THE REACTION OF NITROGEN ATOMS WITH PROPANE

by

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CONTENTS

CONTENTS (Continued)

PH.D. CHEMISTRY

Leo Breitman

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ABSTRACT

The reaction of nitrogen atoms with propane has been found to produce hydrogen cyanide, ethane, ethylene, methane and hydrogen in the temperature range 75°C. - 292°C. The rate of hydrogen cyanide formation at a constant nitrogen atom flow rate increased with increasing propane flow rate; no corresponding increase was observed for the rates of formation of the other hydrocarbons. Second order specific rate constants were calculated from the rates of disappearance of propane. The average value for the constant at 75°C. was found to be 6.3×10^5 litre $mole^{-1}$ sec^{-1}; the mean deviation from the average was 0.9×10^5 litre $mole^{-1}$ sec^{-1}. From the temperature coefficient of the specific rate constants, the activation energy was estimated at 2.1 kilocalories per mole. A mechanism for the reaction has been proposed, involving formation of a collision complex which splits off hydrogen cyanide and an ethyl radical, which in turn undergoes reaction with nitrogen atoms.

INTRODUCTION

Unquestionably, one of the greatest advances in chemical kinetics in recent years has been in the study of elementary reactions involving atoms and free radicals.

Such studies have been the subject of extensive reviews, particularly that represented by Steacie's(1) recent book on "Atomic and Free Radical Reactions". Since such excellent and detailed treatments of the subject are available, it would surely be inappropriate, and fortunately it is not necessary, to attempt in the limited scope of this thesis, any comprehensive survey of atomic and free radical reactions. The following survey is therefore limited entirely to those aspects of the subject which may bear directly or indirectly on the reactions of nitrogen atoms with hydrocarbons, particularly propane.

Active Nitrogen and Nitrogen Atoms

On subjecting nitrogen to a condensed discharge, Lewis(2) found that a yellow cloud filled the discharge tube and that it persisted for several seconds after the current was broken. This afterglow differed from that obtained by other workers who used an induction coil in air. It could be excited only by inserting a condenser and spark gap in the secondary circuit. Furthermore, the nitrogen had to be free of oxygen and contain a trace of water vapour as a wall-poisoning agent. The spectrum of the afterglows was also different: the spectrum of the afterglow produced in air was continuous whereas that of Lewis' was banded and identified with the nitrogen spectrum.

Burke(3), Constantinides(4) and Strutt(5) found that the yellow cloud travelled past wire gauzes charged to high potentials, which showed that no ions were present in the stream. Strutt found that the nitrogen which had been subjected to a discharge could not be condensed by liquid air and that the afterglow disappeared more quickly at lower temperatures.

Small traces of oxygen, water vapour, hydrogen sulphide and hydrocarbons enhanced the afterglow. Bonhoeffer and Kaminsky(6) were unable to detect these gases in the spectrum, which was interpreted to mean that the afterglow intensification was due to a wall effect. The authors measured the intensity of the afterglow as a function of the relative concentrations of active and normal nitrogen. Excellent agreement was obtained between the experimentally observed intensities and those calculated on the basis that the afterglow resulted from a bimolecular process. This was taken as evidence that the afterglow was excited by recombination of nitrogen atoms in the bimolecular reaction

$$N + N \longrightarrow N_2 + \text{afterglow.}$$

The role of three-body collisions was also investigated.

$$N + N + (N_2) \longrightarrow N_2 + (N_2)$$

The rate of decay of the afterglow was found to increase with increasing total pressure in the gas, in accord with the observations of Rudy(7). The authors maintained that the increased rates of decay of the afterglow at higher total pressures bore no relation to quenching of the glow by collisions of the second kind. The latter could only have decreased the intensity of the afterglow, but could not have increased its rate of decay.

Herzberg(8) was unable to obtain the afterglow in clean quartz tubes and thoroughly baked out vessels, even in the presence of a little oxygen. Traces of foreign gases apparently served as wall poisoners but large quantities destroyed the glow. This phenomenon was not understood until Strutt demonstrated the great reactivity of nitrogen which had been subjected to a discharge, i.e. "active" nitrogen.

Strutt studied the chemical behaviour of active nitrogen. He obtained nitrides with mercury, zinc, sodium, arsenic, cadmium and sulphur; nitrogen sulphide, $\left[(NS)_x\right]$, and carbon monosulphide, $\left[(CS)_x\right]$, from carbon disulphide; and hydrogen cyanide from hydrocarbons. Benzene reacted with active nitrogen to give hydrogen cyanide and cyanobenzene, the latter identified by smell alone.

Flames accompanied the reactions of active nitrogen with phosphorous, iodine, various salts, nitric oxide, methane, pentane, acetylene, ethyl alcohol, diethyl ether, ethyl iodide, methyl bromide, ethyl chloride, heptane, benzol, chloroform, bromoform, ethyl dichloride and ethylidene dichloride. The wave length of the luminescence was not equal to that of the nitrogen afterglow. All compounds that contained carbon gave hydrogen cyanide, while those containing carbon and halogen gave the corresponding cyanogen halides. No cyanogen was obtained from hydrocarbons.

The reactions between active nitrogen and methane and pentane were investigated by Koenig and Elöd(9). They observed no reaction with methane, but obtained small amounts of hydrogen cyanide and amylene from pentane.

Strutt repeated the investigations with pentane, heptance and methane. Two samples of the latter were prepared: one from aluminium carbide, the other from sodium acetate and soda lime. A faint flame was obtained by the action of active nitrogen on both methane samples. Heptane reacted with the nitrogen mixture to form hydrogen cyanide while a nitrile was also identified by its odour. Hydrogen cyanide was the only product obtained from pentane.

The remarkable behaviour of active nitrogen soon raised the question as to the identity of the component which was responsible for chemical reaction.

The Nature of Active Nitrogen

Strutt was the first investigator to suggest that the activity of active nitrogen was due to the presence of nitrogen atoms. Saha and Sur(10), from the modern quantum point of view, postulated that metastable nitrogen molecules were responsible for the observed chemical reactions.

The latter theory was favoured by the evidence of Foote, Ruark and Chennault(11). They found that only certain mercury lines could be excited by the active nitrogen mixture: the lines corresponding to 9.52 e.v. could be excited whereas the 9.66 e.v. lines were not observed even after 150 hours of exposure. Strutt himself had found that the yield of active nitrogen was especially high when the fourth positive group of nitrogen appeared in the spectrum. The energy of excitation of this group, 14.8 e.v., is greater than the dissociation energy of nitrogen molecules.

Willey and Rideal(12) showed that active nitrogen attacked ammonia, hydrogen bromide and hydrogen iodide, but not hydrogen, oxygen, water vapour, carbon dioxide, chlorine, bromine, iodine, methane, hydrogen chloride and nitrous oxide. The latter group of compounds required a maximum of 55 kilocalories per mole for dissociation. The authors then concluded that active nitrogen contained metastable molecules having an energy of 2.3 e.v. which preferentially transferred 45 kilocalories per mole to a reacting system. Strutt, however, had shown that active nitrogen excited the 2061Å iodine line which corresponded to an energy of 150 kilocalories per mole. Moreover, the experimental observations of Willey and Rideal were questioned. Strutt found that methane does react with active nitrogen and Steiner(13) later showed that hydrogen was also attacked.

Willey(14) observed that when the afterglow of the active nitrogen was destroyed by an auxiliary discharge, the activity of the mixture measured by thermometers beyond the auxiliary discharge remained constant. He inferred that active nitrogen consisted of atoms and metastable molecules, and that the latter were the chemically active components while the former were responsible for the glow.

Okubo and Hamada(15), however, found that the reactivity of the nitrogen varied with the intensity of the afterglow and that the reactivity disappeared entirely when glowless, pure nitrogen was used.

By direct pressure measurements, Wrede(16) was able to detect the presence of nitrogen atoms in active nitrogen. His determination of nitrogen atom concentrations was based on the different rates of diffusion of molecules and atoms through an orifice, the diameter of which was small compared with the mean free path of the partially dissociated gas.

The atomic arc lines of nitrogen were detected by Bay and Steiner(17) when they applied a high frequency discharge in addition, and externally to the discharge that produced the active nitrogen. They also found that the intensity of the afterglow increased with increasing atom concentration. In fact, when a glowless discharge was used, no atomic arc lines could be found.

Later work showed that the chemical action of active nitrogen was related to the afterglow. Tiede and Chomse(18) noted that glowing active nitrogen reacted with mercury. When the gas was rendered glowless by passage through an auxiliary continuous discharge, mercury was not attacked.

An experiment designed to demonstrate the definite orientations of atoms in an inhomogeneous magnetic field was performed by Stern and Gerlach in 1921. The presence of atoms having magnetic moments can be demonstrated by use of their technique.

Glowing, active nitrogen left a trace due to atomic nitrogen on a metallic silver detector in a Stern-Gerlach experiment.(19)

Rayleigh(20) was able to maintain the luminosity of active nitrogen for six hours in glass bulbs which had been wetted with phosphoric or sulphuric acid. By direct compression of the gas he found that the intensity of the glow varied inversely as the cube of the volume. Metal targets were exposed to active nitrogen and the energy that they acquired was measured. The author deduced that the nitrogen was completely dissociated and that the energy content of the active nitrogen was related to the intensity of the afterglow. However, the energy absorbed by the metal targets greatly exceeded the energy associated with the afterglow. Rayleigh concluded that the afterglow accompanied formation of nitrogen atoms but was not an essential feature in their production.

Debau(21) investigated the nature of the afterglow anew. Two connected glass vessels were filled with nitrogen; the afterglow was excited in one vessel with an electrodeless discharge and the luminosity immediately appeared in the other. The pressure of the system was nearly doubled although the temperature along the walls rose only slightly. When liquid air was applied to a very small portion of the surface of the second vessel, the pressure was restored to its original value; the afterglow was concentrated in a very small region near the cool portion of the second bulb and its intensity was greatly increased, but it disappeared within thirty seconds. Debau attributed the pressure changes to the almost complete dissociation of the nitrogen molecules.

Assuming complete dissociation, Debau concluded from Rayleigh's value for the interaction of active nitrogen with gold that half the atoms were in the normal 4s state and half in the excited 2d state. He postulated the following mechanism for the afterglow excitation.

(1) $N\ (2d) + N\ (4s) \longrightarrow N_2^{*}$ 9.8 e.v. above the ground state of N_2.

(2) $N_2^{*} \longrightarrow N + N$

(3) $N_2^{*} + M \longrightarrow N_2\ (B^3\pi) + M$

(4a) $N_2\ (B^3\pi) \longrightarrow N_2\ (A^3\Sigma) + h\nu$ (afterglow)

(4b) $N_2^{*} + M \longrightarrow N_2\ (1\Sigma) + M$ + heat, non-afterglow radiation, or energy dissipated by transfer of energy to the third body.

Rayleigh showed that the energy associated with the afterglow is small compared with the energy present in active nitrogen so that (4b) was considered to be more probable than (4a).

It appears certain from the evidence to date that active nitrogen contains nitrogen atoms. Wrede gauge measurements and Stern-Gerlach experiments directly indicate the presence of nitrogen atoms in active nitrogen. Most of the observations of Bonhoeffer and Kaminsky, Strutt, Okubo and Hamada, Rayleigh and Debau are in complete accord with the atom theory.

Steiner(13), Speakman and Rodebush(22), and more recently, Greenblatt and Winkler(23) and Blades and Winkler(24) have assumed that nitrogen atoms were responsible for the chemical action of active nitrogen. In fact, this assumption was necessary for the explanation of experimentally observed results.

Douglas and Herzberg(25) have recently obtained absorption lines in the far ultra-violet corresponding to atomic nitrogen, although they have not yet assessed the concentration of atoms present in the mixture.

Nitrogen Atom Reactions

The Reactions of Oxides of Nitrogen with Nitrogen Atoms

Speakman and Rodebush(22) found that when nitric oxide or nitrogen dioxide was added to active nitrogen, the yellow afterglow faded, and gave rise to a faint blue luminosity. A further increase in nitric oxide concentration resulted in liberation of heat and complete extinction of the nitrogen afterglow. A large excess of nitrogen dioxide eliminated the blue luminosity as well.

The authors postulated the following reactions to account for their observations:

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

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

$$O + NO \longrightarrow NO_2 \qquad (3) \quad \text{slow}$$

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

The characteristic blue oxygen afterglow was attributed to reaction (3). Postulation of reaction (3) as slow explained the persistence of the oxygen afterglow, even after the atomic nitrogen afterglow had been eliminated. When nitric oxide was added in excess, the blue afterglow was intensified as a result of the increased rate of reaction (3). When the nitrogen <u>dioxide</u> concentration was increased however, the blue afterglow was quenched as a result of almost complete consumption of the oxygen atoms by reaction (4).

The Reactions of Hydrogen with Nitrogen Atoms

In 1928, Lewis(49) found that nitrogen atoms and hydrogen atoms, prepared by an electrodeless discharge, reacted to form ammonia. Hydrazine was not detected in any of the experiments.

No ammonia was formed when active nitrogen was mixed with molecular hydrogen, or when nitrogen molecules were mixed with hydrogen atoms. These results were taken as proving that the atomic theory of active nitrogen was correct.

According to the author, formation of ammonia from molecular nitrogen and hydrogen atoms required reactions of the type

$$N_2 + H \longrightarrow N_2H \qquad (1)$$

$$N_2H + H \longrightarrow N_2H_2 \qquad (2)$$

$$N_2H_2 + H_2 \longrightarrow N_2H_4 \qquad (3)$$

$$N_2H_4 + H_2 \longrightarrow N_2H_6 \longrightarrow 2NH_3 \qquad (4)$$

Under the conditions of low gas pressures of the experiments, Lewis considered the probability of encounters such as depicted by (2) to be small. Similarly, he maintained that on bringing together unactivated hydrogen and active nitrogen, three or four successive and selective encounters would have been required to produce ammonia, depending on whether the process had commenced with molecular or atomic nitrogen.

There were two possibilities when hydrogen atoms were mixed with active nitrogen. With the metastable nitrogen molecule, the reaction sequence would have been composed of the four reactions given above. On the other hand, if atomic nitrogen were present, only two steps were conceived to have been necessary to produce ammonia:

$$N + H \longrightarrow NH \qquad (5)$$

$$NH + H_2 \longrightarrow NH_3 \qquad (6)$$

The author maintained, further, that neither (5) nor (6) would have been a rare occurrence, since Wood's method of activating hydrogen, which Lewis had used, yielded a considerable amount of atomic hydrogen.

Steiner(13) later re-investigated the behaviour of nitrogen-hydrogen systems. To permit quantitative analysis of reaction products, he prepared nitrogen atoms in greater quantity than had Lewis. The behaviour of the following mixtures was studied:

atomic nitrogen + atomic hydrogen
atomic nitrogen + molecular hydrogen
molecular nitrogen + atomic hydrogen
molecular nitrogen + molecular hydrogen

Experiments were made using low (2%) and high (40%) nitrogen atom concentrations as determined by Wrede gauge measurements. The concentration of atomic hydrogen was estimated at about 10%.

The system containing molecular nitrogen and molecular hydrogen was found to be chemically inert. No hydrazine or ammonia was obtained from molecular nitrogen and atomic hydrogen, in accord with the observations of Lewis.

However, the reaction between atomic nitrogen at a 40% concentration and <u>molecular</u> hydrogen yielded both ammonia and hydrazine in comparable amounts. At the lower nitrogen atom concentration, 2%, only ammonia was detected. The rate of production of ammonia was independent of the nitrogen atom concentration.

When nitrogen atoms at a concentration of 40%

were mixed with hydrogen atoms, hydrazine and ammonia were obtained in larger quantities, but at the 2% nitrogen atom concentration, no hydrazine was detected.

Steiner proposed the scheme

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

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

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

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

to account for the experimental observations. The formation of ammonia from molecular hydrogen and atomic nitrogen was attributed to the diffusion of the gas from the reaction vessel back to the discharge tube. This inference was supported by the observation that the rate of formation of ammonia was essentially independent of the nitrogen atom concentration when the latter was changed from 2% to 40%.

The yield of ammonia could be greatly increased by adding hydrogen containing 15-20% atoms to an active nitrogen mixture. The normally intense nitrogen afterglow was weakened under these conditions, which indicated that nitrogen atoms were being consumed by reaction (1) at a faster rate. The observation that the rate of hydrazine formation is left unaltered by hydrogen atom addition to the mixture is fully in accord with the proposed mechanisms.

The Reaction of Ethylene with Nitrogen Atoms

The reaction between ethylene and nitrogen was studied by Greenblatt and Winkler(23) using the Wood-Bonhoeffer technique. The total pressure was about 0.5 mm.; the nitrogen flow rate was about 1.25 liters per hour (S.T.P.) and the ethylene-nitrogen atom ratio was varied from 0.3 to 1.5. Nitrogen atoms were produced with a condensed discharge. Atom concentrations up to 40% as measured with a Wrede gauge were obtained, using water vapour as a wall poisoner.

The interdiffusion zone of the reactants was luminescent and was marked by rather sharp boundaries. Hydrogen cyanide and ethane were identified as products of the ethylene-nitrogen atom reaction, together with a polymer which was obtained in quantities insufficient for adequate analysis.

The rate of hydrogen cyanide formation was observed to increase linearly with increasing ethylene flow rate to a maximum which depended on the nitrogen atom concentration. The maximum rates of hydrogen cyanide formation were higher, the higher the nitrogen atom concentration. The fact that at a given nitrogen atom concentration, an increase in hydrocarbon-nitrogen atom ratio beyond a critical value did not increase the rate of hydrogen-cyanide formation led the authors to assume that the reaction proceeded by a "clean-up" mechanism. That is, the ethylene was presumed to consume essentially all the nitrogen atoms in the flame when the hydrocarbon was in excess. The yield of ethane increased as the excess of ethylene over nitrogen atoms was increased. The mechanism postulated for the reaction

$$C_2H_4 + N \longrightarrow \text{complex} \longrightarrow HCN + CH_3 \quad (1)$$

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

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

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

accounted reasonably well for the experimentally observed results.

An activation energy of 6.9 kilocalories as an upper limit was calculated from collision yields, with an assumed steric factor of 0.1. The authors pointed out that the value for the activation energy was undoubtedly high on two accounts: (a) recent investigations^(1),(26)^ in atomic reactions point to a much lower value for the steric factor; (b) the nitrogen atom concentrations used in their calculation of collision yields were taken to be the concentrations in the absence of ethylene.

Specific rate constants for the reaction were also determined by the use of Polanyi's(27) diffusion flame technique in the temperature range 273°-377°K. In this study, the widest variation in the rate constants over the complete temperature range led to an upper limit of 3 kilocalories for the activation energy and a steric factor of 10^{-2}.

The Reaction of Methane with Nitrogen Atoms

Blades and Winkler(24) found that no appreciable reaction occurred between nitrogen atoms and methane at temperatures up to 200°C. The only product, hydrogen cyanide, corresponded to one per cent of the methane input and was attributed to impurities.

In the temperature range 350°-450°C., 7-20% of the methane was converted to hydrogen cyanide, the only product that was trapped by liquid air. Non-condensible gases were not analyzed.

Assuming a steric factor 0.1, the authors calculated an activation energy of 14.6 ± 0.4 kilocalories from collision yield data. In addition, independent values of the activation energy and the steric factor, 11 kilocalories and 5×10^{-3} respectively, were calculated from the temperature coefficient of the collision yield.

The suggested mechanism was

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

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

The Reaction of Ethane with Nitrogen Atoms

The reaction between ethane and nitrogen atoms was also studied by Blades and Winkler.(24) The reaction was attended by a lilac-coloured diffuse flame which apparently marked the intermingling of the reactants. The ethane-nitrogen atom ratio was varied from 1:4 to 1:1 to obtain kinetic data. Clean-up of nitrogen atoms occurred at ethane-nitrogen atom ratios higher than 3:1. Under the latter conditions, the yields of hydrogen cyanide were in excellent agreement with the nitrogen atom concentrations which were determined by Wrede gauge measurements.

Hydrogen cyanide was the only product of the ethane-nitrogen atom reaction, and with the unreacted ethane, accounted for 97-98% of the hydrocarbon passed through the reaction system in a single experiment.

Relative specific rate constants for the formation of hydrogen cyanide were calculated at different temperatures in the range 106°-264°C, with assumed second order kinetics. Two sets of rate constants were calculated: one assuming uniform concentrations of reactants in the flame, the other considering the concentration gradients arising from the depletion of reactants faster than their concentration could be restored by diffusion processes.

The former assumption led to an activation energy of 6.2±0.5 kilocalories, the latter to 7.9±0.5 kilocalories. Values of 10^{-3} to 10^{-1} were estimated for the steric factor.

The authors postulated the mechanism

$$N + C_2H_6 \longrightarrow HCN + H_2 + CH_3 \quad (1)$$

$$N + CH_3 \longrightarrow HCN + H_2 \quad (2)$$

for the nitrogen atom-ethane reaction.

The reaction between methyl radicals and nitrogen atoms was presumed to yield molecular hydrogen rather than hydrogen atoms, as proposed by Greenblatt and Winkler(23), since methane, which is formed in reactions between hydrogen atoms and hydrocarbons, was not obtained in the ethane-nitrogen atom reaction.

Non-condensible gases were not analyzed in this study, but in view of the good material balances that were obtained, the authors felt justified in ruling out methane as a product of the reaction.

In the nitrogen atom-ethylene reaction, it was necessary to assume the formation of hydrogen atoms to account for the production of ethane. On the other hand, Blades and Winkler ruled out the presence of hydrogen atoms in the ethane-nitrogen atom reaction on the grounds that ethane is attacked by hydrogen atoms to form methane. Obviously, the possible reactions of hydrogen atoms with hydrocarbons are of interest in mechanisms proposed for nitrogen atom reactions, and it is therefore advisable to review some of the hydrogen atom reactions that might conceivably be involved subsequently to an attack of nitrogen atoms on a hydrocarbon.

Atomic Hydrogen Reactions

In 1922, Wood(28) found that hydrogen, which had been pumped through a continuous discharge, heated metal targets. Bonhoeffer(29) repeated this experiment and found that the hydrogen reduced the oxides of metals and formed hydrides with non-metals. This behaviour was consistent with the behaviour of hydrogen atoms, and it was generally accepted that hydrogen atoms were formed in the discharge tube. Phosphoric acid syrup was used to poison the walls of the reaction vessel, and a half-life of 0.3 seconds was indicated for hydrogen atoms. It was assumed that atom recombination could occur only when a third body accommodated the energy associated with the formation of hydrogen molecules.

A study of hydrocarbon-hydrogen atom reactions indicated that free radicals must be involved in these processes.

The Reaction of Methane with Hydrogen Atoms

Bonhoeffer and Harteck(30) and later von Wartenberg and Schultze(31) found that no appreciable heat was generated on mixing hydrogen atoms and methane. Chadwell and Titani(32) also obtained no indication of reaction.

The mercury photosensitized reaction between methane and deuterium atoms was investigated by Taylor, Morikawa and Benedict(33). Two methods of attack were conceived to be possible:

inversion $CH_4 + D \longrightarrow CH_3D + H$ (1)

hydrogen abstraction $CH_4 + D \longrightarrow CH_3 + DH$ (2)

followed by $CH_3 + D \longrightarrow CH_3D$ (3)

The authors found that deuteromethane was formed and that at least part of the exchange was due to the reactions

$Hg(^3P_1) + CH_4 \longrightarrow Hg(^1S_0) + CH_3 + H$ (4)

$CH_3 + D \longrightarrow CH_3D$ (5)

At low temperatures, they ascribed exchange mainly to reactions (4) and (5); reaction (2) was assumed to become appreciable only at about 300°C.

When the deuterium atoms were produced by the Wood-Bonhoeffer method, Trenner, Morikawa and Taylor(34) found that methane was not attacked up to a temperature of 208°C.

Steacie(35) investigated the reaction by the Wood-Bonhoeffer method and obtained an activation energy of 12.9 ± 2 kilocalories for the process, which was in good agreement with the value calculated from collision yields.

Farkas and Melville(36) interpreted the results of their mercury-photosensitized reaction in terms of the inversion mechanism, but the weight of evidence favoured the abstraction process for the exchange reaction between deuterium atoms and methane.

The Reactions of Ethylene with Hydrogen Atoms

Von Wartenberg and Schultze(31), Klemenc and Patat(59) and Geib and Harteck(37) agreed that ethylene was rapidly converted to ethane by hydrogen atoms; a little acetylene was also formed. The following reactions were postulated to account for these observations:

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

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

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

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

Taylor and Hill(38) found that ethane was practically the sole product of the reaction when the hydrogen atom concentration was high, but that some methane and a considerable quantity of higher hydrocarbons were formed when the ethylene concentration was increased.

Polymerization simultaneously with the formation of ethane had been noted by Bates and Taylor(39). This was attributed to reactions of acetylene, formed by successive dehydrogenations of ethylene.

Ethane is formed rapidly(37) even at liquid air temperatures by reactions (1) and (2) and Steacie(1) assigns an activation energy of less than 5 kilocalories to the reaction

$$C_2H_4 + H \longrightarrow C_2H_5$$

The Reaction of Ethane with Hydrogen Atoms

On mixing ethane with hydrogen atoms, Bonhoeffer and Harteck(30) and von Wartenberg and Schultze(31) found that up to 25% of the hydrocarbon was lost, while the remainder was unchanged ethane. This loss was attributed to the formation of methane which had passed through the liquid air trap in their flow systems, though ethane might also have been lost under the experimental conditions. The main reactions suggested were

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

$$C_2H_5 + H + M \longrightarrow C_2H_6 + M$$

Luminescence in the reaction zone corresponding to C-H and C-C bands was observed, but since a complex mixture of products was not obtained, the authors concluded that little dehydrogenation to C-H and C-C had actually occurred.

Chadwell and Titani(32) identified methane, ethylene and carbon dioxide in the products of the hydrogen atom-ethane reaction. The phosphoric acid or water used as a wall poisoner was the source of oxygen, found as carbon dioxide, in these experiments.

Steacie and Phillips(40) studied the reaction of ethane with deuterium atoms using the Wood-Bonhoeffer technique. An activation energy of 6.3 kilocalories was measured and attributed to the dehydrogenation reaction

$$C_2H_6 + D \longrightarrow C_2H_5 + HD$$

No analysis for methane was made in this study.

From a similar investigation, Trenner, Morikawa and Taylor(34) concluded that up to 100°C., the main reaction was

$$D + C_2H_6 \longrightarrow CH_3 + CH_3D$$

with an activation energy of 7.2 kilocalories. Deuteromethanes, containing about 50% deuterium, were obtained but the ethane was entirely deuterium-free, which suggested the scheme

$$\begin{aligned}
&D + C_2H_6 \longrightarrow CH_3 + CH_3D \\
&CH_3 + D \longrightarrow CH_3D^* \longrightarrow CH_3D \\
&CH_3D^* \longrightarrow CH_2D + H \\
&CH_2D + D \longrightarrow CH_2D_2 \\
&CH_2D \longrightarrow CHD + H \\
&CHD + D \longrightarrow CHD_2 \\
&CHD_2 + D \longrightarrow CHD_3 \text{ etc.}
\end{aligned}$$

The authors ruled out the dehydrogenation reaction

$$D + C_2H_6 \longrightarrow C_2H_5 + HD$$

followed by

$$D + C_2H_5 \longrightarrow CH_3 + CH_2D$$

as the mechanism for methane formation because Taylor and Hill(38) found that ethyl radicals are hydrogenated to ethane by hydrogen atoms without formation of methane. At temperatures above 100°C., Trenner, Morikawa and Taylor assumed that reaction also occurred by hydrogen abstraction.

Steacie and Phillips(40) investigated the photosensitized hydrogen atom-ethane reaction. In the absence of hydrogen, the photosensitized decomposition of ethane yielded methane, propane and butane; in the presence of hydrogen, more methane was formed and hydrogen was consumed. In their opinion, a C-C split followed by a reaction between methyl or ethyl radicals and ethane to consume hydrogen would be too slow, and a C-H cleavage was therefore postulated as the initial step. Methane formation was then accounted for mainly by

$$H + C_2H_6 \longrightarrow CH_4 + CH_3$$

since the alternative

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

was considered by Smith and Taylor(41) to be too slow at room temperature. However, reactions of the type,

$$H + C_2H_6 \longrightarrow CH_4 + CH_3$$

are contrary to the Rice(42) mechanisms which assumed that reactions of the type

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

occurred more readily than reactions such as

$$R + CH_3X \longrightarrow RCH_3 + X$$

As an alternative, formation of methane by the mechanism

$$H + C_2H_5 \longrightarrow 2CH_3$$

$$H + CH_3 \longrightarrow CH_4$$

was suggested by Rice and Teller(43). This mechanism does not conflict with the Rice theory. At the same time it reconciled the activation energies 7.2 kilocalories and 6.3 kilocalories found by Trenner, Morikawa and Taylor, and Steacie and Phillips, respectively, providing the reaction

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

was the initial, rate-determining step.

As in the methane-hydrogen atom reaction, the evidence favoured hydrogen abstraction as the initial act in the hydrogen atom attack on ethane.

The Reaction of Propane with Hydrogen Atoms

Trenner, Morikawa and Taylor(34) reacted propane with deuterium atoms using the Wood-Bonhoeffer technique. Methane and ethane were produced in the ratios 85:15 at room temperature and 65:35 at 109°C.

A similar investigation by Steacie and Parlee(44) showed that at low temperatures methane was the sole product; ethane was first detected at 100°C. while the ethane-methane ratio at 250°C. was 2:1. The formation of only hexane and hydrogen in the photosensitized hydrogen atom-propane reaction studied by Steacie and Dewar(45) showed conclusively that the primary step was dehydrogenation,

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

The authors calculated an activation energy of 10±2 kilocalories for this process. Ethylene and ethane, which were formed at higher temperatures, were attributed to the reactions

$$C_3H_7 \longrightarrow C_2H_4 + CH_3$$

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

Experiments with deuterium atoms and propane at temperatures up to 250°C. showed that while methane and ethane were obtained as deuterized products, the propane contained hydrogen almost exclusively. This observation excluded the exchange reaction

$$C_3H_8 + D \longrightarrow C_3H_7D + H$$

Other Hydrocarbon-Hydrogen Atom Reactions

Hydrogen atoms generally degrade the higher saturated hydrocarbons, where the first step involves hydrogen abstraction. Unsaturated hydrocarbons, such as ethylene, are usually hydrogenated.

Rabinowitch, Davis and Winkler(46) suggested that the reaction

$$C_3H_6 + H \longrightarrow C_3H_7$$

was the first step in the propylene-hydrogen atom reaction and estimated an activation energy of 5 kilocalories for the process.

Acetylene was exchanged with deuterium atoms(30),(31),(37) in discharge tube experiments, but LeRoy and Steacie(47) found ethane, butane and a partially hydrogenated polymer in the products of the mercury photosensitized reactions.

Further evidence that saturated hydrocarbons reacted with hydrogen atoms largely by the mechanism

$$RH + H \longrightarrow R + H_2$$

was provided by the investigations of Schiff and Steacie(48).

Methane was by far the main product in the reactions of benzene, cyclobutane, cyclopentane and cyclohexane with hydrogen and deuterium atoms.

Cyclopentane and cyclohexane underwent considerable exchange with deuterium atoms and primary processes other than dehydrogenation were also believed to occur with these compounds.

Some Reactions of Hydrocarbon Radicals

The existence of radicals in reactions involving hydrocarbon-nitrogen atom reactions, as indicated by Greenblatt and Winkler(23) and by Blades and Winkler(24) confronts the writer with the probability that such radicals play an important role in these reactions. In these circumstances, it seems that a consideration of some of the most probable free radical reactions is essential to any adequate discussion of hydrocarbon-nitrogen atom mechanisms.

The Interactions of Methyl and Ethyl Radicals

Paneth and Hofeditz(50) in their original experiments found that methyl radicals had a half-life of 0.006 sec. under their experimental conditions. Paneth and Lautsch(51) found that the rate of disappearance of methyl radicals was not appreciably different in the presence of nitrogen, helium, neon or argon as carrier gases at room temperature. Studies of the effect of surface showed that recombination of the radicals is mainly a wall reaction. Paneth and Hofeditz and Rice, Johnston and Evering(52) showed that at a temperature of -180°C. all methyl radicals disappear by recombination.

Paneth, Hofeditz and Wunsch(53) investigated the rate of disappearance of methyl radicals from tetramethyl lead in the presence of both hydrogen and helium. At room temperature the products were 1% ethylene, 59% ethane and 40% methane while at 350°C. 90% of the radicals formed methane and 10% ethane. This was strong evidence that at higher temperatures the homogeneous reaction

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

became more important than the recombination reaction at the wall

$$CH_3 + CH_3 + M \longrightarrow C_2H_6 + M \quad (2)$$

The formation of ethylene was presumably due to the disproportionation reaction

$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2 \quad (3)$$

followed by $CH_2 + CH_2 \longrightarrow C_2H_4$

Steacie(1) assigns activation energies of 9±2 kilocalories and approximately zero to reactions (1) and (2) respectively. Little is known at present about reaction (3).

Recombination reactions of the type

$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

$$CH_3 + C_3H_7 \longrightarrow C_4H_{10}$$

apparently occur quite readily with very small activation energies(1) though little is known about them.

The decomposition of the ethyl radical

$$C_2H_5 \longrightarrow CH_4 + H$$

is one of the fundamental steps in the Rice-Herzfeld chain mechanisms. Steacie(1) estimates the activation energy at 38-43 kilocalories, so that it would be of importance only at relatively high temperatures. The observations of Paneth and Loleit(54) indicated that the decomposition of ethyl radicals first becomes appreciable at about 600°C.

Appreciable quantities of butane were obtained from the decomposition of tetraethyl lead by Paneth and Lautsch(51), apparently from the reaction

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$$

Products consisting almost entirely of ethane and ethylene were formed when Meinert(55) decomposed tetraethyl lead in the liquid state at 220°C. The author concluded that only part of the products were formed by disproportionation

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

and that in the liquid state, the complete process was too complex to disentangle. Some information about the disproportionation of ethyl radicals has been obtained by Ivin and Steacie(63). Ethyl radicals were obtained from the photolysis of mercury diethyl vapour and the products were analyzed for ethane, ethylene, butane and butylene. No significant amounts of hydrogen, methane, butylene or higher hydrocarbons were found.

Tabulation(64),(65) of the products of ethyl radical interactions obtained by earlier workers had shown that the percentage of butane formation varied from zero in the ethyl iodide photolysis to 100 in the decomposition of certain solid gold compounds. Ivin and Steacie maintained that in some of these reactions there was no evidence for the intermediate formation of ethyl radicals and that in the remaining cases, the variation in the relative amounts of products must have been due to at least two things: temperature differences, and side reactions.

Velocity constants for the reactions

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \quad \text{activation energy } E_1$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \quad \text{activation energy } E_2$$

$$C_2H_5 + Hg(CH_3)_2 \longrightarrow C_2H_4 + C_2H_6 + Hg + C_2H_5$$

were determined from rotating sector experiments, and the following activation energies were deduced from the velocity constant for the recombination reaction at 150°C. and the calculated collision frequency:

$$E_1 - E_2 = 0.8 \pm 0.2 \text{ kilocalories per mole,}$$

$$E_2 \ngtr 0.65 \text{ kilocalories per mole.}$$

The Reactions of Methyl and Ethyl Radicals with Hydrogen Atoms

The hydrogenation of methyl radicals by hydrogen atoms

$$CH_3 + H \longrightarrow CH_4 \quad (1)$$

has frequently been assumed in free radical mechanisms. Steacie(1) considers it difficult at present to assess its importance in H_2-H-CH_3 systems compared with the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H.$$

but believes it probable that three-body restrictions play some part in reaction (1) because of the relative simplicity of the methane molecule.

Reactions involving ethyl radicals and hydrogen atoms(1) lead to either ethane or methane or both, apparently by the mechanisms

$$C_2H_5 + H \longrightarrow C_2H_6$$

$$C_2H_5 + H \longrightarrow 2CH_3$$

$$CH_3 + H \longrightarrow CH_4$$

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

Steacie and Parlee(44) found it impossible to account for the products of the propane-hydrogen atom reaction at room temperature unless the predominant reactions were

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

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

$$H + C_2H_5 \longrightarrow 2CH_3$$

$$H + CH_3 \longrightarrow CH_4$$

On the other hand Geib and Harteck(37) found that hydrogen atoms reacted with ethylene to give ethane even at liquid air temperatures, apparently by the reactions

$$H + C_2H_4 \longrightarrow C_2H_5$$

$$H + C_2H_5 \longrightarrow C_2H_6$$

Undoubtedly, both reactions

$$C_2H_5 + H \longrightarrow 2CH_3$$

$$C_2H_5 + H \longrightarrow C_2H_6$$

must be considered possible and as having very low activation energies.

In general, there is little evidence of the occurrence at low temperatures of the reaction

$$C_2H_5 + H \longrightarrow C_2H_4 + H_2$$

although Steacie(1) states that in some cases ethylene is formed in systems containing hydrogen atoms and ethyl radicals at higher temperatures. Any ethylene obtained however would be expected to reform C_2H_5 rapidly by the reaction

$$H + C_2H_4 \longrightarrow C_2H_5$$

The Reactions of Methyl and Ethyl Radicals with Hydrogen

The hydrogenation reaction between methyl radicals and hydrogen molecules

$$CH_3 + H_2 \longrightarrow CH_4 + H$$

has been considered by a large number of investigators(1). As might have been expected, the various results were dependent on estimated methyl radical concentrations and were not in good agreement.

Definite information, however, was obtained from the decomposition of mercury dimethyl(56), a proven source of methyl radicals. Ethane and methane were obtained from the reactions.

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

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

$$H + Hg(CH_3)_2 \longrightarrow CH_4 + Hg + CH_3 \qquad (3)$$

$$CH_3 + Hg(CH_3)_2 \longrightarrow C_2H_6 + Hg + CH_3 \qquad (4)$$

On the basis of this mechanism, a steady state treatment of the results gave a value of 8.1 kilocalories for the activation energy of reaction (1) with the assumption that the activation energy for recombination of methyl radicals is zero.

More recently Majury and Steacie(57) have studied the reaction of methyl radicals, obtained from the photolysis of acetone, with deuterium and hydrogen. They obtained an activation energy of 9.7±0.6 kilocalories and a steric factor of 10^{-3} for the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H$$

The most recent assessment of the reaction

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

is that of Wijnen and Steacie(58), who reacted deuterium with ethyl radicals obtained from the photolysis of diethyl ketone. For the deuterium reaction they found an activation energy of 13.4±0.5 kilocalories from which they deduced the value 11.5±1 kilocalorie for the hydrogen reaction.

The Reactions of Methyl and Ethyl Radicals with Hydrocarbons

Reactions of the type

$$CH_3 + RH \longrightarrow CH_4 + R \quad (1)$$

are well known and a fairly large body of literature exists(1) on this subject. For the purpose of this survey it is sufficient to note that reaction (1) occurs quite readily at temperatures above 100°C. and that Steacie(1) assigns an activation energy of 6-8 kilocalories when R = C_3H_7 and

6 kilocalories when R = C_2H_5.

There is no quantitative information concerning reactions such as

$$C_2H_5 + RH \longrightarrow C_2H_6 + R \qquad (2)$$

mainly because of the uncertainty of the mechanisms by which ethyl radicals are produced. Nevertheless, qualitative evidence for the occurrence of reaction (2) has been obtained by a number of investigators(1).

EXPERIMENTAL

Apparatus

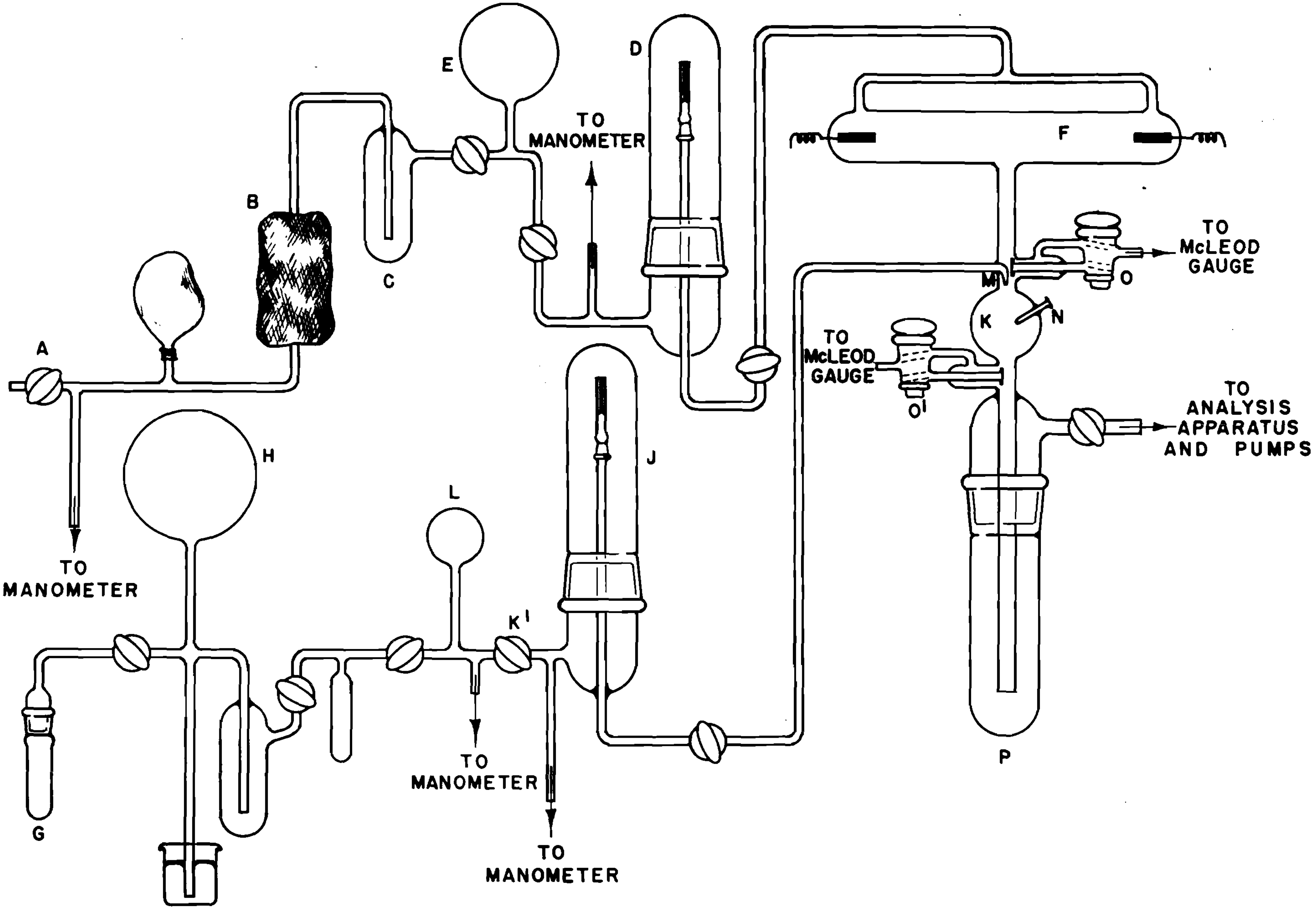
The concensus of others who have worked with nitrogen atoms is that they are produced most efficiently by subjecting oxygen-free nitrogen to a condensed or electrodeless discharge in a tube with poisoned walls. The condensed discharge is preferable at pressures greater than 0.4 mm. of mercury.

An apparatus was constructed consisting essentially of a Wood-Bonhoeffer flow system, an apparatus for the analysis of gaseous products and an electrical circuit to energize the discharge.

These components are illustrated schematically in Figures I, II and III respectively and all descriptions of apparatus are made with reference to these diagrams.

The discharge tube, F, was made of pyrex glass 2.5 cm. in diameter and 57 cm. long. The electrodes were made of sheet aluminium, bent into cylindrical shape. They were attached to tungsten leads which were sealed through the glass so that the inter-electrode distance was about 44 cm. After the inner wall of the discharge tube had been wetted with a 5% solution of phosphoric acid, it was sealed to a pyrex tube, 25 cm. long and 15 cm. in diameter, which in turn was sealed to the reaction vessel.

Fig. I. The flow system


A
B
C
E
D
TO MANOMETER
F
M
O
TO McLEOD GAUGE
K
N
TO McLEOD GAUGE
O'
TO ANALYSIS APPARATUS AND PUMPS
TO MANOMETER
H
L
J
K'
P
G
TO MANOMETER
TO MANOMETER

The linear velocity of gas through this tube at 2 mm. pressure was sufficient to prevent significant diffusion of the hydrocarbon from the jet back to the discharge tube.

The reaction vessel, K, was constructed from a 300 ml. pyrex flask to which two modified Wrede gauges, O and O', were sealed. The gauges were made from filter sticks of "fine" porosity (Fisher Scientific Company) with a pore size of about 5 microns. The pore diameter is of importance, since it should be considerably smaller than the mean free path in the gas. This condition was fulfilled at the operating pressure of about 2 mm. Pressure measurements were made with a McLeod gauge attached to the Wrede gauge through a two-way stopcock.

A removable furnace which fitted the reaction vessel was constructed from two hemispheres of asbestos. The heating element was made of nichrome wire wound uniformly around the hemispherical shells, and the wire was then insulated with several layers of asbestos. The reaction vessel was fitted with a well, N, so that measurements of the temperature in the reaction zone could be made with a copper-constantan thermocouple. The inner wall of the reaction chamber was poisoned with phosphoric acid by drawing a 5% solution of the acid up through the inner tube of the main trap, P.

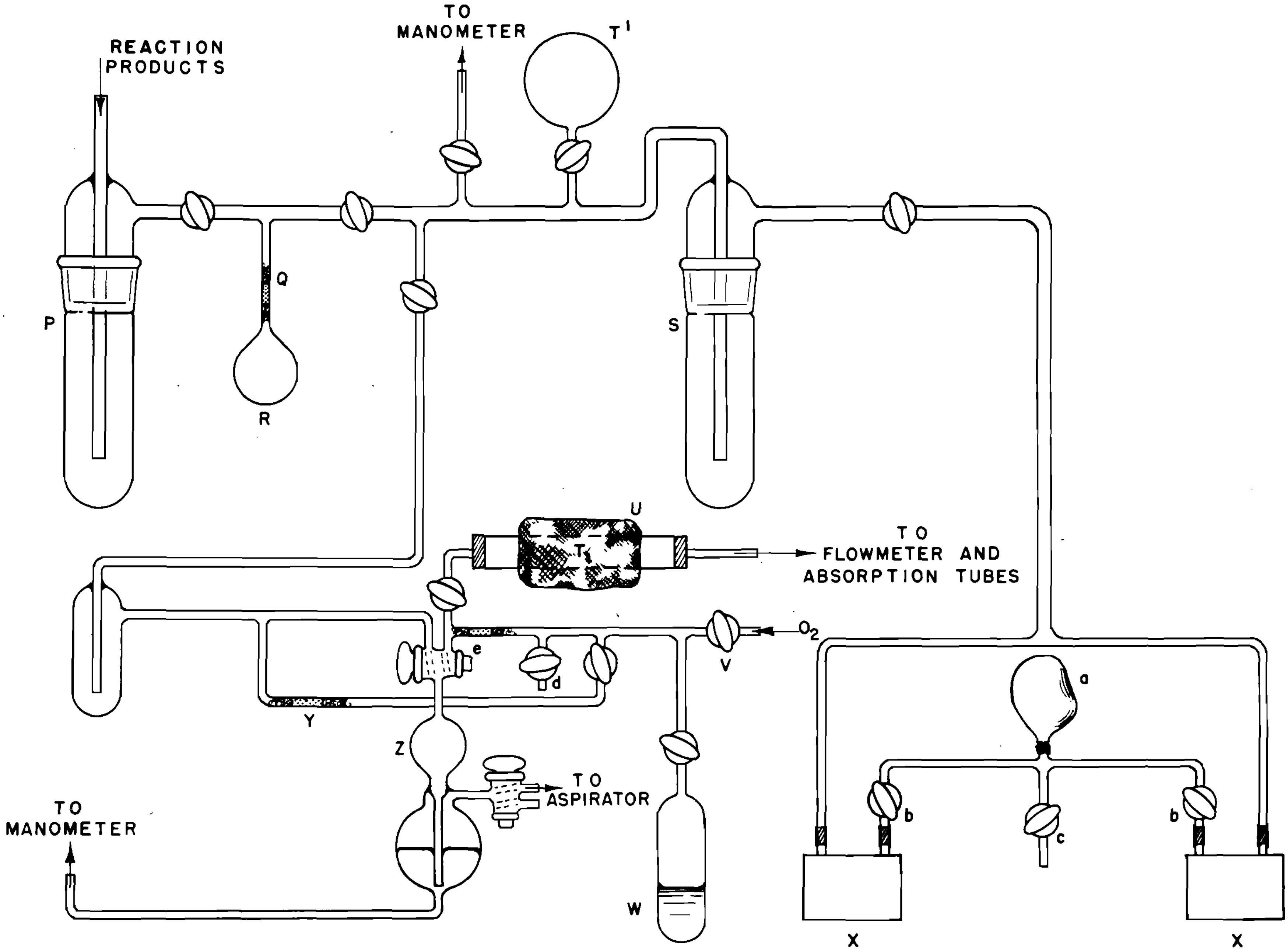
The main trap was 4 cm. in diameter; its inner tube, of 1.8 mm. O.D., was sufficiently large to permit condensation of products without impeding the flow of gas. This trap was connected to the analysis system and two Cenco-Megavac pumps, X, as illustrated in Figure II. All main connections were made with 2.5 cm. O.D. pyrex tubing, and the stopcocks in the pumping line were of correspondingly large bore to ensure a fast pumping speed.

The flow rate of nitrogen was controlled by a removable capillary at D. A known volume, E, was introduced to calibrate this capillary. Nitrogen was pumped from the calibrated volume through the capillary while the pressure changes with time were followed. The flow rate for a given pressure differential across the capillary could then be calculated.

The nitrogen was admitted through two leads near the ends of the discharge tube to ensure uniform sweep of the gas past the electrodes.

The flow rate of the hydrocarbon was controlled by a removable capillary at J. The pressure differential across the flowmeter was kept constant by a stopcock with a scratched plug, K'. The amount of propane passing through the capillary in a given time could be calculated from the pressure change in the calibrated ballast volume, L.

Fig. II. The analysis system


REACTION PRODUCTS
TO MANOMETER
T'
P
Q
R
S
U
T
TO FLOWMETER AND ABSORPTION TUBES
O_2
e
d
V
a
Y
Z
TO ASPIRATOR
TO MANOMETER
b
c
b
W
X
X

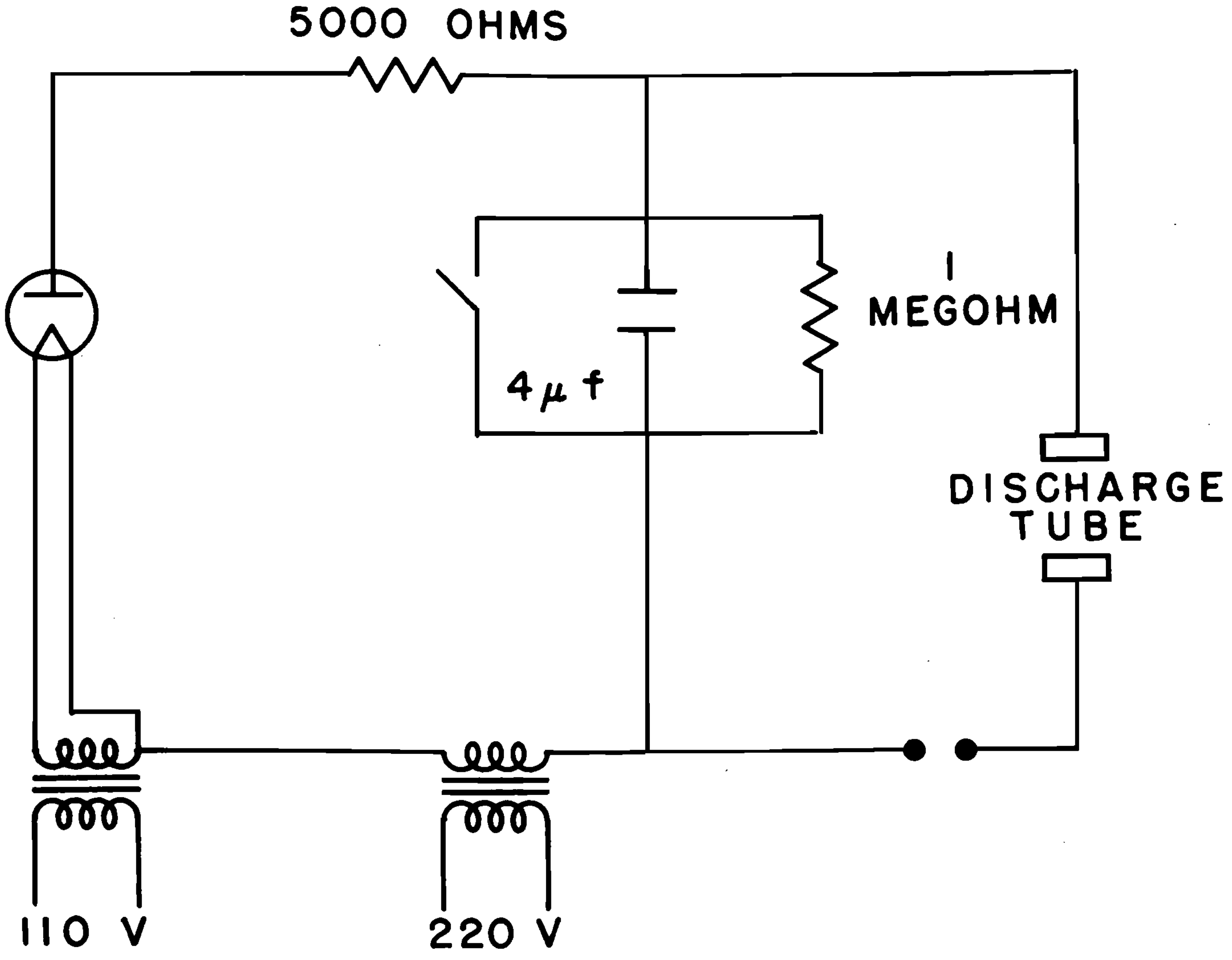
The propane was fed into the reaction vessel through a jet, M, of 3 mm. O.D. "quill" tubing.

The system used for the analysis of products is best described in relation to the experimental procedure, and will be dealt with later.

The circuit used to produce the condensed discharge is shown in Figure III. It consisted of a 4 μf condenser which charged through a high resistor from a half-wave rectifier, and discharged across the aluminium electrodes through a spark gap. The diode rectifier was an 866-A tube, rated for 1 amp. peak load, and the resistor was a coil of about 5000 ohms resistance. A transformer with 220 volts primary and 3500 volts secondary windings fed the condenser-discharge tube circuit. A discharge rate of about seven pulses per second was obtained when the two brass spheres of the spark gap were placed 1-2 mm. apart. At larger separations, the discharges were too infrequent, but the discharge rate stayed virtually constant as the inter-sphere distance was decreased from 2 mm. to zero.

A one megohm bleed resistor was inserted across the capacitor as a safety device. This resistor discharged the condenser within 30 seconds of shutting off the transformer supply voltage.

Fig. III. The electrical circuit


5000 OHMS
1 MEGOHM
4 μ f
DISCHARGE
TUBE
110 V
220 V

Materials

Propane, obtained from the Ohio Chemical and Manufacturing Company, was of C.P. grade. It was condensed in tube G, freed from air by prolonged pumping, then subjected to a bulb to bulb distillation during which the lowest and highest boiling fractions were discarded. The gas was then distilled into the five litre storage vessel, H.

Nitrogen was obtained in cylinders from the Dominion Oxygen Company and the Canadian Liquid Air Company. The gas was stored in a meteorological balloon, A, (Meteorology Department, Dorval) at virtually constant pressure. When fully inflated the balloon was at 1.2 cm. of mercury above atmospheric pressure, and the nitrogen pressure could easily be maintained constant within a few millimeters.

It was noted in preliminary experiments that the character of the nitrogen afterglow was strongly dependent on nitrogen purity. When oxygen was incompletely removed, the yellow afterglow of the nitrogen mixture was masked by the characteristic bluish glow accompanying formation of oxygen atoms. It was possible to demonstrate the presence of these atoms by condensing ozone in a liquid nitrogen trap.

Nitrogen was purified in early experiments by passing the commercial cylinder product through a wash bottle of alkaline sodium hydrosulphite to remove oxygen, then through a solution of potassium hydroxide to scrub out entrained hydrosulphite. The water vapour carried over by the nitrogen served as an excellent wall poisoner, and permitted the attainment of nitrogen atom concentrations up to about 15%. However, carbon dioxide in detectable quantities were trapped out when this method of purifying the nitrogen was used. This was attributed to either incomplete removal of carbon dioxide by the alkaline solution, or decomposition of the water vapour in the discharge tube, followed by reaction with the hydrocarbon. Chadwell and Titani(32) obtained carbon dioxide in the reaction of ethane with hydrogen atoms, and the water used in wall poisoning was undoubtedly the source of the oxygen.

The nitrogen was therefore freed from oxygen by passing it through a tube, B, containing "Chore Girl" copper turnings heated to about 500°C. A liquid nitrogen trap, C, was used to remove carbon dioxide and water. This method of purifying nitrogen proved to be entirely satisfactory.

Phosphoric acid was then used as a wall poisoner and presented no difficulties even at elevated temperatures. The nitrogen atom concentrations obtainable in this way were about 10%, i.e., somewhat smaller than when water vapour was present, but were quite adequate for the purpose at hand.

Experimental Procedure

At a total nitrogen pressure of 2.213 mm., the average nitrogen atom concentration was 7.44%. A single flow rate of nitrogen, 0.4355 moles per hour, was used and the operating pressure, about 2.2 mm. remained essentially constant throughout the study.

Nitrogen atom concentrations were calculated from the expression,

$$\%N = \frac{100(P_2-P_1)}{P_2(1-0.5\sqrt{2})}$$

where P_2 is the steady state pressure of the nitrogen atom-nitrogen molecule mixture in the reaction vessel, and P_1 is the steady state pressure of nitrogen molecules after the recombination of the atoms in the Wrede gauge.

Initial attempts to obtain concordant measurements were unsuccessful. Satisfactory results were later obtained by (a) allowing about ten minutes for equilibrium to be attained across the Wrede gauge between individual measurements and (b) preventing mercury in the McLeod gauge from rising too quickly near "cut-off". A large number of successive pressure measurements, precise within observational errors, were then averaged and the nitrogen atom concentration calculated.

At temperatures of 75°C. and higher, the differences in concentrations of nitrogen atoms measured on the upper and lower Wrede gauges, O and O' respectively, were small and decreased with increasing temperature.

Various propane flow rates were obtained by using capillaries of different size at J. (Figure I). The choice of capillary was governed by the suitability of the pressure differential it produced at the desired flow rate.

Before each experiment, the system was pumped down to a pressure of about 5×10^{-5} mm. with the two Cenco-Megavac pumps, X, operating in parallel (Figure III). The spherical furnace was placed around the reaction vessel when elevated temperatures were desired. Nitrogen was allowed to pass through the discharge tube and the temperature of the reaction vessel was adjusted continuously by a rheostat in the heating circuit. When the furnace was removed, passage of nitrogen from the discharge tube through the reaction vessel elevated the temperature to about twenty-five degrees above room temperature in ten minutes.

After thermal equilibrium had been attained, pressure measurements were made on Wrede gauges O and O'. The main trap was then surrounded by liquid air. The pressure differential across the capillary, J, was adjusted according to the desired propane flow rate, and the hydrocarbon was admitted to the reaction vessel through jet M.

On mixing the gases, a lilac-coloured flame was produced in the vicinity of the jet. The flame was distended in the direction of flow. It was assumed that this flame approximately delineated the zone in which reaction occurred. Hence the propane flow rates were chosen so as to produce rather diffuse flames. The temperature in the reaction vessel quickly rose about twenty-five degrees after the gases were mixed. Temperature fluctuations occurred throughout the experiment when the reaction vessel was not electrically heated, but much better control was achieved when the experiments were performed at elevated temperatures.

The balloon, E, holding nitrogen at constant pressure, was refilled from a cylinder as required, and the propane flow was maintained uniform by periodically adjusting the scratched stopcock, K'.

The duration of an experiment was about thirty minutes, in which time a convenient quantity of products had accumulated. At the end of this period, the propane flow was shut off, and the quantity of hydrocarbon that had been admitted to the reaction vessel was calculated from the observed pressure decrease in the calibrated volume, L.

The nitrogen flow was continued for several minutes, without the discharge, to sweep out all reaction products. The analysis system was then isolated from the pump by an appropriate stopcock.

The products of the reaction were allowed to warm up and were then recondensed in a bulb, R. A small quantity of occluded nitrogen was liberated in this way, and was pumped off.

The tube, Q, contained anhydrous phosphorous pentoxide which was held in position with two loose plugs of pyrex glass wool at either end. All gases condensed in R were thus freed of water vapour. The bulb was then surrounded with an ether bath which was maintained with liquid nitrogen at a temperature of about -90°C. The low-boiling gas fractions were condensed in another trap, S, kept at liquid air temperature. The vapour pressure of the high boiling fraction was measured at the temperature of freezing ether, -116.3°C., and was found to coincide with that of hydrogen cyanide.

Initially, some difficulty was encountered in estimating the hydrogen cyanide quantitatively. Samples of the gas which had not been passed through phosphoric anhydride almost invariably polymerized to some extent on melting. Even the dry samples left a small amount of solid residue when allowed to sublime, but the liquid or solid hydrogen cyanide seemed to be quite stable.

The sample bulb R was sealed off, dried and weighed. It was then broken open and its contents were absorbed in a 5% solution of potassium hydroxide. The cyanide was titrated to incipient turbidity with 0.1 N silver nitrate solution. The bulb was repeatedly rinsed with distilled water and the washings were added to the original solution until the turbidity was no longer destroyed. The sample bulb and broken tip were thoroughly washed, dried and weighed again. The estimates of hydrogen cyanide by weight and by titration deviated by a maximum of three per cent for any one sample. It may be inferred, therefore, that hydrogen cyanide was essentially the sole constituent of the higher-boiling gas fraction.

The low-boiling material in trap S was warmed to room temperature and expanded into a calibrated volume, T', where its pressure was measured on a manometer.

Analysis of a sample of this gas in a Podbielniack still showed that it contained mostly unreacted propane and a lower-boiling material, presumably ethane. Because of the high propane content of this mixture, the fractions obtained in the still were not sharp enough for quantitative work. The gases were therefore subjected to combustion analysis.

A measured quantity of the gas was passed through a quartz tube, T, surrounded by an electrically heated furnace, U, by means of a Töpler pump, then through two absorption tubes containing anhydrous magnesium perchlorate (Anhydrone) and Ascarite respectively. The combustion tube was kept at about 900°C. by a rheostat in the heating circuit.

Oxygen was purified by passing it through two similar absorption tubes and was fed into the gas stream through a stopcock, V. The oxygen flow rate was controlled with a hosecock and was adjusted so that the oxygen-hydrocarbon ratio in the furnace was about 10:1.

Determination of the carbon dioxide produced gave the proportion of C_3 and C_2 components in the gas sample. Estimation of the water produced in the combustion showed that the C_2 component obtained at lower reaction temperatures was essentially ethane but that it probably contained traces of ethylene. At higher reaction temperatures, there was an appreciable deficiency of hydrogen when the C_2 component of the reaction products was assumed to be 100% ethane. Therefore, some gas samples obtained in the reaction at higher temperatures were analyzed for their ethylene content. The gas was pumped into a bulb, W, containing a solution of mercuric nitrate and nitric acid. The bulb was cooled to liquid air temperature and then isolated from the rest of the apparatus by a stopcock. The solution was warmed to room temperature and stirred electromagnetically for a half hour, after which it was cooled to -95°C. with an ether-liquid air bath. The unabsorbed gas was drawn over phosphoric anhydride , Y, to dry it and its pressure was measured in a calibrated volume. Small quantities of ethylene were found in the reaction products by this method. Analysis for ethylene in a known mixture of ethylene, propane and ethane showed the procedure to be accurate within one per cent.

Analysis for the amount of methane produced involved estimation of the hydrocarbon content of a methane-nitrogen mixture in which the mole ratio was of the order 1:30.

The trap, S, was packed with 6-16 mesh activated silica gel and was cooled with liquid nitrogen while a measured quantity of nitrogen and methane were simultaneously pumped through. After the desired quantity of gases had been passed through the trap, they were desorbed from the silica gel and pumped into the bulb Z, where it was diluted with a large excess of oxygen, then forced through the combustion tube, T, at a rate of 250 cc. per minute. The combustion tube was kept at about 900°C. by the surrounding furnace, U. Only about 50% of the methane was found to have been retained by the silica gel in this experiment. The efficiency was increased somewhat by using a longer and wider trap, but the amounts of methane that were retained varied with the gas flow rate and were not at all reproducible. The defect was not in the combustion procedure itself, since analyses of synthetic methane-nitrogen mixtures were always possible with a precision of ±0.5%, even when nitrogen was present in a fifty-fold excess.

The scheme finally used to isolate the nitrogen-methane mixture is illustrated in Figure III. The oil Fig I chambers of the Cenco-Megavac pumps were fitted with flat brass plates having central tubular openings. Oil-resistant gaskets, made of neoprene, were used between the lower plate surfaces and the oil chambers, and the upper surfaces were covered with plasticene. A meteorological balloon, a, was connected to the brass tubes by snugly fitting rubber stoppers. The system was conveniently tested for leakage by inflating the balloon to a measured pressure and allowing it to stand for twelve hours. Wads of glass wool were inserted in the tubing between the pump and stopcocks, b, to exclude oil vapour and foreign particles which might be entrained by the effluent gases.

All the non-condensible gases formed during a nitrogen atom reaction were isolated in the balloon and the free volume of the pumps. The latter volume was determined experimentally.

At the end of an experiment, stopcocks b were closed, and the contents of the balloon were transferred with a Töpler pump into the calibrated volume, Z, through stopcocks c, d and a drying tube, e. Before combustion, the pressure of each portion of gas was measured on a manometer connected to the Töpler pump. The volume of bulb Z was 525 cc. while the volume of methane and nitrogen collected in an experiment was of the order 4-7 litres.

The balloon was then again connected to the pumps and nitrogen alone was passed through the apparatus under the experimental conditions. The collected gas was analyzed in the same way as the methane-nitrogen mixture. The blank corrections were usually small, but varied slightly from day to day.

Before each determination involving gas collected in the balloon, nitrogen was passed through the apparatus for about twenty minutes to flush out any hydrocarbon present in the pump.

An appropriate correction for the blank determination was applied to all subsequent determinations of the methane content of the reaction products.

When a known quantity of methane in a large excess of nitrogen was pumped through the balloon and analyzed, 99.5% of the methane was found by the combustion procedure.

RESULTS AND DISCUSSION

Experiments were first made to determine the effect of varying the hydrocarbon flow rate at constant atomic nitrogen flow rates. The average temperature of the reaction vessel during experiments 1-10 was 75°C. The flow rates of molecular and atomic nitrogen were 0.436 moles per hour and 3.24×10^{-2} gm. atoms per hour respectively, while the flow rate of propane was varied from 5.47×10^{-3} to 3.79×10^{-2} moles per hour. The corresponding range of atomic nitrogen to propane flow rate ratios was therefore 0.85 to 5.9.

The experimental conditions and analytical data are given in Table I, while in Table II are brought together the rate of formation of hydrogen cyanide and the rate of disappearance of propane at corresponding hydrocarbon flow rates. These data are illustrated graphically in Figures IV and V.

The rates of propane disappearance and hydrogen cyanide formation increase with increasing propane flow rate and the two curves (IV and V) have the same general appearance. They are not identical because not all of the reacted propane appeared as hydrogen cyanide; some was degraded by the nitrogen atom reaction to lower hydrocarbons.

TABLE I

EXPERIMENTS 1-10 AT 75±5°C

Experiment Number	Total pressure mm.	Propane flow molesx10^3	Propane recovered molesx10^3	Hydrogen cyanide formed molesx10^3	Ethane* formed molesx10^4	Methane formed molesx10^3	Duration of Experiment Seconds	Carbon recovered (÷ 3) gm.atomsx10^3
10	2.186	3.433	1.123	3.622	2.31	1.880	2261	3.111
8	2.186	5.789	2.405	7.788	2.02	1.364	1952	5.588
3	2.153	5.210	1.680	7.656	5.41	1.060	1418	4.946
9	2.186	6.430	2.314	8.514	4.71	1.410	1606	5.936
4	2.082	6.985	3.384	7.044	4.74	1.012	1360	6.385
7	2.132	5.538	2.515	5.380	4.19	1.212	980.0	4.991
1	2.274	6.913	3.080	6.768	5.35	2.398	1023	6.492
5	2.274	7.089	4.066	5.930	4.66	1.411	836.0	6.824
2	2.274	7.104	4.046	4.616	5.20	1.371	682.7	6.422
6	2.153	6.395	4.000	3.922	4.60	1.350	608.0	6.064

* Includes small undetermined amounts of ethylene

TABLE II

DATA USED IN FIGURES IV AND V FOR EXPERIMENTS 1-10

Experiment	Propane flow rate	Propane recovered	Propane consumed	Hydrogen cyanide produced
Number	moles per hour	moles per hour	moles per hour	moles per hour
10	5.471×10^{-3}	1.789×10^{-3}	3.682×10^{-3}	5.772×10^{-3}
8	1.068×10^{-2}	4.426×10^{-3}	6.254×10^{-3}	1.434×10^{-2}
3	1.320×10^{-2}	4.265×10^{-3}	8.935×10^{-3}	1.944×10^{-2}
9	1.442×10^{-2}	5.189×10^{-3}	9.231×10^{-3}	1.908×10^{-2}
4	1.849×10^{-2}	8.960×10^{-3}	9.530×10^{-3}	1.865×10^{-2}
7	2.034×10^{-2}	9.239×10^{-3}	1.110×10^{-2}	1.976×10^{-2}
1	2.433×10^{-2}	1.084×10^{-2}	1.349×10^{-2}	2.381×10^{-2}
5	3.053×10^{-2}	1.751×10^{-2}	1.302×10^{-2}	2.554×10^{-2}
2	3.746×10^{-2}	2.133×10^{-2}	1.613×10^{-2}	2.434×10^{-2}
6	3.786×10^{-2}	2.369×10^{-2}	1.417×10^{-2}	2.322×10^{-2}

Fig. IV. Graph illustrating the rate of formation of hydrogen cyanide as a function of propane flow rate.

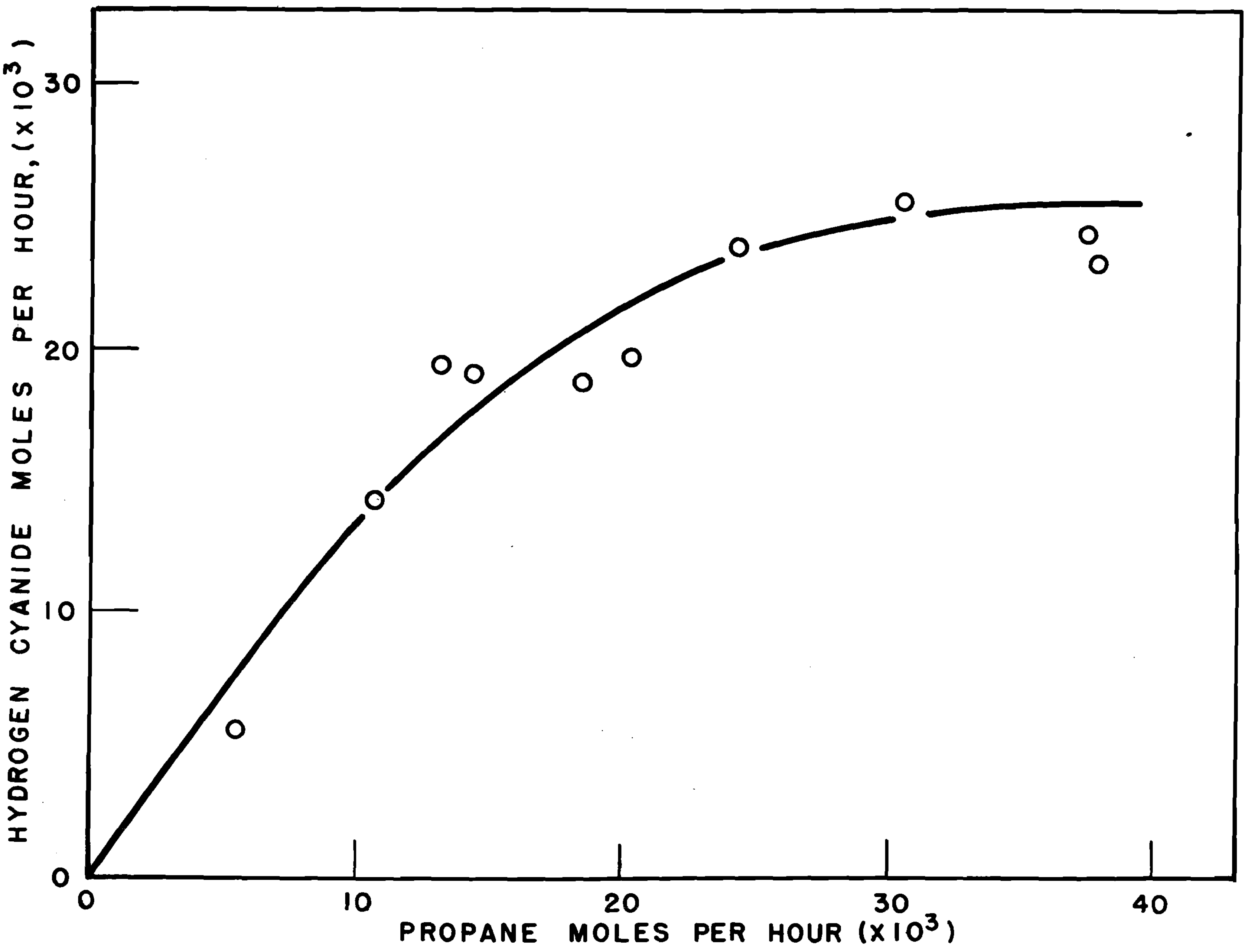
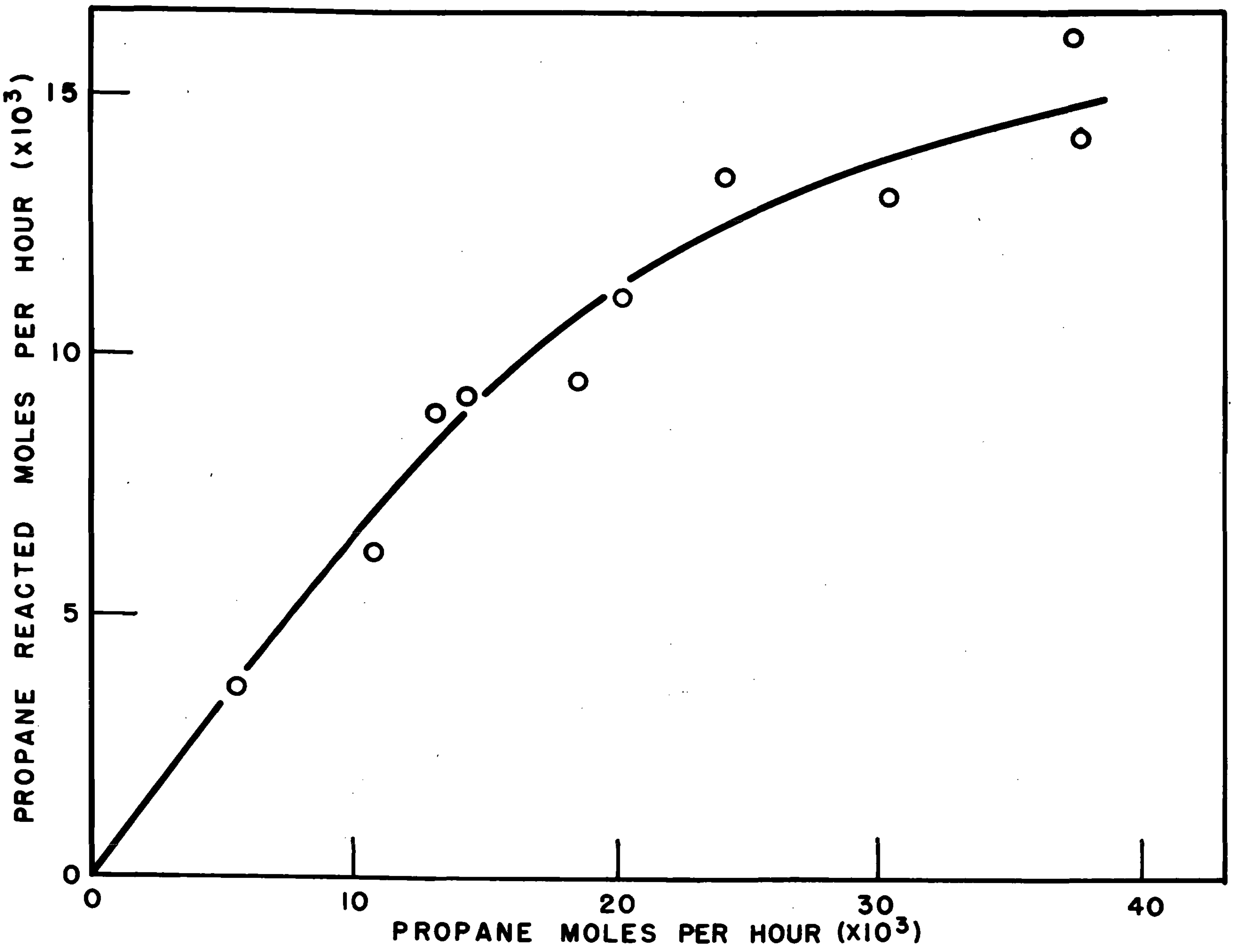

HYDROGEN CYANIDE MOLES PER HOUR, (x10^3)
30
20
10
0
0
10
20
30
40
PROPANE MOLES PER HOUR (x10^3)

Fig. V. Graph illustrating the rate of disappearance of propane as a function of propane flow rate.


PROPANE REACTED MOLES PER HOUR (X10^3)
PROPANE MOLES PER HOUR (X10^3)
0
5
10
15
0
10
20
30
40

In Table I are recorded the amounts of ethane and methane produced. It was not possible to obtain a simple relation between the quantities of the latter hydrocarbons that were recovered and the propane flow rate.

This was probably a result of either, or both of,

(a) insufficient accuracy in the determinations of methane and ethane produced in the reactions.

(b) the complex dependence of their rates of formation on the concentrations of fragments which were involved in competing reactions.

The latter is the more compelling explanation since free radicals can undergo a variety of reactions, and at least some of these are quite dependent on wall conditions, and on local thermal and concentration gradients.

Calculation of rate constants of a reaction are usually made on the basis of the rate of appearance of a product, or the rate of disappearance of a reactant.

When more than one product is obtained as a result of successive reactions, the rate equation for the appearance of a product is based on an assumed mechanism. It is then necessary to estimate, e.g. by the "steady-state" treatment, the concentrations of the various components involved in those reactions which yield the designated product.

If the reaction between nitrogen atoms and a hydrocarbon is followed by the rate of disappearance of the hydrocarbon, the rate equation involves only the concentrations of the initial reactants, providing the hydrocarbon is neither attacked by an intermediate, nor regenerated in the course of the reaction.

The latter assumption was made and rate constants were calculated from the second order expression

Rate of disappearance of propane $= k[N][C_3H_8]$

where k is the specific rate constant,

$[N]$, $[C_3H_8]$ are the effective nitrogen atom and propane concentrations, respectively.

The data used for the calculation of the rate constants for experiments 1-10 are shown in Table III. These calculations involve certain approximations and assumptions which may now be considered.

The reaction between nitrogen atoms and ethylene(23) is a "clean-up" reaction: that is, the volume in which nitrogen atoms attack ethylene bears no relation to the size of the reaction vessel. Flames with rather sharp boundaries are obtained and the actual volume to which the reaction is confined presumably corresponds to the flame size. The latter is determined completely by the extent of interdiffusion and rate of reaction of the gaseous components. In these circumstances, the method of "diffusion flames" is

TABLE III

DATA USED IN CALCULATION OF SPECIFIC RATE CONSTANTS EXPERIMENTS 1-10

Experiment Number	I Propane flow rate moles per hour	II Nitrogen atom flow rate gm. atoms per hour	III Total nitrogen flow rate (no discharge) moles per hour	IV Total gas flow rate (I +$\frac{1}{2}$II + III) moles per hour	V Total Pressure mm.	VI Reaction Time seconds
1	2.433x10^{-2}	3.24x10^{-2}	0.4355	0.476	2.274	0.257
2	3.746x10^{-2}	3.24x10^{-2}	6.4355	0.489	2.274	0.251
3	1.320x10^{-2}	3.24x10^{-2}	0.4355	0.465	2.153	0.250
4	1.849x10^{-2}	3.24x10^{-2}	0.4355	0.470	2.082	0.239
5	3.053x10^{-2}	3.24x10^{-2}	0.4355	0.482	2.274	0.254
6	3.786x10^{-2}	3.24x10^{-2}	0.4355	0.490	2.153	0.237
7	2.034x10^{-2}	3.24x10^{-2}	0.4355	0.472	2.132	0.243
8	1.068x10^{-2}	3.24x10^{-2}	0.4355	0.462	2.186	0.255
9	1.442x10^{-2}	3.24x10^{-2}	0.4355	0.466	2.186	0.253
10	5.471x10^{-3}	3.24x10^{-2}	0.4355	0.457	2.186	0.258

TABLE III (Continued)

Experiment Number	VII Hydrogen cyanide produced moles per hour	VIII Propane recovered moles per hour	IX Initial propane partial pressure P_P^o mm.	X Initial nitrogen atom partial pressure P_N^o mm.	XI Initial propane concentration n_P^o moles	XII Final propane concentration n_P^f moles	XIII $\Delta(n_P)$ moles	XIV Initial nitrogen atom concentration n_N^o gm. atoms	XV Hydrogen cyanide concentration moles
1	2.318×10^{-2}	1.084×10^{-2}	1.16×10^{-1}	1.55×10^{-1}	1.739×10^{-6}	7.749×10^{-7}	9.64×10^{-7}	2.32×10^{-6}	1.657×10^{-6}
2	2.434×10^{-2}	2.133×10^{-2}	1.74×10^{-1}	1.50×10^{-1}	2.607×10^{-6}	1.485×10^{-6}	1.12×10^{-6}	2.25×10^{-6}	1.691×10^{-6}
3	1.944×10^{-2}	4.265×10^{-3}	6.11×10^{-2}	1.50×10^{-1}	9.147×10^{-7}	2.954×10^{-7}	6.19×10^{-7}	2.24×10^{-6}	1.346×10^{-6}
4	1.865×10^{-2}	8.960×10^{-3}	8.25×10^{-2}	1.44×10^{-1}	1.234×10^{-6}	5.980×10^{-7}	6.36×10^{-7}	2.15×10^{-6}	1.236×10^{-6}
5	2.554×10^{-2}	1.751×10^{-2}	1.44×10^{-1}	1.53×10^{-1}	2.156×10^{-6}	1.237×10^{-6}	9.19×10^{-7}	2.29×10^{-6}	1.807×10^{-6}
6	2.322×10^{-2}	2.369×10^{-2}	1.67×10^{-1}	1.43×10^{-1}	2.492×10^{-6}	1.559×10^{-6}	9.33×10^{-7}	2.13×10^{-6}	1.529×10^{-6}
7	1.976×10^{-2}	9.239×10^{-3}	9.19×10^{-2}	1.46×10^{-1}	1.375×10^{-6}	6.246×10^{-7}	7.50×10^{-7}	2.19×10^{-6}	1.337×10^{-6}
8	1.434×10^{-2}	4.426×10^{-3}	5.14×10^{-2}	1.53×10^{-1}	7.688×10^{-7}	3.195×10^{-7}	4.49×10^{-7}	2.29×10^{-6}	1.014×10^{-6}
9	1.908×10^{-2}	5.189×10^{-3}	6.76×10^{-2}	1.52×10^{-1}	1.013×10^{-6}	3.645×10^{-7}	6.49×10^{-7}	2.27×10^{-6}	1.340×10^{-6}
10	5.772×10^{-2}	1.789×10^{-3}	2.62×10^{-2}	1.55×10^{-1}	3.916×10^{-7}	1.280×10^{-7}	2.64×10^{-7}	2.32×10^{-6}	4.134×10^{-7}

NOTE: Concentrations refer to number of moles in the reaction volume (325cc.)

TABLE III (Continued)

Experiment Number	XVI Final nitrogen atom concentration (XIV-XV) n_N^f gm. atoms	XVII Average propane concentration $n_P^{av.} = \frac{n_P^o + n_P^f}{2}$ moles	XVIII Average nitrogen atom concentration $n_N^{av.} = \frac{n_N^o + n_N^f}{2}$ moles	XIX Specific rate constant k litre mole^{-1} sec^{-1} x 10^{-5}
1	6.59 x 10^{-7}	1.26 x 10^{-6}	1.49 x 10^{-6}	6.5
2	5.60 x 10^{-7}	2.05 x 10^{-7}	1.41 x 10^{-6}	5.1
3	8.97 x 10^{-7}	6.05 x 10^{-7}	1.57 x 10^{-6}	8.5
4	9.12 x 10^{-7}	9.16 x 10^{-7}	1.53 x 10^{-6}	6.2
5	4.86 x 10^{-7}	1.70 x 10^{-6}	1.39 x 10^{-6}	5.0
6	6.04 x 10^{-7}	2.03 x 10^{-6}	1.37 x 10^{-6}	4.6
7	8.54 x 10^{-7}	1.00 x 10^{-6}	1.52 x 10^{-6}	6.6
8	1.28 x 10^{-6}	5.44 x 10^{-7}	1.79 x 10^{-6}	5.9
9	9.34 x 10^{-7}	6.88 x 10^{-7}	1.60 x 10^{-6}	7.6
10	2.06 x 10^{-6}	2.60 x 10^{-7}	2.19 x 10^{-6}	7.0
			Average	6.3
			Mean deviation	0.9

appropriate to the study of the kinetics of the reaction.

When nitrogen atoms react with ethane(24), completely diffuse flames can be obtained. The flame boundaries are then uniquely determined by the walls of the enclosing vessel, and the space in which reaction occurs corresponds to the volume of the reaction vessel.

The flame produced by the nitrogen atom-propane reaction was neither sharp nor completely diffuse. The intensity of the lilac-coloured glow was highest at the hydrocarbon inlet, and decreased in the direction of gas flow. In most of the experiments, a faint flame could be seen against a dark background just above the level of the liquid air in the trap. When either nitrogen atoms or propane was in large excess however, no luminosity was observed near the exit of the reaction vessel. Apparently, the volume of the flame was a function of the flow rates of the reactants. The latter were chosen to produce minimal variations of visible flame size in successive experiments. Hence, in a restricted range of flow rates, the reaction volume was assumed to be constant. Equating this volume to the volume of the reaction vessel may affect the absolute accuracy of the calculated specific rate constants, but the reliability of their relative values depends only on the degree of constancy of the various flame volumes. The lilac-coloured flame which is obtained in nitrogen atom-hydrocarbon reactions has been identified with the cyanogen spectrum(5). Since hydrogen cyanide is always the main product of these reactions, it is reasonable to assume that the size of the flame is a true measure of the volume in which nitrogen atoms can attack propane.

The reaction time for each experiment was calculated from the operating pressure, temperature, reaction volume and the total gas flow rate. The total flow rate was taken as the sum of the flow rates of the individual gases in the absence of reaction, i.e. without taking into account stoichiometric changes resulting from nitrogen atom attack. These changes had little effect on the total gas flow rate because of the large excess of molecular nitrogen. The latter accounted for about 90% of the gases that were passed through the reaction vessel.

The initial partial pressures of nitrogen atoms and propane were calculated from the experimentally determined total pressures and mole fractions. The "final" partial pressures were evaluated from the observed conversion of nitrogen atoms to hydrogen cyanide and disappearance of propane.

Some uncertainty arose in the estimation of the effective concentrations of the reactants in the reaction zone. Generally, the concentrations of reactants can be expressed as a function of time, and the amount of reaction in time <u>t</u> is expressed as an integral of the rate expression between the limits $t = 0$ and $t = t$.

In the propane-nitrogen atom reaction, changes in concentration with time are reflected in concentration gradients throughout the flame. A rigorous calculation of the specific rate constant requires a knowledge of the concentrations of reactants as a function of their position in the flame. In the limiting case of streamline flow uncomplicated by diffusion processes, the calculation reduces to a simple integration of the rate expression over the reaction time.

When one gas issues into another from a point source to produce a spherical flame or reaction zone, i.e. when mass flow can be neglected, the concentration gradients are radially symmetrical and can be related to the specific rate constant and the diffusion coefficient of the gases. When one reactant is in large excess so that its concentration is essentially constant throughout the reaction zone, the rate expression is simple and involves the diffusion coefficient of only one gas. This is the basis of the Polanyi "diffusion flame" technique.(27)

A condition of turbulence in which there is complete mixing of reactants in the flame represents another limiting case. There are no concentration gradients; the concentrations of reactants are independent of time. The rate equation then assumes the simple form

$$\Delta[C_3H_8] = kt\ [C_3H_8][N]$$

The specific rate constants recorded in Table III were calculated on the basis of complete turbulence. The effective concentrations of propane and atomic nitrogen in the flame were taken to be $\frac{n_P^o + n_P^f}{2V}$, $\frac{n_N^o + n_N^f}{2V}$ respectively,

where V is the volume in which reaction occurs,

$\frac{n_P^o}{V}$ is the concentration of propane in the absence of chemical reaction,

$\frac{n_P^f}{V}$ is the concentration of propane outside the flame,

$\frac{n_N^o}{V}$ and $\frac{n_N^f}{V}$ are the corresponding nitrogen atom concentrations.

The assumption of uniform concentrations will affect the relative magnitudes of the specific rate constants only insofar as this approximation deviates non-uniformly from reality for different propane flow rates.

The temperature of the reactants was assumed to be constant throughout the reaction vessel and equal to the temperature of the thermocouple at N. (Fig. I). This is a simplification on three accounts:

(a) thermal gradients in the flame resulted from concentration gradients,

(b) the thermocouple was not in physical contact with the flame and therefore did not give the true flame temperature,

(c) at the lowest experimental temperature, viz. 75°C., the reaction vessel was not electrically heated so that temperature fluctuations occurred in the course of a reaction. In addition, the mean temperature of individual experiments varied somewhat with the propane flow rates. The temperature of experiments 1-10 is therefore given as $75 \pm 5^{\circ}$C.

The average value of the ten specific rate constants was 6.3×10^5 litre mole^{-1} sec^{-1}. The lowest and highest calculated values were 4.6×10^5 and 8.5×10^5 respectively and the mean deviation was 0.9×10^5.

Apart from inaccuracies inherent in the experimental methods, some of the variation between individual specific rate constants may be attributed to lack of validity in some, at least, of the assumptions made in their calculation.

The effect of a variation of temperature was studied with a narrow range of hydrocarbon flow rates, since it was apparent from the previous studies that part of the variation of the specific rate constants could be traced to the fact that errors of different magnitude were involved at different experimental flow rates of propane.

The results of these experiments, 11-17, are shown in Table IV, while Table V illustrates the use of the data in calculating the specific rate constants.

An Arrhenius plot for the results of the experiments at different temperatures is shown in Figure VI. The average value, $k = 6.3 \times 10^5$ litre $mole^{-1}$ sec^{-1} at 348°K., is included as a point on the diagram, and a "best" straight line was drawn to pass through this point. An activation energy of 2.1 kilocalories per mole was calculated from the slope of the log k vs. $\frac{1}{T}$ curve.

The lowest and highest k values obtained were 4.6×10^5 for experiment 6 at 348°K. and 2.3×10^6 for experiment 15 at 555°K, respectively. When these two values alone were considered an activation energy of 2.9 kilocalories per mole was calculated. The experimental data thus indicated that the activation energy of the process which involves the disappearance of propane in the propane-nitrogen atom reaction has a probable value of 2.1 and an upper limited of 2.9 kilocalories per mole.

The frequency factor was estimated from the Arrhenius equation

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

TABLE IV

EXPERIMENTS 11-17

Experiment Number	Temperature °K	Total pressure mm.	Propane total flow moles x 10^3	Propane recovered moles x 10^3	Hydrogen cyanide produced moles x 10^3	Methane produced moles x 10^3	Ethane produced moles x 10^4	Ethylene produced moles x 10^4	Duration of experiment seconds	Carbon recovered (÷3) gm.atoms x 10^3
11	440	2.254	5.573	2.031	7.751	1.601	1.13	1.30	1581	5.378
12	460	2.254	5.687	2.376	7.682	1.277	0.41	1.85	1348	5.515
13	493	2.254	5.650	2.199	8.640	0.518	1.00	0.70	1392	5.365
14	515	2.254	5.669	2.137	8.949	0.865	1.32	2.67	1406	5.674
15	555	2.254	5.241	1.262	8.927	1.010	*6.63		1747	5.032
16	565	2.254	5.588	2.006	9.206	0.932	*3.65		1389	5.629
17	393	2.254	5.610	2.137	8.949	1.010	*3.04		1394	5.658

* C_2 total; ethylene content not analyzed.

TABLE V

DATA USED IN CALCULATION OF SPECIFIC RATE CONSTANTS EXPERIMENTS 11-17

Experiment Number	I Temperature °K.	II Propane flow rate moles per hour	III Nitrogen atom flow rate gm. atoms per hour	IV Total nitrogen flow rate (no discharge) moles per hour	V Total gas flow rate (II + $\frac{1}{2}$III + IV) moles per hour	VI Total pressure mm.	VII Reaction time seconds
11	440	1.269×10^{-2}	3.24×10^{-2}	0.4355	0.464	2.254	0.207
12	460	1.578×10^{-2}	3.24×10^{-2}	0.4355	0.467	2.254	0.197
13	493	1.461×10^{-2}	3.24×10^{-2}	0.4355	0.466	2.254	0.184
14	515	1.452×10^{-2}	3.24×10^{-2}	0.4355	0.466	2.254	0.176
15	555	1.080×10^{-2}	3.24×10^{-2}	0.4355	0.463	2.254	0.165
16	565	1.447×10^{-2}	3.24×10^{-2}	0.4355	0.466	2.254	0.161
17	393	1.449×10^{-2}	3.24×10^{-2}	0.4355	0.466	2.254	0.231

TABLE V (Continued)

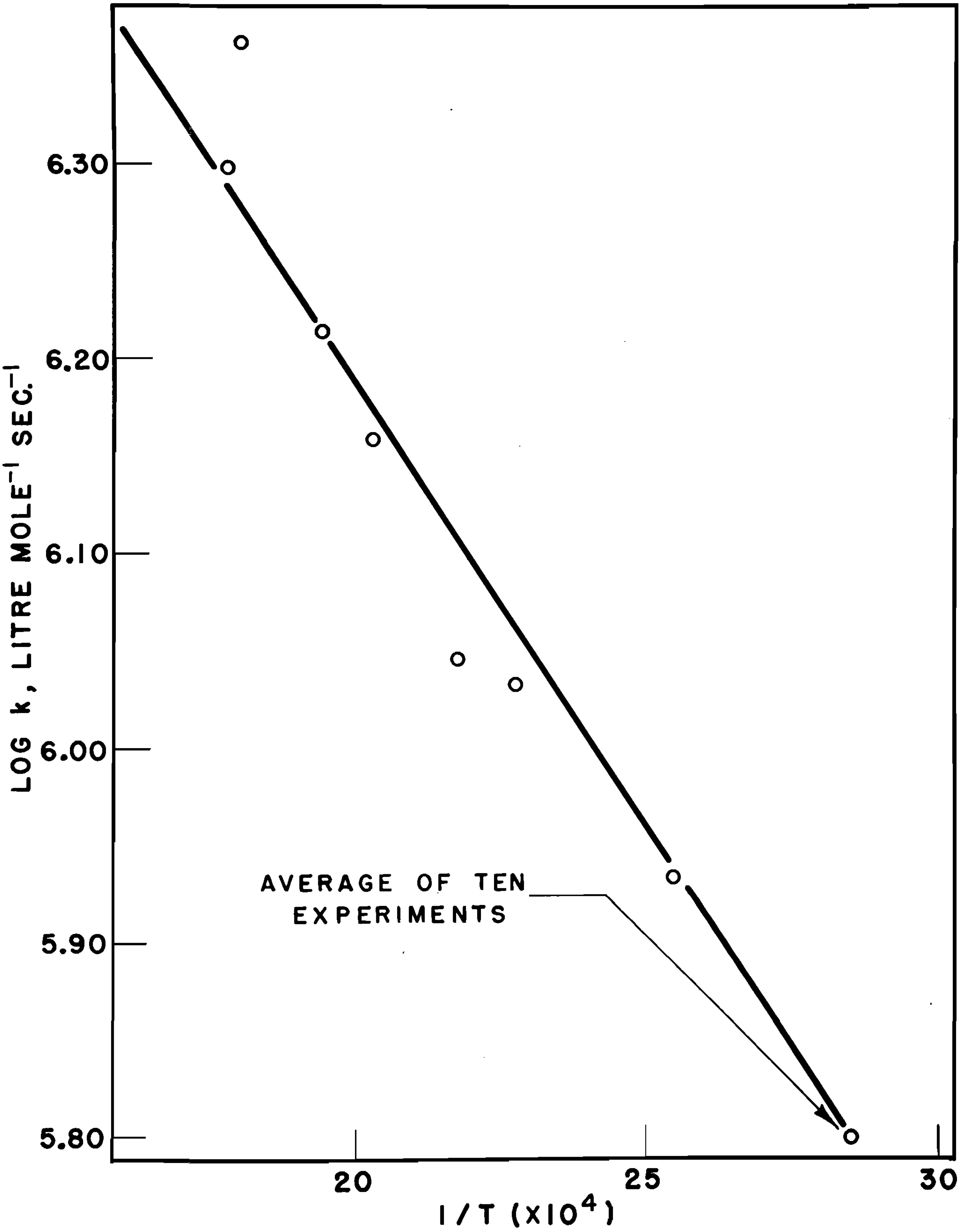
Experiment Number	VIII Hydrogen cyanide produced moles per hour	IX Propane recovered moles per hour	X Initial propane partial pressure P_P^o mm.	XI Initial nitrogen atom partial pressure P_N^o mm.	XII Initial propane concentration n_P^o moles	XIII Final propane concentration n_P^f moles	XIV $\Delta(n_P)$ moles	XV Initial nitrogen atom concentration n_N^o gm.atoms	XVI Hydrogen cyanide concentration moles
11	$1.765\text{x}10^{-2}$	$4.625\text{x}10^{-3}$	$6.16\text{x}10^{-2}$	$1.57\text{x}10^{-1}$	$7.291\text{x}10^{-7}$	$2.657\text{x}10^{-7}$	$4.634\text{x}10^{-7}$	$1.86\text{x}10^{-6}$	$1.015\text{x}10^{-6}$
12	$2.099\text{x}10^{-2}$	$6.949\text{x}10^{-3}$	$6.94\text{x}10^{-2}$	$1.48\text{x}10^{-1}$	$7.854\text{x}10^{-7}$	$3.596\text{x}10^{-7}$	$4.258\text{x}10^{-7}$	$1.67\text{x}10^{-6}$	$1.136\text{x}10^{-6}$
13	$2.235\text{x}10^{-2}$	$5.685\text{x}10^{-3}$	$7.06\text{x}10^{-2}$	$1.56\text{x}10^{-1}$	$7.464\text{x}10^{-7}$	$2.903\text{x}10^{-7}$	$4.561\text{x}10^{-7}$	$1.65\text{x}10^{-6}$	$1.141\text{x}10^{-6}$
14	$2.291\text{x}10^{-2}$	$5.474\text{x}10^{-3}$	$7.02\text{x}10^{-2}$	$1.56\text{x}10^{-1}$	$7.099\text{x}10^{-7}$	$2.676\text{x}10^{-7}$	$4.423\text{x}10^{-7}$	$1.58\text{x}10^{-6}$	$1.120\text{x}10^{-6}$
15	$1.849\text{x}10^{-2}$	$2.601\text{x}10^{-3}$	$5.26\text{x}10^{-2}$	$1.58\text{x}10^{-1}$	$4.941\text{x}10^{-7}$	$1.191\text{x}10^{-7}$	$3.750\text{x}10^{-7}$	$1.49\text{x}10^{-6}$	$8.484\text{x}10^{-7}$
16	$2.385\text{x}10^{-2}$	$5.196\text{x}10^{-3}$	$7.00\text{x}10^{-2}$	$1.57\text{x}10^{-1}$	$6.455\text{x}10^{-7}$	$2.317\text{x}10^{-7}$	$4.138\text{x}10^{-7}$	$1.57\text{x}10^{-6}$	$1.153\text{x}10^{-6}$
17	$2.002\text{x}10^{-2}$	$5.692\text{x}10^{-3}$	$7.01\text{x}10^{-2}$	$1.56\text{x}10^{-1}$	$9.290\text{x}10^{-7}$	$3.649\text{x}10^{-7}$	$5.641\text{x}10^{-7}$	$2.08\text{x}10^{-6}$	$1.283\text{x}10^{-6}$

NOTE: Concentrations refer to number of moles in the reaction volume (325cc.)

TABLE V (Continued)

Experiment Number	XVII Final nitrogen atom concentration (XV-XVI) n_N^f gm. atoms	XVIII Average propane concentration $n_P^{av.} = \frac{n_P^o+n_P^f}{2}$ moles	XIX Average nitrogen atom concentration $n_N^{av.} = \frac{n_N^o+n_N^f}{2}$ moles	XX Specific rate constant k litre mole^{-1} sec^{-1} x 10^{-6}
11	8.46×10^{-7}	4.49×10^{-7}	1.35×10^{-6}	1.0_8
12	5.37×10^{-7}	5.73×10^{-7}	1.11×10^{-6}	1.1_1
13	5.11×10^{-7}	5.18×10^{-7}	1.08×10^{-6}	1.4_4
14	4.62×10^{-7}	4.89×10^{-7}	1.02×10^{-6}	1.6_3
15	6.37×10^{-7}	3.04×10^{-7}	1.06×10^{-6}	2.2_8
16	4.12×10^{-7}	4.39×10^{-7}	9.88×10^{-7}	1.9_8
17	7.91×10^{-7}	6.47×10^{-7}	1.43×10^{-6}	0.8_6

Fig. VI. Plot of log k vs. $\frac{1}{T}$ for experiments 11-17.


6.30
6.20
6.10
6.00
5.90
5.80
LOG k, LITRE MOLE⁻¹ SEC.⁻¹
20
25
30
1/T (X10⁴)
AVERAGE OF TEN
EXPERIMENTS

where k is the specific rate constant (litre mole^{-1} sec^{-1})
A, the frequency factor (litre mole^{-1} sec^{-1})
E, the activation energy (kilocalories per mole)
R, the gas content (kilocalories mole^{-1} deg.^{-1})
and T, the absolute temperature.

For E = 2.1 kilocalories per mole, $A_{348^{o}K.} = 1.3 \times 10^{7}$ litre mole^{-1} sec^{-1}.

E = 2.9 kilocalories per mole, $A_{348^{o}K.} = 3.1 \times 10^{7}$ litre mole^{-1} sec^{-1}.

A "specific" collision rate for atomic nitrogen and propane may be calculated from the expression

$$Z = N_A \, \sigma_{NP}^{2} \left[8\pi RT \left\{ \frac{M_N + M_P}{M_N M_P} \right\} \right]^{\frac{1}{2}}$$

where Z is the specific collision rate (cc. sec^{-1} mole^{-1})
σ_{NP}^{2}, the effective $(\text{collision diameter})^{2}$ (cm.^{2} molecule^{-1})
R, the gas constant (gm.cm^{2} sec^{-2} mole^{-1} deg.^{-1})
T, the absolute temperature
M_N, the "molecular" weight of atomic nitrogen
M_P, the molecular weight of propane
and N_A, the Avogadro number.

The effective collision diameter, σ_{NP}, is defined as the mean of the collision diameters for nitrogen atoms and propane molecules. The value $\sigma_N = 3.0 \times 10^{-8}$ cm. was calculated by Greenblatt(23) from Rayleigh's(20) assumed value for the coefficient of self-diffusion of nitrogen atoms. The collision diameter of propane was taken as 4.2×10^{-8} cm.(66)

Using $\sigma_{NP}^{2} = 1.3 \times 10^{-1}$ cm.^{2} molecule^{-1}, the above expression yielded $Z = 2.0 \times 10^{14}$ cc. sec^{-1} mole^{-1}.

The corresponding probability factor, $P = \frac{A}{Z}$, took the values $P = 6.5 \times 10^{-5}$ and 1.6×10^{-4} for the lower and higher values of A, respectively.

The theory of absolute reaction rates relates the probability factor to the entropy of activation. An estimate of the entropy cannot be made for any but the simplest of systems. However, both simple collision and absolute reaction rate theories indicate that, in general, the probability factor decreases with increasing complexity of reactants. This general trend has been established(67) for reactions involving atoms or free radicals and also for bimolecular reactions between non-radical particles.

The following table compares the probability factors and activation energies for a series of reactions involving nitrogen atoms and a hydrocarbon.

Hydrocarbon	Probability Factor	Activation Energy
Methane	5×10^{-3}	11 kilocalories/mole
Ethane	10^{-1}-10^{-3}	6-8 kilocalories/mole
Ethylene	10-2	3-5 kilocalories/mole
Propane	10^{-4}	2-3 kilocalories/mole

Disregarding the "abnormal" hydrocarbon, methane, the value of the probability factor for the nitrogen atom-propane reaction relative to the other nitrogen atom-hydrocarbon reactions is in accord with expectation. The activation energies also decrease with ascending order in the hydrocarbon series.

Comparisons of the frequency factors and activation energies are, of course, valid only insofar as the mechanisms of the nitrogen atom-hydrocarbon reactions are similar. In this respect the unsaturated hydrocarbon, ethylene, may well be exceptional. For the saturated series, however, qualitative comparisons are probably meaningful; decreases in activation energy correspond to increases in reactivity of the hydrocarbon with respect to nitrogen atoms.

There now arises the question of what process should be identified with the calculated activation energy. An attempt to formulate a mechanism for the nitrogen atom propane reaction suffers generally from the lack of a large body of kinetic data for nitrogen atom reactions, and particularly from the uncertainty in the strength of bonds involving nitrogen. However, it is possible to suggest a mechanism which can account for the experimentally observed results.

If the initial act in the nitrogen atom-propane reaction were analagous to that of hydrogen atom-hydrocarbon reactions, the NH radical would be liberated:

$$C_3H_8 + N \longrightarrow C_3H_7 + NH$$

This possibility must be excluded on both theoretical and experimental grounds. Recent estimates(1) of the C-H bond energy in saturated hydrocarbons indicate a value of 95-100 kilocalories. Pauling(68) and Szwarc(69) calculated values of 83.7 and 95 kilocalories respectively for the average N-H bond energy in ammonia. The latter quantities depended on the energy assumed for the dissociation of nitrogen, the value of which is somewhat uncertain at present. Fortunately, approximate estimates of the strength of the N-H bond in the NH radical which are independent of the nitrogen dissociation energy have recently been made by Warhurst and Scanlan(70) and Glockler(71). They obtained values of 87.3 kilocalories and 86.2 kilocalories respectively.

No experimental evidence for the existence of NH radicals in the mixture was obtained. Unless virtually all the radicals were consumed by reactions of the type

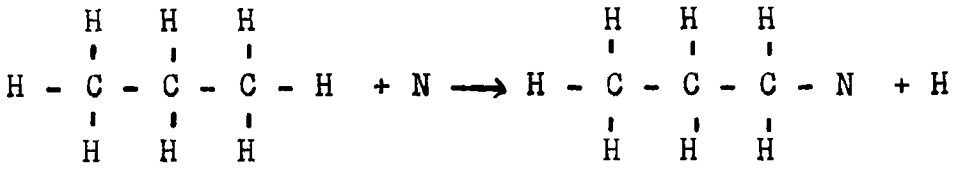
$$NH + N \longrightarrow N_2 + H$$

$$NH + H \longrightarrow N + H_2$$

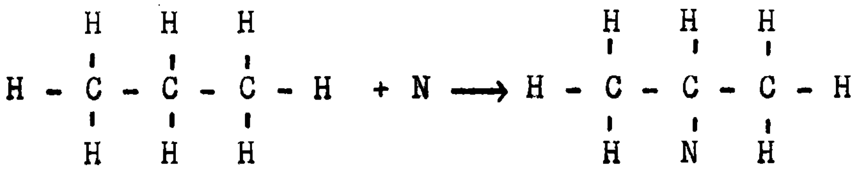
$$NH \longrightarrow N + H$$

their presence might have been inferred from formation of nitrogenous products other than hydrogen cyanide. Such products have never yet been obtained in any nitrogen atom-hydrocarbon reaction.

Reactions involving replacement of a hydrogen atom by nitrogen,



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H + N \longrightarrow H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-N + H$$



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H + N \longrightarrow H-\underset{H}{\overset{H}{C}}-\underset{N}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

are improbable on a thermochemical basis. Palmer(72) found a value of 58 kilocalories for the C-N bond energy in methylamine, assuming a value of 88.5 kilocalories for the N-H bond in his calculation. Almost the same energy, 59 kilocalories was calculated for the average strength of the C-N bond in trimethylamine. An upper limit for the energy of the C-N bond in C_3H_7N is therefore about 59 kilocalories from which it might be inferred that the reaction leading to formation of C_3H_7N is about 40 kilocalories endothermic.

Reactions of the type

$$C_3H_8 + N \longrightarrow C_2H_5 + CH_3N$$

$$C_3H_8 + N \longrightarrow C_3H_7N + CH_3$$

are energetically more favourable than the reaction

$$C_3H_8 + N \longrightarrow C_3H_7N + H$$

However, the rupture of a C-C bond and formation of a C-N bond still requires an expenditure of about 25 kilocalories, taking the value 85 kilocalories(1) for the C-C bond strength in propane.

All reactions involving hydrogen atom abstraction or replacement, or C-C bond ruptures do not appear to be plausible initial processes in the light of present bond energy data.

A possible alternative is the formation of a collision complex in an exothermic process,

$$C_3H_8 + N \longrightarrow C_3H_8N^* \qquad (1)$$

followed by an intermolecular rearrangement to split off hydrogen cyanide,

$$C_3H_8N^* \longrightarrow HCN + C_2H_5 + H_2 \quad (2a)$$
$$C_3H_8N^* \longrightarrow HCN + C_2H_6 + H \quad (2b)$$

On an energy basis, the probabilities of reactions (2a) and (2b) are of the same order of magnitude. The possibility of reaction (2b), however, must be considered negligible if analogy is to be retained with the ethane-nitrogen atom reaction in which no methane was formed. Mechanisms such as depicted by (2a) are, of course, unattractive in that they do not obey the principle of "least action". However, Bawn and Milsted,(60) and Bawn and Dunning(61) have found it necessary to suggest a "one-step" mechanism to explain the formation of ethylene in the reaction between dihalogenated ethane and atomic sodium:

$$CH_3CHX_2 + Na \longrightarrow CH_3CHX + NaX$$

$$CH_3CHX + Na \longrightarrow NaX + C_2H_4.$$

Even when hydrogen was used as the carrier gas only ethylene was obtained. The authors excluded the presence of ethylidene radicals, CH_3CH, because of their failure to obtain ethane.

The ethyl radicals resulting from reaction (2a) might also have reacted with a nitrogen atom to produce another molecule of hydrogen cyanide:

$$C_2H_5 + N \longrightarrow HCN + CH_3 + H \qquad (3a)$$

$$C_2H_5 + N \longrightarrow HCN + CH_4 \qquad (3b)$$

Reaction (3a) seems more plausible than (3b) since a methyl radical would be expected to have a finite life as the result of rupture of the C-C bond in the ethyl radical.

Methane undergoes no appreciable reaction with nitrogen at temperatures up to 350°C.,(24) but methyl radicals are a possible source of additional hydrogen cyanide according to the scheme:

$$CH_3 + N \longrightarrow HCN + H_2 \qquad (4a)$$

$$CH_3 + N \longrightarrow HCN + 2H \qquad (4b)$$

Reaction (4b) has been postulated by Greenblatt and Winkler(23) to account for the formation of ethane in the nitrogen atom-ethylene reaction. Blades and Winkler(24) have rejected the possibility of reaction (4b) because they found that methane was not a product of the reaction between nitrogen atoms and ethane. They maintained that hydrogen atoms would have attacked ethane to produce ethyl radicals and ultimately, methyl radicals and methane. Nevertheless, their failure to obtain methane can be explained equally well on the basis of almost complete consumption of ethyl and methyl radicals by nitrogen atoms rather than by hydrogen atoms. Though no direct evidence has been found for the formation of hydrogen atoms in hydrocarbon-nitrogen atom reactions, the high probability that they are formed is evident from the detection of ethane and propane in the reactions between nitrogen atoms and ethylene and nitrogen atoms and propylene,(73) respectively.

In the mechanism proposed for the nitrogen atom-propane reaction the suggested formation of hydrogen atoms from reaction (3a),

$$C_2H_5 + N \longrightarrow CH_3 + HCN + H$$

appears reasonable and does not conflict with the results of other nitrogen atom-hydrocarbon studies.

The following reactions involving free radicals have low activation energies(1) and are correspondingly probable:

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad (5)$$

$$CH_3 + H \longrightarrow CH_4 \quad (6)$$

$$C_2H_5 + H \longrightarrow 2CH_3 \qquad (7)$$

$$C_2H_5 + H \longrightarrow C_2H_6 \qquad (8)$$

$$C_2H_5 + CH_3 \longrightarrow C_3H_8 \qquad (9)$$

Ethyl radicals can recombine to form butane. This hydrocarbon might have been formed in small quantities in the propane-nitrogen atom reaction, but was not detected. The fate of ethyl radicals in a complex mixture is strongly dependent on temperature and the nature of possible side reactions(63). The formation of ethylene and ethane from the disproportionation reaction

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \qquad (10)$$

might well have occurred in preference to the recombination reaction

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$$

under the conditions that obtained in the nitrogen atom-propane reaction. Reaction (1) would have been favoured by a higher temperature and this is in accord with the experimental results. At the lower experimental temperature, 75°C., only traces of ethylene in the products were obtained. Some ethylene might also have resulted from the reactions

$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2 \qquad (11)$$

$$CH_2 + CH_2 \longrightarrow C_2H_4 \qquad (12)$$

Although there is evidence that the disproportionation reaction of methyl radicals does not occur(74),(75) Paneth, Hofeditz and Wunsch(62) found that small amounts of ethylene were formed during the decomposition of lead tetramethyl.

Reactions of radicals with hydrogen such as

$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (13)$$

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \qquad (14)$$

would have had to compete with the corresponding nitrogen atom reactions (3) and (4). Reactions (13) and (14) have an activation energy of about 9 kilocalories(1),(58) and would have occurred to a significant extent only when the nitrogen atom concentration was small, i.e. at high hydrocarbon flow rates.

Similar activation energies, 6-8 kilocalories,(1) are associated with reactions of the type:

$$C_3H_8 + H \longrightarrow C_3H_7 + H_2 \qquad (15)$$

$$C_3H_8 + CH_3 \longrightarrow CH_4 + C_3H_7 \qquad (16)$$

At present there is no quantitative information concerning reactions such as

$$C_3H_8 + C_2H_5 \longrightarrow C_2H_6 + C_3H_7 \qquad (17)$$

but they are believed possible(1).

In the flame produced by the nitrogen atom-propane reaction there undoubtedly existed regions of relatively high propane concentration and low nitrogen atom concentration at all hydrocarbon flow rates. In these circumstances reactions (15), (16) and (17) could have competed to some extent with the corresponding nitrogen atom reaction.

Propyl radicals produced in the above reactions were presumably degraded by nitrogen atoms in a process analagous to the ethyl radical-nitrogen atom reaction:

$$C_3H_7 + N \longrightarrow HCN + C_2H_5 + H \quad (18)$$

In summary, therefore, a reasonable interpretation of the reaction between nitrogen atoms and propane might be formulated by the following principal reactions:

$$C_3H_8 + N \longrightarrow C_3H_8N^* \longrightarrow HCN + C_2H_5 + H_2$$
$$C_2H_5 + N \longrightarrow HCN + CH_3 + H$$
$$CH_3 + N \longrightarrow HCN + H_2$$
$$R + H \longrightarrow RH$$
$$CH_3 + CH_3 \longrightarrow C_2H_6$$
$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$$

and reactions of secondary importance

$$R + H_2 \longrightarrow RH + H$$
$$C_3H_8 + R \longrightarrow RH + C_3H_7$$
$$C_3H_8 + H \longrightarrow C_3H_7 + H_2$$
$$C_3H_7 + N \longrightarrow HCN + C_2H_5 + H$$

where R is a methyl or ethyl radical.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. An apparatus, suitable for a study of the nitrogen atom-propane reaction was constructed.
2. Hydrogen cyanide, ethane, ethylene, methane and hydrogen were identified and analyzed as products of the reaction in the temperature range 75°C-292°C.
3. Hydrogen cyanide was the main product of the nitrogen atom-propane reaction. Up to 70% of the hydrocarbon which had reacted (experiment 9) was converted to the cyanide at 75°C., 85% of the consumed propane was nitrogenated at 292°C. (experiment 16). About 8% of the propane that disappeared in the reaction at 75°C. was recovered as C_2 hydrocarbons which contained traces of ethylene. At higher temperatures ethane and ethylene were produced in quantities of the same order of magnitude, amounting to about 2-4% of the propane which had reacted. The yield of methane was lower at the higher temperatures: about 20% at 75°C. (experiments 1-10) and 10% above 120°C. (experiments 11-17).
4. Experiments were made at 75°C. to study the effect of varying the hydrocarbon flow rate at a constant atomic nitrogen flow rate. The rates of formation of hydrogen cyanide and disappearance of propane

were found to increase with increasing propane flow rate. The curves relating the rates of hydrogen cyanide formation and propane disappearance to hydrocarbon flow rate had the same general appearance. The amounts of lower hydrocarbons formed in the reaction could not be simply related to the propane flow rate and this was attributed to the complex dependence of the rates of formation of the lower hydrocarbons on the concentrations of fragments which were involved in competing reactions.

5. The use of rate expressions which are appropriate to some types of gas reactions were discussed and the nature of the assumptions and approximations involved were noted. A simple rate expression for the disappearance of propane in the nitrogen atom reaction was chosen; the concentrations of reactants were assumed to be uniform in the reaction zone, a situation which prevails in strongly turbulent flow. On this basis second order specific rate constants were calculated for the reactions at 75°C. and were found to apply reasonably well to the rates of disappearance of propane in the presence of nitrogen atoms. The mean value of the specific rate constants for ten experiments was 6.3×10^5 litre mole^{-1} sec.$^{-1}$ and the mean deviation was 0.9×10^5 litre mole^{-1} sec^{-1}.

6. Experiments were made to study the effect of temperature on the rate of reaction. A restricted range of hydrocarbon flow rates was used to minimize the errors resulting from the assumptions and approximations involved in the calculation of specific rate constants.

   An Arrhenius plot was made from the specific rate constants obtained for the reactions in the temperature range 75°-292°C. (Figure VI). The points in the diagram, including that representing the average of ten specific rate constants calculated for the reactions at 75°C. were found to fit a straight line fairly well. A probable value of 2.1 and an upper limit of 2.9 kilocalories per mole was obtained from the temperature coefficient of the specific rate constants. Values of the steric factor were deduced from the frequency factors and specific collision rates, calculated from the simple collision theory: $P_{348^{\circ}K} = 6.5 \text{ x } 10^{-5}$, and $1.6 \text{ x } 10^{-4}$, corresponding to the lower and higher values of the activation energy, respectively.

7. Some general mechanisms for nitrogen atom-hydrocarbon reactions were discussed. Assuming that unexcited nitrogen atoms were involved in these reactions, all initial processes requiring rupture of a C-C bond, or replacement or abstraction of a hydrogen atom by a nitrogen atom were found to be improbable on a thermochemical basis.

An initial step has been proposed in which a collision complex $C_3H_8N^*$ was formed, then underwent intermolecular rearrangement to split off hydrogen cyanide, hydrogen and an ethyl radical:

$$C_3H_8 + N \longrightarrow C_3H_8N^* \qquad (1)$$

$$C_3H_8N^* \longrightarrow HCN + C_2H_5 + H_2 \qquad (2)$$

The ethyl radical underwent degradation in another nitrogen atom reaction, and liberated a methyl radical capable of conversion to hydrogen cyanide

$$C_2H_5 + N \longrightarrow HCN + CH_3 + H \qquad (3)$$

$$CH_3 + N \longrightarrow HCN + H_2 \qquad (4)$$

A consideration of free radical reactions and the experimentally obtained results led to the conclusion that the following reactions occurred:

$$R + H \longrightarrow RH$$

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$$

and, to a lesser extent,

$$R + H_2 \longrightarrow RH + H$$

$$C_3H_8 + R \longrightarrow C_3H_7 + RH$$

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

$$C_3H_7 + N \longrightarrow HCN + C_2H_5 + H$$

where R is a methyl or ethyl radical.

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