be written as:

$$2N + C_2H_6 \longrightarrow 2HCN + 2H_2 \qquad (1)$$

which is non-committal of reaction mechanism.

Before attempting to obtain a rate expression it is necessary to examine the conditions under which reaction takes place. The reactants are mixed together just as they enter the reaction chamber but from this point on, the reaction conditions are unknown. However, the two extremes to which the process might go can be described.

The are:

(I) The "integrated form" where there is streamlined flow through the reaction chamber with no interdiffusion of reaction zones. At the top of the chamber the concentrations of reactants would then have the values resulting simply from mixing, while at the exit from the chamber they would have values determined only by how much reaction occurred in the time of flow, from the top to the bottom of the reaction chamber.

(2) The "uniform concentration form" where there is turbulence and interdiffusion of reactants so that their concentration throughout the chamber is the same and remains constant. The concentration of reactants throughout the contact time would then be constant at values equal to those found in the gas leaving the chamber.

In work on the reaction of hydrogen atoms with methane (43) a similar experimental procedure, with the reactants mixed in a reaction chamber at elevated temperatures, was used. However, with hydrogen atoms the uncertainty in atom concentration at high temperatures and the complexity of the products found make the above considerations unnecessary. With nitrogen atoms, however, the atom concentration was known with some precision and, with ethane at least, the products were simple and capable of accurate determination.

It is certain that the reaction could not proceed as described in case (I) because the rate of diffusion, under the conditions found in the reaction chamber, is at least faster than the linear flow velocity. This fact was well demonstrated by using a hydrocarbon inlet which extended to the centre of the reaction chamber. When acetylene, which reacts very rapidly to produce a clearly defined flow, was admitted and active nitrogen was passed through the chamber the acetylene could be regulated to produce a nearly spherical flame with the inlet for acetylene at its centre. This means that the rate of diffusion of acetylene was much faster than the linear velocities encountered in the reaction chamber. The diffusion rate of ethane should not be sufficiently different from that of acetylene to invalidate the conclusion that streamlined flow through the reaction chamber did not obtain under the conditions used in studying the ethane reaction. In addition to diffusion any turbulence, which probably was considerable, would promote further mixing and tend to drive conditions to those of case (II).

Whether or not the conditions of case (II) are completely realized will depend on the velocity of reaction. If reaction is slow, as it is at low temperatures, the conditions of case (II) will be more nearly fulfilled than if the reaction is fast, as it is at higher temperatures. It is also true that, at lower temperatures where the extent of reaction is small, the divergence between (I) and (II) will be correspondingly small.

The actual conditions of reaction probably lie between (I) and (II). Calculation of rate constants and other kinetic data can be made for the two extremes. Since (I) assumes concentrations for a portion of the process which are higher than they actually are, the rate constants calculated will be too small and will diverge increasingly from the time values at higher temperatures. Consequently the activation energies and the probability factor will be too low. Conversely, when (II) is assumed the concentrations used will be smaller than they should be and the activation energy and steric factors so calculated will be too large. The true values should lie somewhere in between.

To determine the validity of a given rate expression as a description of the kinetics of a given reaction, it is common procedure to apply it to experimental data obtained at a given temperature. In the present experiments, however, no rate curve at a single temperature is available, nor was it convenient to make a series of experiments with different concentrations at a single temperature.

The procedure, therefore, has been to assume a rate expression and calculate the corresponding rate constant for each experiment performed. Such a constant should be independent of concentration and flow rate but should, of course, depend on temperature. However, the temperature relation is known from the Arrhenius equation:

$$k = Ae^{-E/RT}$$

where: k is the rate constant
A " " frequency factor
E " " activation energy for the process
R " " gas constant
T " " temperature

Thus, if the rate expression used to calculate k, is valid, a plot of the logarithm of k against 1/T should yield a straight line regardless of the concentration of the reactants involved. This same plot will also yield a value for the activation energy, E.

The following rate expressions were tested with the data as outlined above:

(a) Third order rate expression corresponding to the stoichiometry of the over all reaction.

$$\frac{dx}{dt} = k(a-x)^2(b-x/2)$$

where:

x is the partial pressure of the hydrogen cyanide produced

a is the partial pressure of atomic nitrogen

b is the partial pressure of ethane

k is the rate constant.

For the "integrated form" of case (I), where there is no diffusion from one reaction zone to another, this integrates to the form:

$$k = \frac{-1}{a-2b} \quad \frac{x}{a(a-x)t} - \frac{1}{t(a-2b)} \quad \ln \frac{b(a-x)}{a(b-x/2)}$$

When tested, the data did not conform to this expression.

The "uniform concentration form" or case (II) take the form:

$$k = \frac{x}{(a-x)^2(b-x/2)t}$$

which also failed to describe the process.

(b) Second order rate expression

$$\frac{dx}{dt} = k(a-x)(b-x/2)$$

where a, b, x and k are as defined above.

For the "integrated form" this integrates to:

$$k_1 = \frac{1}{(a-2b)t} \ln \frac{b(a-x)}{a(b-x/2)}$$

The "uniform concentration form" is:

$$k_2 = \frac{x}{(a-x)(b-x/2)t}$$

t, being the average time spent in the reaction chamber by the reactants.

The calculations for these expressions are given in table VI, and the log k versus 1/T plots in figure IV and V. Within the experimental deviations both these plots are linear but, as predicted, the absolute values of k differ and the two lines tend to diverge as the temperature rises. The data are not sufficiently accurate to distinguish the superiority of one plot over the other.

The activation energy obtained by measuring the slope is 6,200 calories for plot IV and 7,900 calories for plot V. The uncertainties in these figures, obtained graphically by drawing lines through the most scattered points on each side of the mean line, is only ±500 calories The two figures obtained here then represent limits within which the true activation energy for the process may be presumed to lie.

In determining the mechanism of the ethane-atomic nitrogen reaction there are three points which must be taken into account

(I) The active species is atomic nitrogen

(II) The only product formed is hydrogen cyanide

(III) The reaction is second order

There are several mechanisms which appear possible for this reaction; they are discussed in turn below.

<u>Dehydrogenation</u>

$$N + C_2H_6 \longrightarrow C_2H_5 + NH \qquad (1)$$

$$N + C_2H_5 \longrightarrow HCN + CH_3 + H \qquad (2)$$

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (3)$$

The primary step here is analogous to that generally accepted in hydrogen atom reactions. The objections to this mechanism are that there are no products indicating the NH radical or its resulting reactions. If it breaks down to leave no trace of its formation, there is still one nitrogen atom consumed in reaction (1) which could not produce hydrogen cyanide. But it has been shown that under the proper conditions all the atoms react to produce hydrogen cyanide.

<u>Figure IV</u> Plot of log k_1 (velocity constant for the "integrated form") versus I/T for the nitrogen atom - ethane reaction.

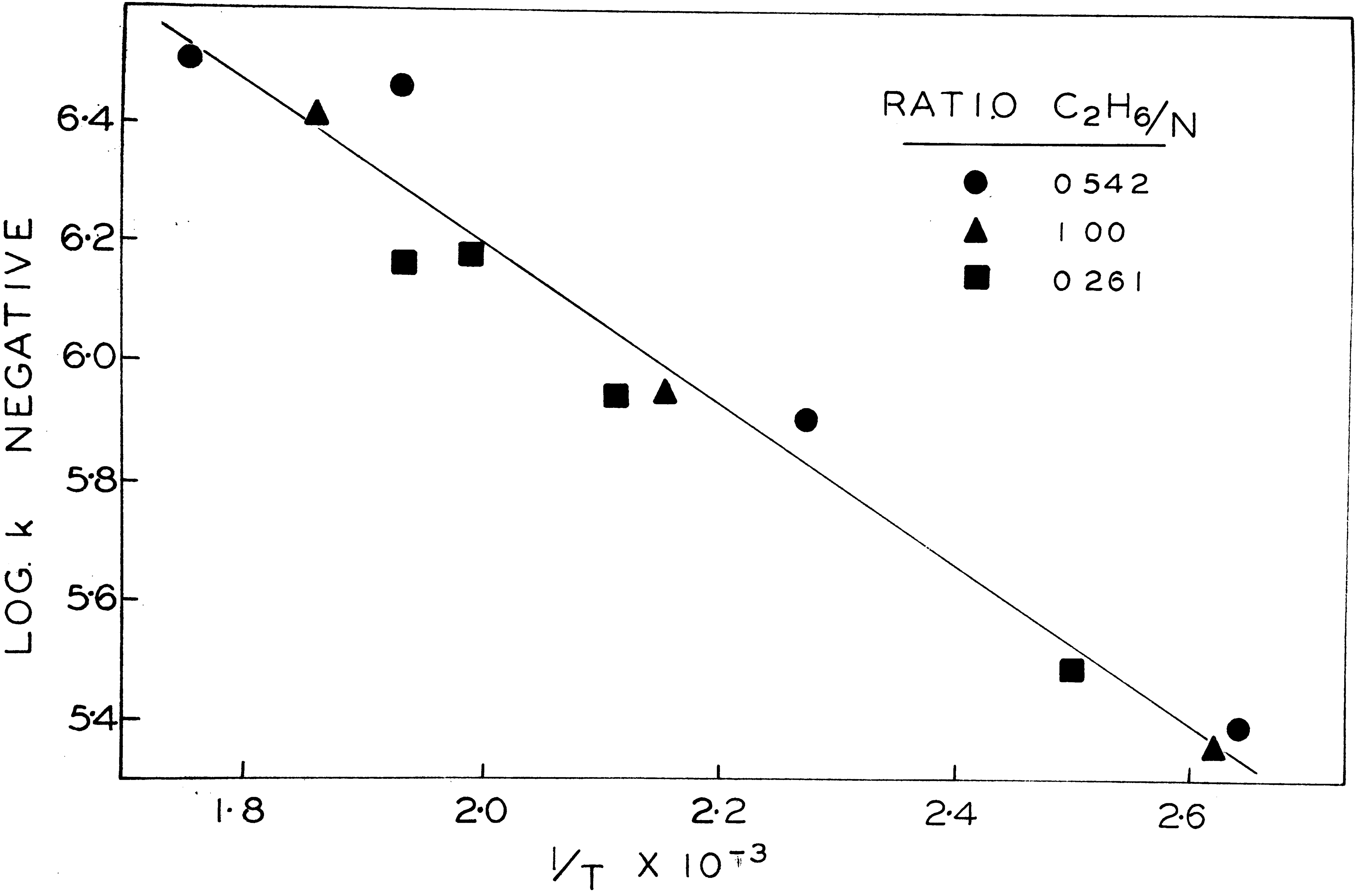
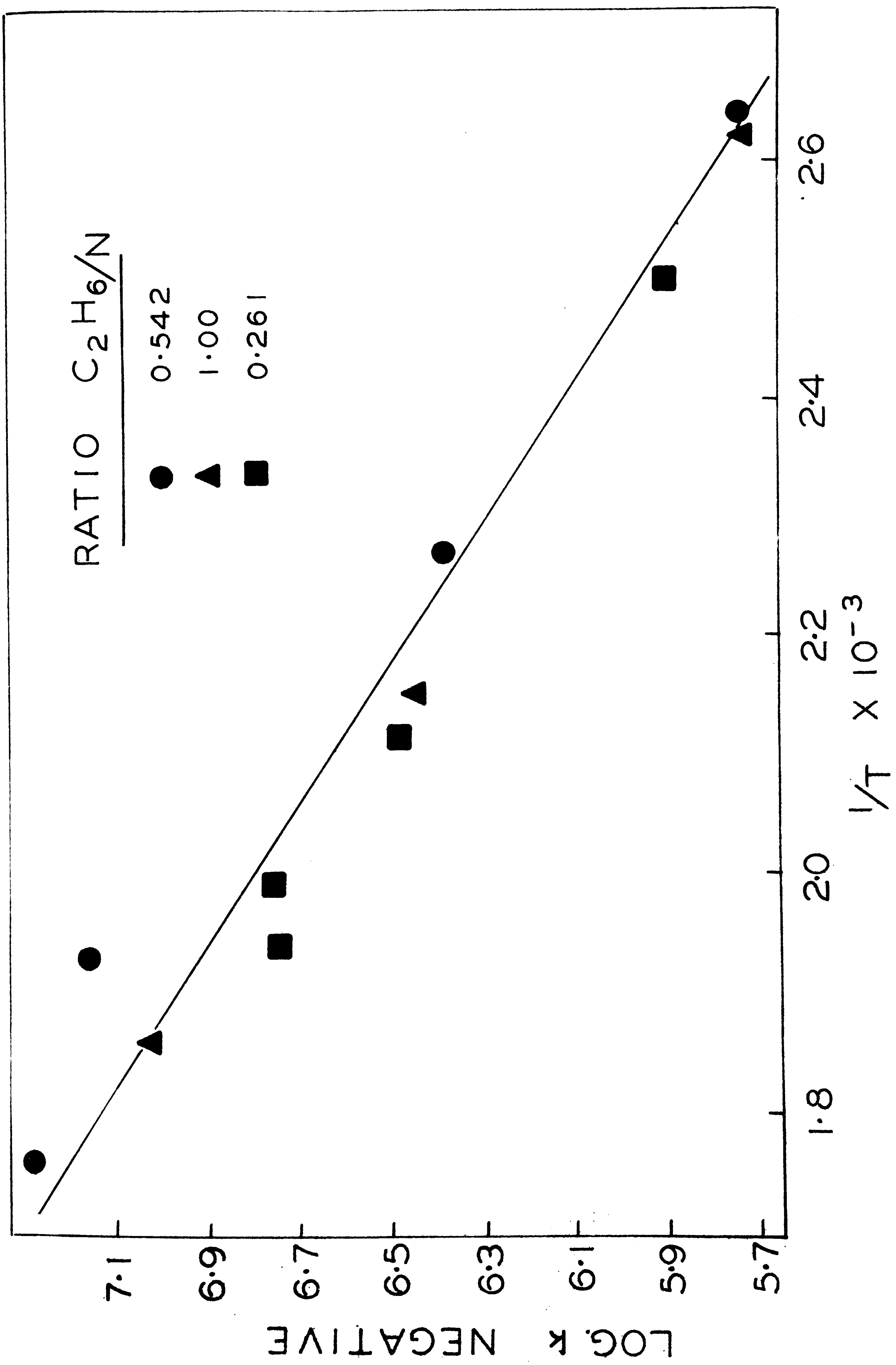

RATI.O C_2H_6/N
● 0 542
▲ 1 00
■ 0 261
LOG. k NEGATIVE
6·4
6·2
6·0
5·8
5·6
5·4
1·8
2·0
2·2
2·4
2·6
$1/T \times 10^{-3}$

Figure V Plot of log k_2 (velocity constant for the "uniform concentration form") versus I/T for the nitrogen atom - ethane reaction.


RATIO C$_2$H$_6$/N
● 0·542
▲ 1·00
■ 0·261
LOG. K NEGATIVE
7·1
6·9
6·7
6·5
6·3
6·1
5·9
5·7
$^1/_T$ × 10^{-3}
1·8
2·0
2·2
2·4
2·6

Dehydrogenation must be discarded then as a possible first step.

Formation of a Complex

$$N + C_2H_6 \longrightarrow C_2H_6N^{\star} \qquad (4)$$

$$C_2H_6N^{\star} \longrightarrow C_2H_6 + N \qquad (5)$$

$$C_2H_6N^{\star} + N \longrightarrow 2HCN + 2H_2 \qquad (6)$$

This mechanism is attractive because it can explain the production of the single product, hydrogen cyanide. To have a sufficient concentration of the complex, reaction (4) would have to be rapid. Also if the complex does not represent a stable molecule (see later), reaction (5) would also be fast. The result is an equilibrium where the concentration of the complex is given by the relation:

$$\left[C_2H_6N^{\star}\right] = K\left[N\right]\left[C_2H_6\right]$$

Reaction (6) then becomes the rate controlling step, the rate being given by:

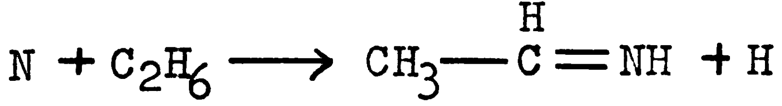
$$\frac{dx}{dt} = kK\left[N\right]^2\left[C_2H_6\right]$$

where $\frac{dx}{dt}$ is the rate of production of hydrogen cyanide.

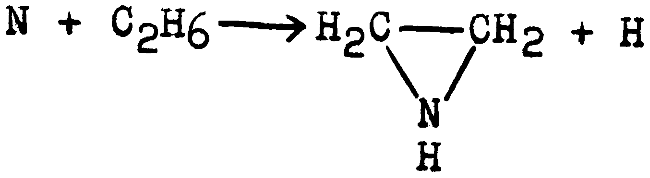
But this is the third order equation tested above and the rate of reaction is not described by this relation. Hence this mechanism must also be discarded as a possibility.

Formation of a Stable Intermediate Molecule

The formation of a stable molecule with a nitrogen atom must produce a hydrogen atom



$$N + C_2H_6 \longrightarrow CH_3-\overset{H}{C}=NH + H \qquad (7)$$



(8)

$$N + C_2H_6 \longrightarrow H\ C = CNH_2 + H \qquad (9)$$

Of the compounds listed here only ethylenimine as indicated in reaction (8) is known and it is thermally stable up to 400°C. and boils at 55°.

If any such stable compound were formed, appreciable quantities of it should have condensed in the trap under conditions of excess ethane flow, when there would not be enough atomic nitrogen to remove it completely from the system. No indication of a nitrogen containing product, other than hydrogen cyanide, was ever observed.

Further objection to stable intermediate compound formation is had in the accompanying production of atomic hydrogen, which is known to react with ethane, at the temperature used here, to produce methane (10). However, measurable amounts of methane were not found in the products of reaction.

Thus a mechanism involving the formation of a stable intermediate must also be rejected.

Rupture of the Carbon Carbon Bond

$$N + C_2H_6 \longrightarrow HCN + CH_3 + H_2 \qquad (10)$$

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (11)$$

$$CH_3 + C_2H_6 \longrightarrow C_2H_5 + CH_4 \qquad (12)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (13)$$

To make this mechanism conform to the conditions outlined previously, reaction (11) must have a low activation energy and be very fast so that virtually all the methyl radicals are consumed by it.

Assuming this, reaction (10) becomes the rate controlling step and the rate would be second order. Hydrogen cyanide would be the only product formed in significant quantities.

Reactions (11) and (12) compete for methyl radicals. Reaction (12) has been studied (45) and has an activation energy of 8,300 calories. The relative rates of these two reactions can be expressed as:

$$\frac{\text{rate of reaction (12)}}{\text{rate of reaction (11)}} = \frac{C_2H_6}{N} e^{\frac{-(8.3-E_{11})}{RT}}$$

where E_{11} is the activation energy for reaction (11).

If E_{11} is assigned a value of 4,000 calories the value of the factor $e^{\frac{-(8.3-E_{11})}{RT}}$ is about 10^{-2}. The ratio $\frac{C_2H_6}{N}$ in reactions where nitrogen atoms were not quantitatively consumed was never larger than 2 or 3. Thus, if reaction (11) has an activation energy of 4,000 calories, the extent of reaction (12) would be so small as to be undetectable.

In experiments where ethane was in large excess and nitrogen atoms were removed quantitatively, the situation is a little more difficult to appraise. In experiment 6, Table (III), for example, the ratio $\frac{C_2H_6}{N}$ is 3.4 at the beginning of the reaction but it increases to infinity before the reaction is complete. However, a substantial part of the reaction proceeds under conditions where reaction (II) is favoured and, even if reaction (12) is favoured towards the end of the reaction when the concentration of atomic nitrogen is low, the production of methane would probably not be large and might well escape detection.

Recombination of methyl radicals by (13) would, of course, merely yield the original reactant, ethane.

In the reaction scheme shown above, all reactions involving the displacement of hydrogen have postulated its formation in the molecular form. This is energetically more favourable than the production of atomic hydrogen. Greenblatt assumed, however, that reaction of methyl radicals with atomic nitrogen produced atomic hydrogen. The consequences of the presence of atomic hydrogen must then be examined here. It might be produced by any one of the following reactions:

$$N + C_2H_6 \longrightarrow HCN + H + CH_4 \qquad (18)$$

$$N + C_2H_6 \longrightarrow HCN + CH_3 + 2H \qquad (19)$$

$$N + CH_3 \longrightarrow HCN + 2H \qquad (20)$$

$$N + C_2H_5 \longrightarrow HCN + CH_3 + H \qquad (21)$$

Reaction (18) appears to be the most probable source of atomic hydrogen in the ethane system, but it can be ruled out since a significant quantity of methane was not produced. If one or all of reactions (19), (20), (21) took place, there would be produced a large concentration of atomic hydrogen in the reaction zone, since for each ethane molecule consumed, two to four hydrogen atoms are produced. At elevated temperatures then the hydrogen atom concentration would be comparable with and even greater than the atomic nitrogen concentration. This would presumably lead to reactions of atomic hydrogen with ethane:

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \qquad (22)$$

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5 \qquad (23)$$

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (24)$$

$$H + CH_3 \longrightarrow CH_4 \qquad (25)$$

Since methane is not formed, reaction (22) may be ruled out. Ultimately in the presence of a high concentration of hydrogen atoms the other atom reactions should lead to the production of considerable quantities of methane. The absence of methane in the products may be taken to indicate that a mechanism of the type suggested by Greenblatt is not operative.

The fact that the atomic nitrogen-ethane system gives a second order rate is another serious argument against atomic hydrogen production. At higher temperatures where reaction of hydrogen stoms with ethane becomes possible (and such temperatures were used in the present study) a chain reaction might be expected and the resulting rate would not be second order. Moreover, the steric factor should be larger than the value 10^{-2} found for the overall reaction.

If the production of hydrogen atoms by reaction of nitrogen atoms with free radicals is ruled out, the production of small amounts of saturated hydrocarbons in the ethylene-atomic nitrogen reaction must be explained by some other process than atomic hydrogenation of ethylene. As pointed out above in the review on the ethylene-nitrogen atom reaction these saturated hydrocarbons might arise from reaction between methyl radicals and ethylene but in this event no ethane would be produced.

A single experiment was performed, using the techniques and apparatus described above, where ethylene and atomic nitrogen were mixed together, with ethylene in about twofold excess.[x] After removal of hydrogen cyanide the products of reaction were analysed by distillation in a Podbielniak still. Ethylene alone was found, and in a quantity which, with the hydrogen cyanide produced, accounted for all the ethylene passed into the reaction chamber.

The absence of ethane indicates that atomic hydrogen is not produced by the reaction of methyl radicals with atomic nitrogen.

Taking all the available information into consideration the only mechanism which appears to be tenable for the

---

[x] Courtesy of J. Versteeg, now reinvestigating the ethylene-atomic nitrogen reaction in this laboratory.

reaction between ethane and nitrogen atoms is:

$$N + C_2H_6 \longrightarrow HCN + H_2 + CH_3 \qquad (10)$$

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (11)$$

where reaction (11) is very fast and (10) is the rate controlling step. The measured activation energy of 7,100 ± 900 calories can then be ascribed to (10).

The steric factor in the expression

$$k = PZe^{-E/RT}$$

was calculated for the limiting values of k at 450° K, the values of k being obtained from figures IV and V. Since k is the specific rate constant and is expressed as moles per litre per second, the collision number, Z, must be expressed as moles of collisions per litre per second at unit concentration of reactants. This values was calculated from the expression given on page 41, assuming collision diameters of 3.75Å for ethane and 3.0Å for atomic nitrogen. At 450° K. and unit concentration, Z = 2.49 moles of collisions per litre.

For the "integrated form" $k = 8.04 \times 10^5$ moles per litre per second, E = 6,170 calories and $P = 3.0 \times 10^{-3}$.

For the "uniform concentration form" $k = 2.69 \times 10^6$ moles per litre per second, E = 7,900 calories and $P = 7.0 \times 10^{-2}$.

A Possible Application of Nitrogen Atom Reactions for the Resolution of Reaction Mechanisms

In the brief review of the reactions of atomic hydrogen with methane and ethane outlined previously it was indicated that some reagent which was reactive with methyl radicals and unreactive with hydrogen might be used to resolve certain uncertainties in the mechanisms of these reactions. It is postulated in the mechanisms for the reactions of both ethane and ethylene with nitrogen atoms that methyl radicals react rapidly with atomic nitrogen while the nitrogen atom-hydrogen systems are known to react to only a very small extent. Thus, if the reactions of atomic nitrogen with methane and ethane are sufficiently slower than the analogous atomic hydrogen reactions, it might serve as the desired reagent. The possible application is illustrated by the following discussion.

Hydrogen Atom-Nitrogen Atom -Methane System

A mixture of atomic nitrogen and atomic hydrogen, produced in separate discharge tubes, could be led into a reaction chamber similar to that described earlier. The following reactions might then be postulated:

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

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

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

$$N + CH_4 \longrightarrow HCN + H_2 + H \qquad (4)$$

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (5)$$

The activation energy for reaction (1) or (2) has been estimated as 13,000 ± 2,000 calories, assuming a steric factor of 0.1. This means that reaction (1) and (2) are probably faster than (4) and that (4) might well be a relatively unimportant source of hydrogen cyanide in the presence of methyl radicals.

Now, if atomic hydrogen reacts with methane by reaction (1), the yield of hydrogen cyanide would be that corresponding to reaction of nitrogen atoms with methane and would not be increased over the yield when no atomic hydrogen is present. If reaction (2) takes place and reaction (5) is fast, as postulated, then the yield of hydrogen cyanide should be much higher when atomic hydrogen is present. Thus it might be possible, using atomic nitrogen, to determine whether atomic hydrogen reacts with methane by reaction (1) or by reaction (2).

Hydrogen Atom-Nitrogen Atom-Ethane System

In the hydrogen atom-ethane reaction it has never been directly determined which of the following mechanisms is correct for the production of methane:

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad (1)$$

I

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (2)$$

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

or

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \qquad (4)$$

II

$$H + CH_3 \longrightarrow CH_4 \qquad (5)$$

If atomic nitrogen were introduced into the reaction zone, as was suggested above for methane the following reactions might result for mechanism II:

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (6)$$

$$N + C_2H_6 \longrightarrow HCN + H_2 + CH_3 \qquad (7)$$

The activation energy for reaction (4) or (1) is 7,600 ± 1,000 calories while the activation energy for reaction (7) is 7,900 when the steric factor is 0.1. Hence these two processes probably have approximately the same rate. This would make the information obtained more difficult to interpret but not too difficult to be useful. If methane is produced by mechanism II the rate of its production should be reduced one half when atomic nitrogen was present.

If mechanism I is correct, then the following reactions might take place:

$$N + C_2H_6 \longrightarrow HCN + CH_3 + H_2 \qquad (7)$$

$$N + CH_3 \longrightarrow HCN + H_2 \qquad (6)$$

$$N + C_2H_5 \longrightarrow HCN + CH_4 \qquad (8)$$

$$N + C_2H_5 \longrightarrow HCN + CH_3 + H \qquad (9)$$

If reaction (8) takes place then methane would be produced even in the presence of atomic nitrogen and the resulting information would be difficult to interpret. If reaction (9) takes place to the exclusion of (8) then little or no methane would be produced, and mechanism I would be established. The success of the scheme depends on which of reactions (8) and (9) take place. This problem will probably be solved when the reaction between propane and atomic nitrogen is studied. Then, the mechanism will probably be:

$$\begin{array}{ll} & N + C_3H_8 \longrightarrow HCN + C_2H_5 \\ \text{I} & N + C_2H_5 \longrightarrow HCN + CH_3 + H \\ & CH_3 + N \longrightarrow HCN + H_2 \end{array}$$

or

$$\begin{array}{ll} & N + C_3H_8 \longrightarrow HCN + C_2H_5 \\ \text{II} & N + C_2H_5 \longrightarrow HCN + CH_4 \end{array}$$

If methane is produced mechanism II would be established and atomic nitrogen could not be used to determine the mechanism of the atomic hydrogen-ethane system.

Admittedly, the foregoing discussion is highly speculative and might be based on arguments which further studies of nitrogen atom reactions will prove untenable. Nevertheless, there is an indication that more information about the behaviour of nitrogen atom systems might well assist materially in elucidating the mechanisms of other atomic reactions.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

The reactions between active nitrogen and ethane and methane have been studied in a flow system. Active nitrogen was produced in a condensed discharge and allowed to react with a hydrocarbon at various temperatures.

Methane reacts at temperatures above 300° C to produce hydrogen cyanide. The reaction probably proceeds by a simple one step mechanism without the intervention of reaction chains. An activation energy of 11,000 calories and a steric factor of 5×10^{-3} were calculated for the process.

Ethane reacts only slowly at room temperature, and the reaction was investigated up to 295° C. At high temperatures and with excess ethane, nitrogen atoms are completely consumed. This permits a chemical determination of the concentration of active nitrogen. The concentration of active nitrogen so determined is the same as the concentration of atomic nitrogen determined with a Wrede gauge. Chemically active nitrogen is, therefore, atomic nitrogen.

The ethane-nitrogen atom reaction is second order and produces only hydrogen cyanide. The primary reaction probably involves rupture of a carbon-carbon bond, the methyl radical so formed reacting very rapidly with nitrogen atoms.

$$N + C_2H_6 \longrightarrow HCN + CH_3 + H_2$$

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

An activation energy of 7,100 ± 900 calories and a steric factor with a value between 10^{-1} and 10^{-3} were calculated.

The reaction of atomic nitrogen with methyl radicals would appear to have an activation energy less than 4,000 calories.

An alternative mechanism for the ethylene atomic nitrogen reaction is proposed and suggestions are made for the possible use of atomic nitrogen to clarify the mechanisms of atomic hydrogen reactions with methane and ethane.

BIBLIOGRAPHY

1. Wrede, Z. Physik., 54, 53 (1929).
2. Jackson and Broadway, Proc. Royal Soc., A127, 678 (1930)
3. Strutt, Proc. Royal Soc., A85, 219 and 377 (1911)
    ibid. A86, 56, 105 and 262 (1912)
    ibid. A87, 179, and 302 (1912)
    ibid. A88, 539 (1913
    ibid. A91, 303 (1915)
    ibid. A92, 438 (1915)
    ibid. A93, 254 (1917)
    ibid. A102, 453 (1922)
4. Wood, Phil. Mag., VI 44, 538 (1922)
5. Bonhoeffer, Z. Phys. Chem., 113, 199 (1924
6. Bonhoeffer and Harteck, Z. Physik. Chem., 139, 64 (1928)
7. Paneth and Hofeditz, Ber. 62, 1335 (1929)
8. Rice, J.A.C.S. 53, 1959 (1931)
9. Steacie, Atomic and Free Radical Reactions.
    Reinhold Publishing Corporation, New York.
10. Trenner Morikawa and Taylor, J. Chem. Phys., 5, 203 (1937)
11. Rice and Teller, J. Chem. Phys. 6, 489 (1938)
12. Taylor, J. Phys. Chem., 42, 763 (1938)
13. Steacie and Parlee, Trans. Faraday Soc., 35, 855 (1939)
    Can. J. Research, B17, 371 (1939)
14. Steacie and Trost, J. Chem. Phys., 16, 361 (1948)
15. Mons and Pease, J. Chem. Phys., 3, 796 (1935)
16. Harteck and Kopsch, Z. Phys. Chem., B1

17. Steacie and Parlee, Can. J. Research, 16, B203 (1938)

18. Kuschnerev and Schnechter, Compt. Rend. Acad. Sci. U.R.S.S.
32, 560 (1941)

19. Schwab and Friess, Z. Elektrochem., 39, 586 (1933)

20. Kistiakowsky and Artsdalen, J.Chem.Phys., 12, 469 (1944)

21. Lewis, Ann. Phys. Chem., (4), 2, 459 (1900)

22. Knaus and Murray, Rev. Sci. Instruments, 11, 78 (1940)

23. Koenig and Elod, Ber., 47, 4, 516 (1914)

24. Baxter, Willey and Rideal, J.C.S. 669 (1927)
J.C.S. 336 and 1146 (1930)

25. Tiede and Chomse, Ber., 63, 1839 (1930)

26. Debau, Phys. Review, 61, 668 (1942)

27. Bay and Steiner, Z. Phys. Chem., (B), 3, 149 (1929)

28. Rayleigh, Proc. Royal.Soc., A189, 296 (1947)

29. Greenblatt and Winkler, Can. J. Research, B, 27, 721 (1949)

30. Steiner, Z. Elektrochem., 36, 807 (1930)

31. Spealman and Rodebush, J. Am. Chem. Soc., 57, 1474 (1935)

32. Hertz, Z. Physik, 19, 35 (1923)

33. Kennard, Kinetic Theory of Gases.

34. MacGillvray, J.C.S., 941 (1932)

35. Bedel, Compt. Rend., 176, 168 (1923)

36. Lescouer et Rigout, Compt. Rend., 89, 310 (1879)

37. Bamberg, Ber., 35, 1083 (1902)

38. Scott, Standard Methods of Chemical Analysis
Van Nostrand Co., New York.

39. Taylor and Baker, Sidgwick's Organic Chemistry of Nitrogen
Oxford Clarendon Press (1937)

40. Gryszkrewicz - Trochimowski
Toczniki Chem., 8, 165 (1928)
C.A. 22, 4475.

41. U.S. Patents, 2, 194, 370 March 19, 1940

42. Steacie, Darwent and Trost, Discussions of the Faraday Society, 2, 80 (1947)

43. Steacie, Can. J. Research, 15B, 264 (1937)

45. Taylor, J. Chem. Phys., 7, 390 (1939)

46. Breck and Rust, J. Chem. Phys. 9, 480 (1941)

47. Hartel and Polyanyi, Z. Phys. Chem. B11, 97 (1930)