

THE REACTIONS OF ACTIVE NITROGEN WITH ACETYLENE,
METHYLACETYLENE AND DIMETHYLACETYLENE

by

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INTRODUCTION

Preparation of Active Nitrogen

Strutt, in particular, made valuable contributions to the development of appropriate apparatus for the production of active nitrogen. In 1916 he published a diagram of a discharge tube apparatus in which aluminum electrodes were used (1), and this metal still remains the favoured electrode material for the production of active nitrogen.

By varying the dimensions of the discharge tube, Strutt was led to conclude that more active nitrogen was produced in narrow than in wide tubes, and that the optimum length of travel for the gas from the discharge was about twelve centimetres. When direct current was used, the concentration of active nitrogen proved to be greatest near to the cathode. Strutt found that a circuit containing a condenser was more effective than one in which an induction coil was used.

From the results of several investigations it has been shown that the generation of active nitrogen by means of an electric discharge can be described only in terms of several variables, such as, the pressure, temperature, and previous history of the gas, the presence of impurities, and the voltage, current density, inductance, capacitance, duration, and geometry associated with the discharge (1 to 14).

Active nitrogen can also be produced by an electrodeless discharge (15 to 18), by the use of α -rays (19), and by the catalytic activity of metals of the platinum group (20).

Properties of Active Nitrogen

Lewis used pure nitrogen in a discharge tube, and described the appearance of a chamois-yellow glow, the typical afterglow of active nitrogen (21 to 25). Three bands were reported with the glow: red, double yellow, and green.

Many investigations have been made on the decay of the afterglow from active nitrogen. The process seems to be second-order in the active species and third-order if the pressure of the inactive nitrogen is varied (26 to 35). Angerer (36) and Willey (37) found that the square root of the glow intensity varied linearly with the distance measured along the cylindrical tube in which the afterglow was contained. The spectrum and order of decay of the afterglow did not change as the glow proceeded.

Strutt has reported that, by cooling or compressing the gas, he was able to intensify the afterglow (38). Such a behaviour is consistent with a third-body process (39).

The appearance of the afterglow bands and the order of the glow decay have displayed a dependence on heterogeneous, as well as homogeneous, processes (40 to 44). The suggestion has been made that the impurities in the flowing nitrogen gas poison the wall against nitrogen atom recombination, thus allowing the slower, gas-phase reaction to exhibit its typical decay characteristics.

The effects of impurities on the spectra produced in active nitrogen are variable. Oxygen, added to very pure nitrogen, causes the

formation of the brightest glow at about 0.1 per cent concentration; at larger concentration, the glow is diminished, and is practically extinguished by an oxygen content of 2 per cent (2). Additional oxygen causes the appearance of a greenish-yellow afterglow (45,46).

With vapours of H_2O , Hg, and many metals, small amounts are sufficient to quench the typical spectra, while with H_2 and He, larger amounts are required (24). In a discharge through nitrogen containing argon, negative band spectra are not visible, while they appear if the inert gas is neon, and are even more intense if helium is used (40,47).

There is some evidence to indicate that very pure nitrogen does not produce an intense afterglow (22,29,48 to 54). It has been suggested that many different types of impurities have an effect similar to that of oxygen in aiding the formation of the afterglow, for example, H_2 , He, CO, CO_2 , H_2O , O_3 , and oxides of nitrogen (4,5,7, 55 to 60).

Lewis has reported (3) that, in a self-inductive electrical discharge, negative bands become more prominent and spectral lines more sharp, while discharge current density decreases. Several workers have reported that active nitrogen, subjected to a mild second discharge, exhibits a spectral glow of greatly reduced intensity (1,3, 61 to 64). The typical spectra of the glow appear also when nitrogen is activated by an electrodeless discharge or by an electron stream of controlled energy (17,65 to 72).

Spectroscopy of Active Nitrogen

From the time of the discovery of active nitrogen its spectroscopic properties have been studied in an attempt to understand the gas more thoroughly. Such studies have been especially appropriate, for the species which determine the spectroscopic behaviour of active nitrogen bear a significant relation to processes that occur in the discharge, in the afterglow, and in the reactions characteristic of active nitrogen.

In 1885 and the years that followed Deslandres described and classified the spectra that could be excited in nitrogen and its oxides (73 to 77). He determined the regions in which were to be found the members of the first, second, and third groups of the spectra of nitrogen, and found that the members of the groups could be set into arithmetic progressions if they were designated according to their wave-numbers. With improved dispersion many of the bands were resolved more closely and shown to be series of regular triplets, belonging to one of the positive groups.

Birge, in 1914, made a comprehensive analysis of the first Deslandres group of the positive band spectrum of nitrogen (78). He found that each series could be described by the laws which Deslandres had formulated, except for small deviations which became apparent near the violet end of the group.

After the first observations, that active nitrogen was associated with its typical afterglow, studies were made to explain, in greater detail, the spectra which were observed (6,12,25,79 to 82). It was found that the

spectrum of the afterglow invariably included bands associated with four heads belonging to the first positive group of the spectra of nitrogen. The second positive group occurred only in the spectrum from the discharge. Experimental investigations have also been made far into the red regions of the band spectra of nitrogen (83 to 86).

There was, for several years, considerable uncertainty and disagreement over the origins of the bands which occur in the typical nitrogen afterglow; some hypotheses favoured the spectra to originate from nitrogen atoms, others preferred a molecular species as the source. It has now been proved definitely that the positive and negative band lines arise from molecules of nitrogen, which are respectively neutral and singly, positively ionized (6,66,80,87 to 92).

Selection rules have been proposed to explain the series of positive and negative band spectra of nitrogen (93 to 96). It has been shown that the first positive bands of nitrogen are emitted by molecules of excited nitrogen during transitions from the tenth, eleventh, and twelfth vibrational levels of the B state to one of the fifth, sixth, seventh or eighth levels of the A state (67,90,97 to 99).

Exhaustive analyses have been made of the bands corresponding to the spectra observed in the afterglow of active nitrogen (5,21,100 to 102). These include the distribution of nitrogen molecules among the intermediate molecular vibrational and rotational states (84,99, 103 to 107).

There has been considerable variation of opinion regarding the part played by metastable atoms or metastable molecules in the spectral

properties. In 1925 Birge, from a thorough analysis of the afterglow spectrum, concluded that spectra of the first positive group originate from metastable excited nitrogen molecules (90,97,108). Some later studies have favoured the presence of metastable states, while others have given no indication of such states or indicate that, at best, the concentrations of metastable species are negligibly low under the normal conditions of observation of the afterglow (58,70,99,109 to 116).

Investigations have also been made of the systematic variations of intensities across bands, of the role played by perturbations among the electronic energy levels, and of the importance of predissociative processes among those which lead to the formation of atoms (117 to 125).

The Nature of Active Nitrogen

Many workers have suggested that active nitrogen is an active form of molecular nitrogen. According to Saha and Sur active nitrogen in the afterglow consists mainly of excited molecules, produced by inelastic collisions of the second kind (126). The energy content of such an excited molecule was estimated to be 8.5 e.v., and the lifetime about 10^{-8} seconds. Other evidence was available at this time to indicate that the spectral carrier was of a neutral, diamagnetic character (6,66,87,127). Later, a photographic investigation of the spectrum of active nitrogen in the infra-red region was also used to support the molecular theory of active nitrogen (84,86,111,122,128 to 131).

No single theory of active nitrogen explains completely the full

range of phenomena which have been observed experimentally. However, it may be noted that recent theories increasingly emphasize the participation of atomic nitrogen.

From the relative simplicity of the active nitrogen spectrum in the visible region, and the failure of active nitrogen to condense when cooled by liquid air, Strutt reasoned that the active species was probably monatomic (132), rather than molecular. Similar deductions have been made by other investigators through the discovery of spectral lines originating from nitrogen atoms (87,89,133 to 136). Some theories require the dissociation of molecular nitrogen into atoms which are in an excited, rather than in a ground state (137).

Evidence exists to support the presence of atomic nitrogen in active nitrogen, and attempts have been made to measure the concentration of atoms. Bay and Steiner, working with active nitrogen prepared by a condensed discharge, reported that the concentration of the active, atomic species was proportional to the capacity in the discharge, that is, to the expenditure of energy in the flashes (138). From measurements of pressure differences across a fine capillary, one end of which was in contact with active nitrogen, Wrede found nitrogen atom contents of thirty to fifty per cent in nitrogen issuing from a discharge (63).

Jackson and Broadway have interpreted the results of a Stern-Gerlach experiment with active nitrogen to indicate that the gas contained nitrogen atoms in a $^2P_{1/2}$ state (139,140). Jackson and Schiff have obtained qualitative indications of the presence of nitrogen atoms in active nitrogen

by analyses with a mass spectrometer (141,142).

Oldenberg has found nitrogen atom lines in very pure nitrogen in a low-pressure discharge, but not in air. He concluded that nitrogen atoms may be easily removed by impurities, such as oxygen (59).

Harteck studied the variation of the atom yield in relation to the pressure of nitrogen in the discharge. With pure nitrogen he could obtain nitrogen atoms only at pressures of one millimetre or less; however, if up to twenty millimetres of neon were added, he obtained almost complete dissociation of nitrogen molecules into atoms (143). In contrast, Herbert, Herzberg, and Mills reported that the amount of nitrogen in 2P or 2D metastable states was not greater than a minute fraction of the total gas present (144).

In 1926 Birge and Sponer suggested that a molecule of nitrogen could dissociate into two atoms, one of which was in its ground state, the other in an excited state (137). The emission of the afterglow bands was regarded as a secondary effect following the association of the active atomic species to form nitrogen molecules excited with sufficient energy to emit the yellow glow. Many workers have subsequently corroborated, modified, and improved this early theory of active nitrogen (42,58,99,109,110,112 to 114,122,133,138,145,146).

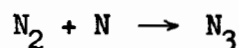
Cario and Kaplan in 1930 proposed metastable nitrogen atoms as a component of active nitrogen. The afterglow was presumed to arise from metastable molecules of nitrogen, excited by collisions of the second kind

with metastable nitrogen atoms (109,112). Other investigators have also concluded that metastable atoms are more actively involved in the behaviour of active nitrogen than are nitrogen molecules (70,99,113,114).

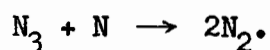
According to Debeau active nitrogen contains nitrogen atoms in 2D and 4S states which can combine to form a collision complex that may be stabilized by collision with a third body to the B state of the molecule N_2 , and give rise eventually to the afterglow emission by transition to the A state (147). Mitra has suggested that excited nitrogen atoms combined in a preassociative process which occurs more readily as the temperature is lowered (148).

Willey discussed the catalytically-accelerated decay of active nitrogen and its reactions with several gases. He concluded that there exists, in the afterglow, a statistical equilibrium among several types of active particles having energies centred about the 2 e.v. level. Subsequent work by other authors, however, does not lend support to Willey's theory (27,37,61,132,145 to 154).

The suggestion has also been made that active nitrogen owes its activity to the triatomic radical, N_3 (155 to 157). According to Trautz the fast reaction



is followed by the measurable, rate-controlling decay step



When the glow of active nitrogen is destroyed by heat, the remaining dark form is capable of exciting the D lines of sodium vapour,

and possesses an undiminished capacity for chemical reactivity. In subsequent reports, however, the correctness of such observations has been questioned (64,109,158).

Since it possesses significant electrical conductivity, active nitrogen has been considered by some authors to consist of charged particles (132,159). The failure of the afterglow to be affected by passage through an ion trap has, on the other hand, provided rather serious evidence against the existence of an ionic form of active nitrogen (13,15). Other views suggest that N_2^+ ions are required for the formation of active nitrogen or that there is in the gas one free electron for 2.3×10^8 molecules of N_2 (160 to 162).

The results of considerable research into the chemical behaviour of active nitrogen have been interpreted, in the major part, on the assumption that atomic nitrogen is the active species (92,163,164). A comprehensive review of pertinent facts has been presented by Evans and Winkler (165).

Chemical reactions of active nitrogen

Strutt discovered that most elements and compounds reacted with active nitrogen (2, 166). Na, K, Mg, I_2 , Hg, $SnCl_4$, HgI_2 , Cu_2Cl_2 , S, H_2S , CS_2 , $(CN)_2$, and As were excited to characteristic spectral emission, or formed compounds which, on alkaline hydrolysis, yielded ammonia. The assumption was made that nitrides might have been the original products. With CS_2 the products were a deep indigo deposit on the walls, which was insoluble in benzene, and a brown deposit on the cooled condenser. It

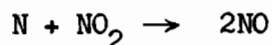
was suggested that the products were polymeric $(NS)_x$ and $(CS)_x$ respectively. $SnCl_4$ and $TiCl_4$ formed amounts of an unknown white substance.

Strutt obtained some peculiar results when he fed a stream of nitrogen, laden with phosphorus vapour, into glowing active nitrogen (136). The glow died out within a short distance after the introduction of the phosphorus. After a short, dark interval, a luminous region reappeared, characterized by a continuous spectrum, attributed to nitrogen and phosphorus. When the phosphorus jet was pushed further in the direction of flow, the whitish flame continued to appear, although less intensely. No further reference has been made to this experiment, and no attempts have been made to explain the phenomena observed.

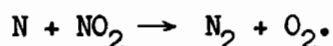
The formation of metal nitrides from the reaction of metals with active nitrogen has been found also by other investigators. Moldenhauer and Dorsam¹¹ have reported that the reaction with phosphorus leads to the formation of the compound PN (167).

Other reactions of active nitrogen with inorganic compounds have been investigated. Spectral effects have been reported for reactions with LiF , Li_2CO_3 , $BeCO_3$, BeO , $BaPt(CN)_4$, $MgCO_3$, $Ca(N_3)_2$, $Ba(N_3)_2$, molybdic acid, CuF , $CuCl_2$, $CuBr$, CuI , PbI_2 , $HgBr$, $UO_2(NO_3)_2$, ZnS , $BaCl_2$, $SrCl_2$, $CaCl_2$, $CaCl$, NaI , KI , Na_2CO_3 , $SrBr_2$ (54,168,169). The appearance of spectra of $CuCl$, $SnCl$, and $AuCl$ with, respectively, $CuCl_2$, $SnCl_4$, and $AuCl_3$, has been used to indicate the quantity of energy available in active nitrogen (170). In other experiments tubes lined with $NaCl$, $LiCl$, or KCl , after exposure to active nitrogen, turned first blue, then black; washed with water, these coatings yielded alkaline solutions (171).

Oxygen or nitric oxides, added to active nitrogen, cause the appearance of blue and shorter wavelength radiations. For the addition of either NO or NO₂ Spealman and Rodebush (172) have suggested the occurrence of two main reactions:



followed by a third, slower one,



An interesting observation was reported in 1934 for the interactions between active nitrogen and hydrogen halides (173). In the presence of water vapour HBr caused the appearance of a strong yellow-orange afterglow, and the products were solid NH₄Br and Br₂. With HI a strong blue flame was developed, while there was no glow below the inlet if HCl was added.

The chemical reactivity of active nitrogen with hydrogen has been studied in some detail (174 to 177). Ammonia is a main product only if both nitrogen and hydrogen are present in the reaction space in atomic form. Dixon and Steiner have shown that a third body is required by experiments in which increased yields of ammonia were obtained when the streams of gases met on a metal surface (178). If active nitrogen is reacted with molecular hydrogen, hydrazine is a main product.

Freeman (179) has studied the reaction of active nitrogen with both ammonia and hydrazine. The main products were nitrogen and hydrogen.

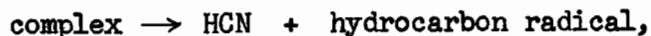
Wiles investigated the reaction of active nitrogen with phosphine,

and reported that the main product was an amorphous polymeric material, designated by the formula $(\text{PN})_x$ (180). The formation of molecular hydrogen in this experiment was ascribed to the recombination of NH radicals, following their formation by N-atom abstraction of H atoms from PH_3 .

Studies have been made of the reactions of active nitrogen with organic, as well as with inorganic compounds. Strutt investigated, for the first time, the reaction of hydrocarbons with active nitrogen (2,4,181). He believed that benzene yielded phenyl isocyanide, and found that chloroform and carbon tetrachloride both formed products which showed strong positive tests for the presence of cyanate; cyanide ion was determined using the volumetric method of Liebig. By bubbling the active gas through concentrated sulphuric acid containing dissolved indigo, the dye substance was decolorized, and from methane, n-pentane, and n-heptane, hydrogen cyanide was recovered as one of the main products. With acetylene Strutt noted that a characteristic lilac cyanogen flame appeared, and that tarry substances were among the products.

Winkler and his co-workers (182 to 192) have investigated several reactions between active nitrogen and hydrocarbons, using a fast flow system, with appropriate provision for trapping and analysing the products. In a comprehensive summary and discussion of the reactions studied, Freeman, Evans, and Winkler (193) have proposed a unified mechanism, in which it is assumed that the initial attack of a nitrogen atom on a hydrocarbon molecule leads to the formation of a nitrogen-hydrocarbon complex. The stability of the complex determines its lifetime and the subsequent reactions

which it undergoes. A short-lived complex may dissociate according to



while a more stable complex might react as follows,



The excited hydrocarbon molecule might subsequently dissociate into hydrogen atoms, hydrocarbon radicals, or unsaturated hydrocarbon molecules.

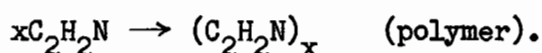
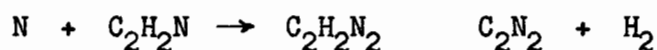
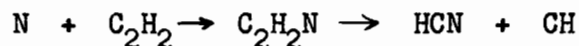
In all such reactions hydrogen cyanide is the main product, in yields which vary with the amount of active nitrogen available, and with the reaction temperature. The observed reaction flames are thought to originate from excited CN radicals or, perhaps, from the reaction of CH or CH₂ with nitrogen atoms.

Assuming both streamlined and turbulent gas flow through the reaction vessel, second order rate constants have been calculated for the production of hydrogen cyanide from active nitrogen and saturated hydrocarbons. Activation energies and steric factors of the reactions have been estimated from the temperature dependence of the rate constants.

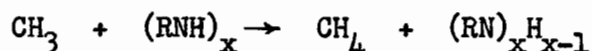
It has not been possible to obtain any values of the activation energies and steric factors for the reactions of active nitrogen with unsaturated hydrocarbons, since the rates are several times higher than for saturated hydrocarbons.

For the reaction of active nitrogen with acetylene, which is of particular interest in this work, Versteeg (186) found that the main product was HCN, that yields of C₂N₂ and CH₄ passed through maximal values as the flow rate of acetylene was increased, and proposed the following

mechanism:



Methane formation was explained by a combination of reactions which involved addition of molecular hydrogen or abstraction of atomic hydrogen from polymeric material:



The table on the following page lists the products obtained from the reactions of active nitrogen with pure hydrocarbons.

The reactions of all the alkyl chlorides yield hydrogen cyanide and hydrogen chloride as main products, and small amounts of cyanogen and a polymer that contains carbon, hydrogen, nitrogen and chlorine (194,195). All the chlorides, except methyl chloride, yield small amounts of C_2 hydrocarbons, while propyl chlorides also give small yields of C_3 hydrocarbons.

From the reaction of active nitrogen with methyl cyanide the main product is hydrogen cyanide (196). Smaller amounts of cyanogen, methane, ethane, ethylene, acetylene and (probably) methyl isonitrile are also produced.

Methylamine reacts with active nitrogen to yield hydrogen cyanide and a polymer, together with traces of cyanogen, methane, ethane, ethylene and acetylene (179).

Hydrocarbon	Products
CH_4	HCN
C_2H_6	HCN
C_3H_8	HCN, C_2H_2 , C_2H_4 , C_2H_6
n- C_4H_{10}	HCN, C_2H_2 , C_2H_4
iso- C_4H_{10}	(propylene)
neo- C_5H_{12}	HCN, C_2H_2 , C_2H_4 , C_3H_6 , C_3H_8
cyclo- C_3H_6	HCN, C_2H_2 , C_2H_4 , C_2H_6
cyclo- C_4H_8	HCN, C_2H_2 , C_2H_4
C_2H_2	HCN, C_2H_2 , CH_4 , H_2 , polymer
C_2H_4	HCN, C_2N_2 , CH_4 , C_2H_2 , C_2H_6
C_3H_6 (propylene)	HCN, C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8
1- C_4H_8	(propylene)
cis-2- C_4H_8	
iso- C_4H_8	
	HCN, CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_{10}

The purpose of the present work was twofold, firstly, to determine, if possible, why not more than half of the carbon atoms in acetylene are converted into hydrogen cyanide, and to obtain more information about the interactions of nitrogen atoms with acetylenic bonds. The second objective was approached by studying the reactions of methylacetylene and dimethylacetylene, where it was of particular interest to examine the effect of replacing the hydrogen atoms of acetylene successively by methyl groups.

EXPERIMENTAL

Reagents:

Dry-pumped nitrogen, 99.9% pure, was obtained from high-pressure cylinders (Canadian Liquid Air). Small residual amounts of oxygen and water vapour were removed, respectively, by passage of the gas over hot copper metal C, and through a liquid-air-cooled trap N (Fig. 1).

Acetylene was obtained from the Matheson Company. Methylacetylene and dimethylacetylene were both obtained through the courtesy of the Air Reduction Chemical Company.

The three reactant gases used were purified according to the procedure of Versteeg (186); each gas was passed successively through scrubbers containing water to remove acetone, calcium chloride to remove water, ascarite to remove carbon dioxide, and magnesium perchlorate to remove residual water. It was condensed in a liquid nitrogen cooled trap and recycled through the same purification train before being condensed into the large supply bulb.

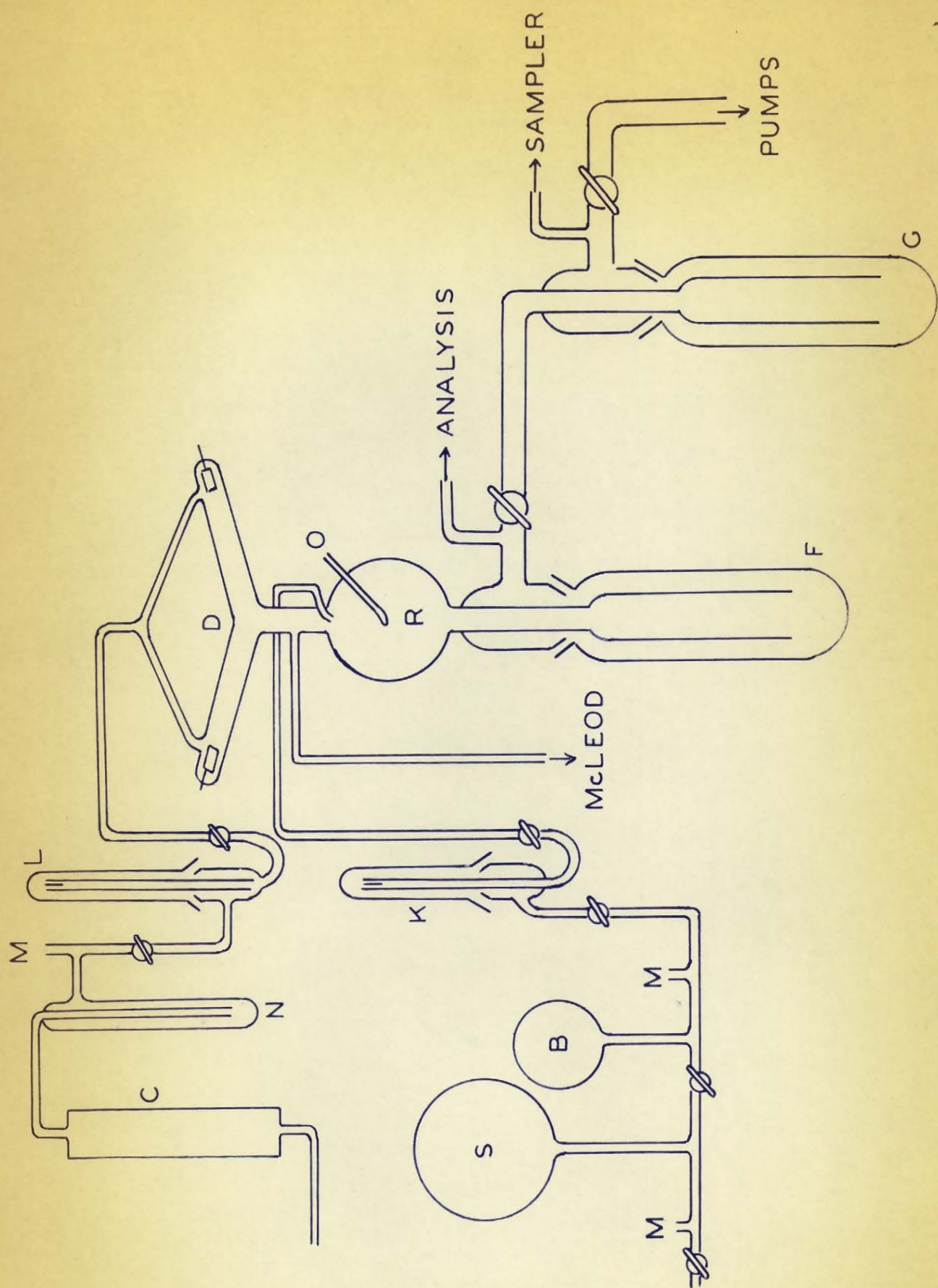
In all cases probably a little more than half of the gas originally fed in was eventually stored; the rest was rejected in the original and final fractions that might have contained more or less volatile impurities.

Apparatus:

Fig. 1 is a diagram of the flow system used in this investigation. A low pressure valve and needle valve, connected to a tank of nitrogen,

FIGURE 1

DIAGRAM OF APPARATUS



served to maintain a slight excess flow of the gas through a dibutyl phthalate bubbler to the heated (400-425°C) copper furnace, C. The head of dibutyl phthalate was adjustable so that a nitrogen feed pressure of 770 ± 1 mm., downstream of the furnace, could be obtained under all variations of atmospheric pressure. By such means a constant flow head, and constant flow rate of molecular nitrogen were assured.

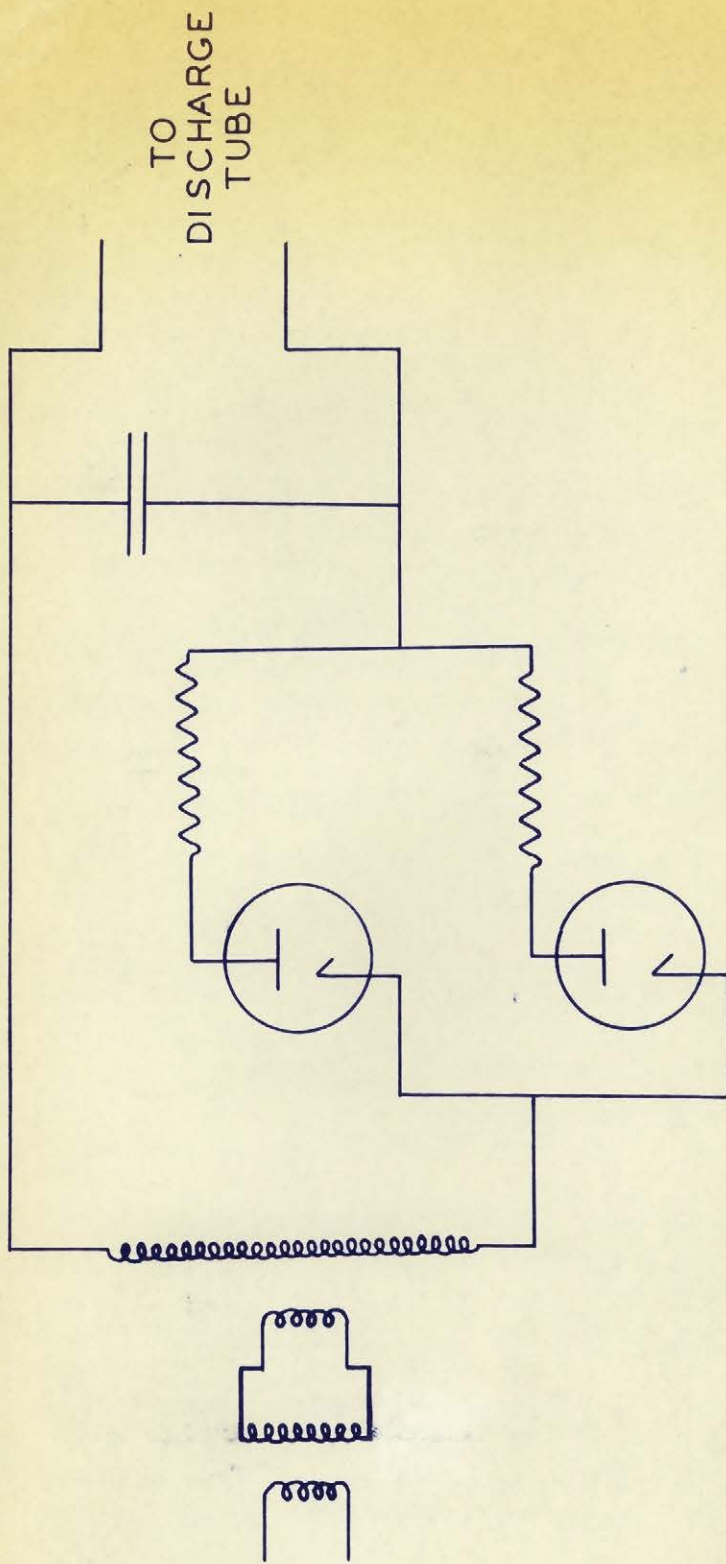
After passing the furnace C and the cold trap N, the nitrogen passed through a capillary flowmeter L into the two ends of the discharge tube D. The discharge tube was made of Pyrex glass 2.5 cm. in diameter, with high purity aluminum electrodes about 55 cm. apart, attached to tungsten leads which, in turn, were sealed through the Pyrex tube by sheathing pieces of Nonex glass. The discharge tube was bent into a V shape so that it could be cleaned and re-poisoned with a solution of phosphoric acid, without wetting the electrodes.

The nitrogen stream, emerging from the electrical discharge, flowed through a glass tube 16 mm. in diameter and 19 cm. long into the reaction chamber R. To R were also attached the thermocouple probe OR (chromel-alumel), the McLeod gauge, and the nozzle through which the reagent gas was introduced. After leaving the reaction chamber, the reacting gases passed into two traps, F and G, each of which was cooled with liquid nitrogen up to its ground glass joint.

Between the traps and the connection to the pumps are shown tubes labelled 'ANALYSIS' and 'SAMPLER'; to these were connected bulbs for condensing hydrogen cyanide or cyanogen, a Toepler pump for collection of 'non-condensables', and a LeRoy still for analysis of low-boiling, but

FIGURE 2

DIAGRAM OF ELECTRICAL CIRCUIT



condensable, products (mainly hydrocarbons).

The pumping system consisted of a Cenco Megavac pump and a Welsh Duoseal pump; these operated in parallel, and provided an adequate vacuum of less than five microns.

Fig. 2 indicates the nature of the electrical system used for the discharge tube. A variac, connected to the 110 volt alternating source, fed 40 V across its secondary winding to two parallel-connected 866A mercury rectifier tubes. The rectifier current flowed through a 5000 ohm resistor and was collected across the plates of a 4 μ fd. condenser. Under steady-state operating conditions the voltage across the condenser rose quickly enough for the discharge tube to fire about six times per second. At the end of each experiment the main power switch was turned off and the residual charge across the capacitor shorted by a manually-operated conductor connected to one of its terminals.

A five-litre flask was used to store the hydrocarbon gas. From this vessel the gas passed into a one-litre flask, entered a ballast bulb through a scratched stopcock, thence through a capillary flow meter into the reaction chamber R. During a reaction a manometer attached to the ballast volume was kept at a constant level by judicious adjustment of the scratched stopcock, and the amount of gas used was calculated from the pressure change in the one-litre supply vessel.

The flow meter for molecular nitrogen was calibrated by determining the rate of removal of the gas from a calibrated bulb, under reaction-like conditions, but without any reactant hydrocarbon. The rate of nitrogen flow was estimated to be 104 micromoles per second.

From the known volumes of the storage and ballast vessels used, the ambient temperature, and the initial and final manometer levels, it was possible to calculate, for each trial, the amount of reagent gas consumed.

When desired, the reaction vessel was cleaned with alkali (usually 5% NaOH, but on some occasions 7% NH_4OH). This treatment was followed by repeated rinsing with distilled water, re-poisoning with a 1% solution of phosphoric acid, and continuous evacuation at room temperature to hasten evaporation of water and leave a fresh film of metaphosphoric acid on the glass surface. A furnace, moulded from asbestos to surround the reaction vessel, was heated to 490°C for at least one hour after the poisoning procedure to remove traces of moisture.

Procedure for Experiments:

For an experiment the temperatures of the furnace C and the heating mantle around the reaction vessel were adjusted, and the power tubes for the discharge circuit were turned on to allow them to attain stable operation. The traps for receiving products and protecting the pump were cooled with liquid nitrogen, the nitrogen gas was allowed to pass through bubbler, furnace, trap and capillary into the discharge tube, and the discharge circuit was actuated with 40 V supplied from a variac. Manometers of the ballast and supply chambers were adjusted for the desired flow rate and gas consumption.

When the temperature within the reaction chamber had become constant, manometer readings were taken, and the reaction begun by simultaneously

opening the capillary stopcock with one hand and pressing an electric timer with the other.

During the course of a reaction from five to eight thermocouple readings were taken, the ballast pressure head was maintained at constant level by intermittent adjustment of the scratched stopcock, and monitory checks were made on the variac voltage. At least one McLeod gauge pressure measurement was also made, at about the mid-point of the experiment; in all properly-performed trials, regardless of reagent flow rate, this pressure was 1.43 mm. Experiments were usually of 200 seconds duration.

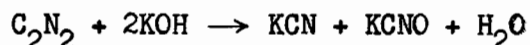
About ten seconds before the end of an experiment the scratched stopcock was closed completely. The reactant flow and the electric timer were then shut off at the same time to terminate the experiment, after which the discharge was disconnected and the nitrogen flow to the system was stopped. The pumps were allowed to operate on the system for about a minute longer. When the system was shut off from the pumps, the reaction products were distilled into a bulb containing an appropriate solution for analysis of HCN, or transferred to a LeRoy still for identification by distillation.

Analyses:

For analysis of HCN 10 ml. of approximately 1N NaOH solution was frozen in a wide glass bulb, attached to a ground glass joint following the cold traps. During the experiment this trap was kept cooled in liquid nitrogen and separated from the flow system by a closed stopcock. After the experiment, when the system had been closed off from the pump, the

stopcock was opened to allow transfer of HCN to the frozen NaOH solution, and liquid nitrogen was removed from the two main product traps. The first product trap was immersed for ten seconds in a cylinder of carbon tetrachloride, some of which froze to form a sheath around the trap and retard the evaporation of HCN. This procedure has been found in this laboratory to minimize polymerization of HCN during its transfer. After distillation was complete, the bulb containing NaOH was removed and carefully warmed by continuous shaking in hot water. When the solid melted the HCN dissolved with a minimum of polymerization, as indicated by virtual absence of discoloration in the solution. The top of the trap was then removed, and its cyanide content determined by the modified Liebig-Deniges method in use in this laboratory: 1.5 cc. of concentrated ammonium hydroxide was added to the solution, together with a few small crystals of potassium iodide, and the titration made with standardized AgNO_3 (0.05N) until the first permanent turbidity resulted.

Analyses for cyanogen were made using the method described by Forst (196). Condensable products were frozen in a detachable trap, on the surface of frozen, acidified silver nitrate. The trap was then connected to a train for analysis, and the frozen products allowed to evaporate and pass successively through a solution of silver nitrate, to trap any residual hydrogen cyanide, and two dilute solutions of potassium hydroxide, in which the following reaction quickly occurred:



The alkaline solutions were titrated, using the modified method of Liebig in use in this laboratory, and the amount of C_2N_2 present was calculated from the measured titration of AgNO_3 solution.

In a few initial trial experiments polymer was removed by drawing a dilute sodium hydroxide solution up into the reaction vessel. Since the polymer was insoluble in the alkaline solution, and the caustic impossible to remove except by a tedious process of dilution, sedimentation of polymer, and decantation of supernatant liquid, a search was made to find another reagent for use in removal of polymer. Solutions of ammonium hydroxide (2 M) were effective in loosening the coating of polymer sufficiently that it could be dislodged easily from the reaction vessel by means of a long-handled brush with bristles. The polymer was then dried by evaporating the aqueous ammoniacal solution.

Condensable products, other than hydrogen cyanide and cyanogen, were analysed with a LeRoy still (197). Condensable products, distilled and frozen into the evacuated still (through connections made to the tube marked 'ANALYSIS' in Fig. 1), were vapourized by slowly raising the temperature of the still. Co-ordinated readings of temperature and pressure were made at appropriate small intervals of temperature. The condensable products were identified, and their amounts determined, by comparing the results of each distillation with the vapour pressures of known compounds.

From the tube marked 'SAMPLER' a connection led to a Toepler pump of about 250 ml. capacity, which was used to compress samples of flowing gas, during an experiment, into small glass storage tubes. From mass-spectrometric analyses of the contents of such tubes the non-condensable products were identified and their amounts estimated.

RESULTS

Reaction of Active Nitrogen with Acetylene

For the reaction of active nitrogen with acetylene, the reaction flame appeared to be as described by Versteeg. The bright, somewhat reddish flame zone, at the smallest flow rates of acetylene, formed an approximately hemispherical cap at the exit of the hydrocarbon inlet. When the flow rate of acetylene passed through a small characteristic value (about one micromole/second), the flame zone shifted abruptly and appeared as a slightly curved, diffuse disc at the inlet for active nitrogen. With increasing flow rates of acetylene the zone continued to rise against the stream of active nitrogen, but was never more than one centimetre above the upper end of the reaction vessel.

In all reactions with acetylene only one flow rate of active nitrogen was used. The pressure in the reaction vessel was found to be constant at 1.43 mm. Hg over the whole range of flow rates.

The measured temperatures gradually increased with increase in acetylene flow rates, until a flat maximum was reached when about ten micromoles/second were fed into the reaction vessel. Thereafter a steady slow drop in temperature occurred, probably due to absorption of heat by the excess acetylene.

In agreement with Versteeg, hydrogen cyanide was found to be the main product for the reaction of active nitrogen with acetylene. The analytical data are recorded in Tables I and II, and shown graphically in Fig. 3. Several analyses were made for very low flow rates of acetylene

TABLE I
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH ACETYLENE

Temperature 190°C

C_2H_2 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>	Ratio $\frac{\text{HCN}}{\text{C}_2\text{H}_2}$
0.1894	0.0306	0.1616
0.296	0.0112	0.0378
1.393	0.1634	0.1172
1.738	0.452	0.260
1.808	0.260	0.1439
2.65	0.643	0.2425
4.58	1.992	0.435
6.89	3.315	0.481
11.0	4.57	0.415
14.70	4.65	0.316
25.85	5.16	0.1996
35.19	5.31	0.1510
44.9	5.75	0.1280

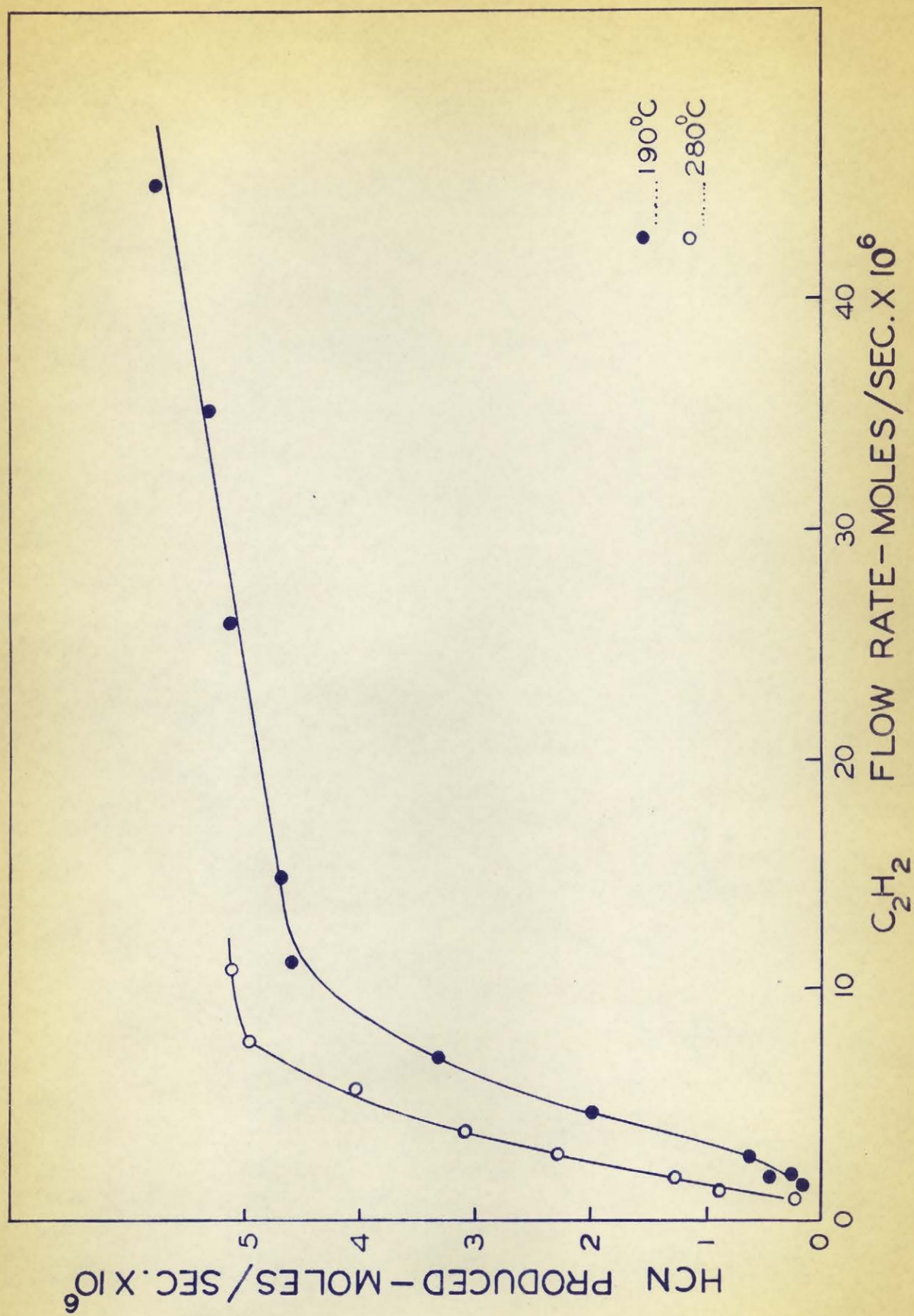
TABLE II
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH ACETYLENE

Temperature 280°C

C_2H_2 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
0.861	0.230
1.235	0.883
1.770	1.288
2.805	2.265
3.68	3.09
5.54	4.03
7.65	4.95
10.75	5.11

FIGURE 3

YIELDS OF HYDROGEN CYANIDE AS A FUNCTION
OF ACETYLENE FLOW RATE



and it is clear from Fig. 3 that the plot of HCN against C_2H_2 is not linear, as suggested by Versteeg, but definitely sigmoid. In Fig. 4 values of the ratio HCN/C_2H_2 are plotted against C_2H_2 to show that several points lie on a straight line. At high flow rates of acetylene the yields of HCN in the present series of experiments continued to rise almost linearly with increasing C_2H_2 , without attaining an obvious plateau, but the largest HCN yields were almost of the same magnitude as values at the plateau reported by Versteeg.

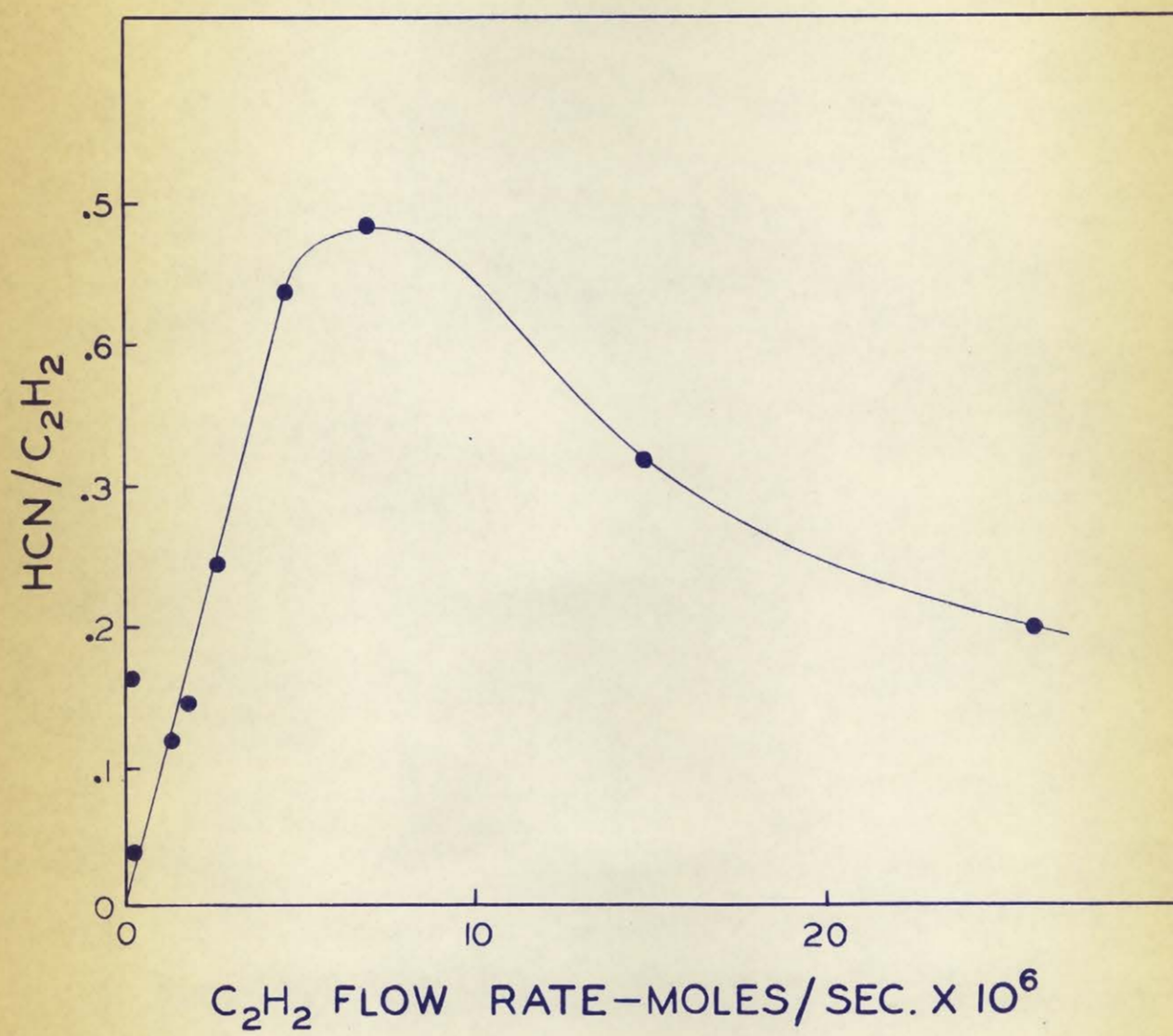
The yield of polymer produced by this reaction was determined for three flow rates of acetylene. The results are recorded in Table III. At very low flow rates of acetylene almost all the polymer was deposited in a uniform layer coating the upper half of the reaction vessel. As the flow rate of acetylene was increased, most of the polymer in the reaction vessel was formed in a dense cylindrical layer starting at the upper edge of the flame zone, while a considerable amount of polymer was also formed in the first cold trap. At large flow rates of acetylene approximately equal amounts of polymer were formed in the reaction vessel and the traps.

TABLE III
YIELDS OF POLYMER FROM THE REACTION OF ACTIVE
NITROGEN WITH ACETYLENE

T°C.	C_2H_2 flow <u>moles/sec. $\times 10^6$</u>	polymer <u>grams/sec. $\times 10^6$</u>
190	7.62	128
190	11.0	98
280	1.74	37

FIGURE 4

THE RATIO $\text{HCN}/\text{C}_2\text{H}_2$ AS A FUNCTION
OF ACETYLENE FLOW RATE



No attempt was made to separate polymer in the trap from that recovered from the reaction vessel. The recovered mixture was found to exhibit the physical and chemical characteristics attributed to it by Versteeg. In addition, the polymer samples were found to be insoluble in chloroform, carbon tetrachloride, carbon bisulphide, concentrated sulphuric acid, methanol, ethanol, pyridine, glacial acetic acid, acetonitrile, nitromethane and dimethylformamide. In a 50:50 (by volume) mixture of HNO_3 and H_2SO_4 the polymer dissolved after several hours' treatment, presumably because of oxidative degradation.

One sample of polymer was analyzed* chemically and found to consist of 67.73% carbon, 25.26% nitrogen, and 7.01% hydrogen. Although an exact comparison cannot be made with the results of Versteeg, who carried out analyses on separate samples of polymer from both traps and reaction vessel, it is to be noted that the percentage of nitrogen given above is almost the average of the values (16% and 32%) obtained by Versteeg, while the ratio of gram-atoms of carbon to gram-atoms of hydrogen is much more nearly unity than the value of 5:1 deduced by Versteeg from a hydrogen balance.

As pointed out by Versteeg, it would appear that, at low flow rates of acetylene, polymer is formed at the expense of other products of reaction, especially HCN. The data in Table III suggest, however, that polymer formation does not become independent of large acetylene flow rates, but, instead, decreases.

* Analyses of polymer samples, derived from acetylene and methylacetylene, were carried out through the courtesy of Dr. Leo Marion, Director, Division of Pure Chemistry, National Research Council of Canada.

Evidence was not found to confirm the suggestion of Versteeg that polymer-covered surface could effectively reduce the available amount of active nitrogen. The yield of HCN was found to rise continuously for values of acetylene flow rate almost twice as great as the largest used by him.

Analyses were not made for other products of the reaction, since the results of Versteeg for these would seem to be adequate (Table IV).

A few experiments, made at a higher temperature, yielded a steeper rise of hydrogen cyanide with acetylene flow rate than observed at the lower temperature (Table II, Fig. 3). However, the curve levelled out sharply at a value of HCN yield near to that obtained from the reaction at the lower temperature. Within the range of acetylene flow rates used, polymer production was less important at the higher than at the lower temperature.

Reaction of Active Nitrogen with Methylacetylene

The colour, contour, and location of the reaction flame with methylacetylene were similar to those for the flame with acetylene.

The pressure in the reaction vessel was also the same as that found in the corresponding reaction with acetylene, and did not change appreciably over the entire range of flow rates of methylacetylene.

In Tables V, VI, VII, and Fig. 5, are shown the yields of hydrogen cyanide, the main reaction product, at three temperatures. At low flow rates of methylacetylene, hydrogen cyanide formation was essentially

TABLE IV*

PRODUCTS OF ACETYLENE REACTION AT 167°C.

<u>C₂H₂ flow</u> <u>moles/sec. x 10⁶</u>	<u>HCN yield</u> <u>moles/sec. x 10⁶</u>	<u>C₂N₂ yield</u> <u>moles/sec. x 10⁷</u>	<u>CH₄ yield</u> <u>moles/sec. x 10⁷</u>	<u>free H₂</u> <u>moles/sec. x 10⁶</u>
1.23	-	0.104	-	-
5.18	3.23	2.69	18.2	negative
5.79	3.45	4.10	3.16	1.54
5.82	3.33	3.60	6.65	0.776
5.89	3.53	4.20	8.63	0.608
6.14	3.90	4.31	13.2	negative
8.98	4.38	4.25	5.62	1.55
9.63	4.82	5.23	8.89	0.998
14.2	5.00	4.50	4.47	2.22
19.5	5.41	2.89	5.21	1.90
26.0	5.30	2.76	4.39	2.28

*from reference 186

TABLE V
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH METHYLACETYLENE

Temperature 168°C

C_3H_4 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
0.056	0.061
0.256	0.041
0.841	0.598
1.053	0.339
1.239	1.436
2.10	3.09
3.47	4.86
6.14	7.54
13.60	8.74
29.0	10.00

TABLE VI
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH METHYLACETYLENE

Temperature 264°C

C_3H_4 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
1.023	1.680
3.83	7.08
8.80	9.94
19.52	10.35
32.3	10.54

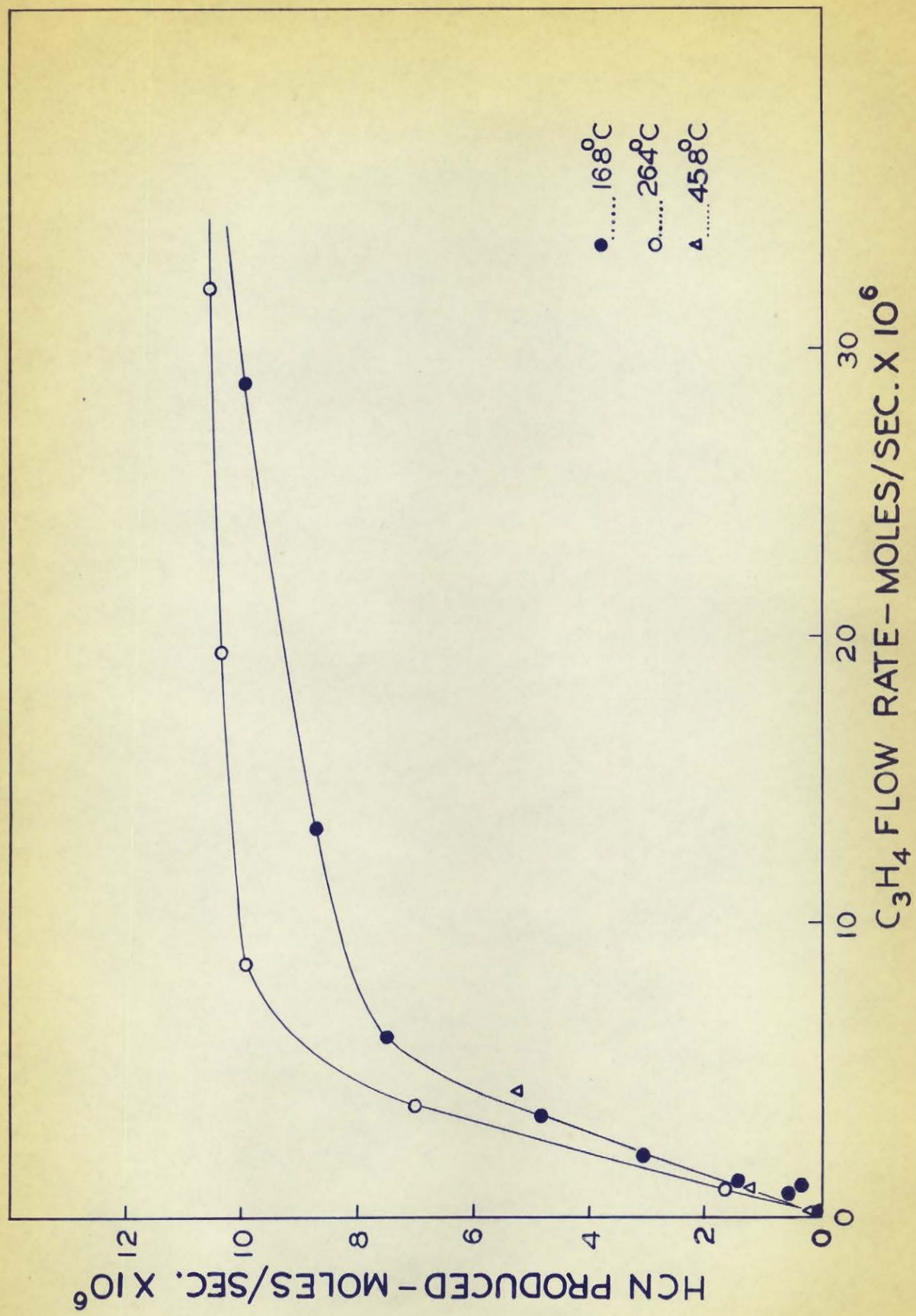
TABLE VII
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH METHYLACETYLENE

Temperature 458°C

C_3H_4 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
0.265	0.174
0.930	1.215
4.30	5.21

FIGURE 5

YIELDS OF HYDROGEN CYANIDE AS A FUNCTION
OF METHYLACETYLENE FLOW RATE



independent of temperature. At higher flow rates, at 168°C, the yield of hydrogen cyanide rose very slowly, and continued to rise within the range of flow rates used, while, at 264°C, the yield quickly reached a plateau.

Careful attention was given to the several experiments at low flow rates of hydrocarbon, since it was of particular interest to determine whether the curves of Fig. 5 showed appreciable curvature as they approached the origin. The results give little justification for assuming other than a linear dependence of HCN yield on flow rate in the low flow rate region.

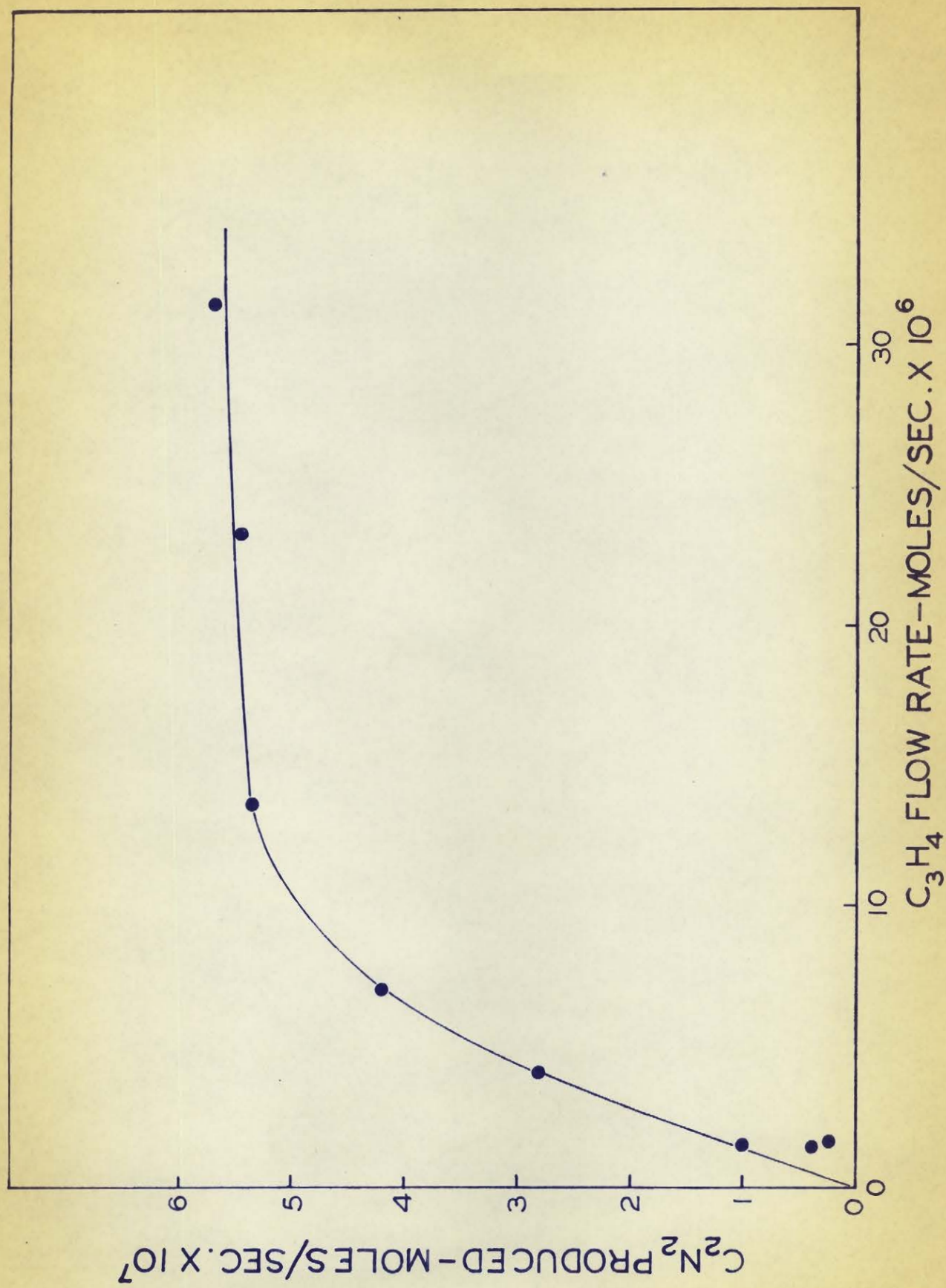
The results of analyses for cyanogen produced at 166°C are shown in Table VIII and Fig. 6. The yields of C_2N_2 rose steadily with increasing flow rate of methylacetylene up to flow rates of about 14 micromoles/second, beyond which they became practically constant.

TABLE VIII
YIELDS OF C_2N_2 FROM THE REACTION OF ACTIVE NITROGEN
WITH METHYLACETYLENE
Temperature 166°C

C_3H_4 flow <u>moles/sec. $\times 10^6$</u>	C_2N_2 yield <u>moles/sec. $\times 10^7$</u>
1.367	0.401
1.558	1.07
1.613	0.239
4.05	2.82
6.99	4.22
13.60	5.38
23.35	5.46
31.55	5.70

FIGURE 6

YIELDS OF CYANOGEN AS A FUNCTION OF
METHYLACETYLENE FLOW RATE



The polymer recovered from the reaction of methylacetylene was lighter brown in colour than the polymer derived from acetylene, and its yield was smaller. The amorphous product was deposited in both the reaction vessel and the first trap, and the data in Table IX indicate that the rate of its formation passed through a maximum value at an intermediate flow rate of methylacetylene.

TABLE IX
YIELDS OF POLYMER FROM THE REACTION OF
ACTIVE NITROGEN WITH METHYLACETYLENE

C_3H_4 flow <u>moles/sec. $\times 10^6$</u>	polymer <u>grams/sec. $\times 10^6$</u>	<u>% nitrogen</u>	<u>% carbon</u>
1.41	21.9	30.2	63.0
6.71	64.7	24.8	68.4
16.12	50.0	-	-

Solubility tests showed no difference between the polymer made from methylacetylene and that obtained from acetylene. The chemical analyses of two samples are given in Table IX.

The low-temperature still was used for the analysis of condensable hydrocarbon products. The results are shown in Table X. At the lowest flow rate of methylacetylene there appeared to be only traces of acetylene, ethylene, ethane, methylacetylene, and C_3 hydrocarbons. At the intermediate flow rate of the alkyne only ethane and propylene were obtained in significant amounts, while at the largest flow rate, in addition

TABLE X

HYDROCARBON PRODUCTS FROM THE REACTION OF
ACTIVE NITROGEN WITH METHYLACETYLENE

Flow rates of C_3H_4 (micromoles/sec. $\times 10^6$)			
	1.608	6.41	20.17
Product Yields (micromoles/sec. $\times 10^6$)			
C_2H_2	trace	trace	1.7×10^{-1}
C_2H_4	trace	trace	trace
C_2H_6	trace	trace	trace
C_3H_4	trace	trace	1.6
C_3H_6	trace	9.5×10^{-1}	3×10^{-1}
C_4H_8	trace	trace	8

to unconsumed methylacetylene, only C_3 and C_4 products were recovered in appreciable amounts. The vapour pressure values indicated that these were probably propylene (with possibly some 1-butene). A carbon balance for the highest flow rate of methylacetylene indicated 80% recovery. The small amount of polymer formed under these conditions may account for the deficit of carbon.

Mass spectrometric analyses* of samples of non-condensable products resulting from low, intermediate, and high flow rates of methylacetylene revealed no hydrogen or methane.

Reaction of Active Nitrogen with Dimethylacetylene

The flame accompanying the reaction of active nitrogen with dimethylacetylene was, in all respects, indistinguishable from those obtained with acetylene and methylacetylene. The pressure in the reaction vessel remained at the same value as for the reactions of the two other alkynes.

The yields of the main product, hydrogen cyanide, determined at three temperatures, are shown in Tables XI, XII, XIII and Fig. 7. For flow rates of dimethylacetylene smaller than 5 micromoles/second the HCN yields at the three temperatures were essentially the same. The relation between HCN yield and dimethylacetylene flow rate was practically linear from the origin up to flow rates of about 5 micromoles/second, beyond which yields levelled out in a plateau for the reaction at the lowest temperature, and

* These were carried out by Mr. G. Verbeke, with the kind permission of Dr. H.I. Schiff.

TABLE XI
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH DIMETHYLACETYLENE

Temperature 149°C

C_4H_6 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
0.085	0.144
0.207	0.214
0.404	0.836
0.501	1.452
0.621	1.906
0.632	2.090
0.652	1.802
0.684	2.27
0.845	2.635
1.945	4.09
2.985	7.26
4.31	9.42
5.01	8.57
5.34	10.06
7.00	10.38
8.98	10.40
11.80	10.95
16.70	10.64
19.60	10.84
20.30	10.88
28.7	10.16
55.6	11.22

TABLE XII
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH DIMETHYLACETYLENE

Temperature 321°C

C_4H_6 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
1.083	3.75
2.61	4.78
4.26	10.00
6.50	9.48
12.90	10.47
18.92	9.89
36.2	7.03

TABLE XIII
YIELDS OF HCN FROM THE REACTION OF ACTIVE NITROGEN
WITH DIMETHYLACETYLENE

Temperature 463°C

C_4H_6 flow <u>moles/sec. $\times 10^6$</u>	HCN yield <u>moles/sec. $\times 10^6$</u>
0.420	1.13
0.866	2.84
1.040	3.43
1.68	4.85
2.87	8.28
4.85	5.53
8.72	10.02
15.9	9.60
36.8	7.88

FIGURE 7

YIELDS OF HYDROGEN CYANIDE AS A FUNCTION
OF DIMETHYLACETYLENE FLOW RATE

decreased for the reactions at the two higher temperatures. The HCN yields determined at the highest flow rates of hydrocarbon were probably subject to considerable error, but the decrease with excess dimethylacetylene, at the higher temperatures, appeared to be real.

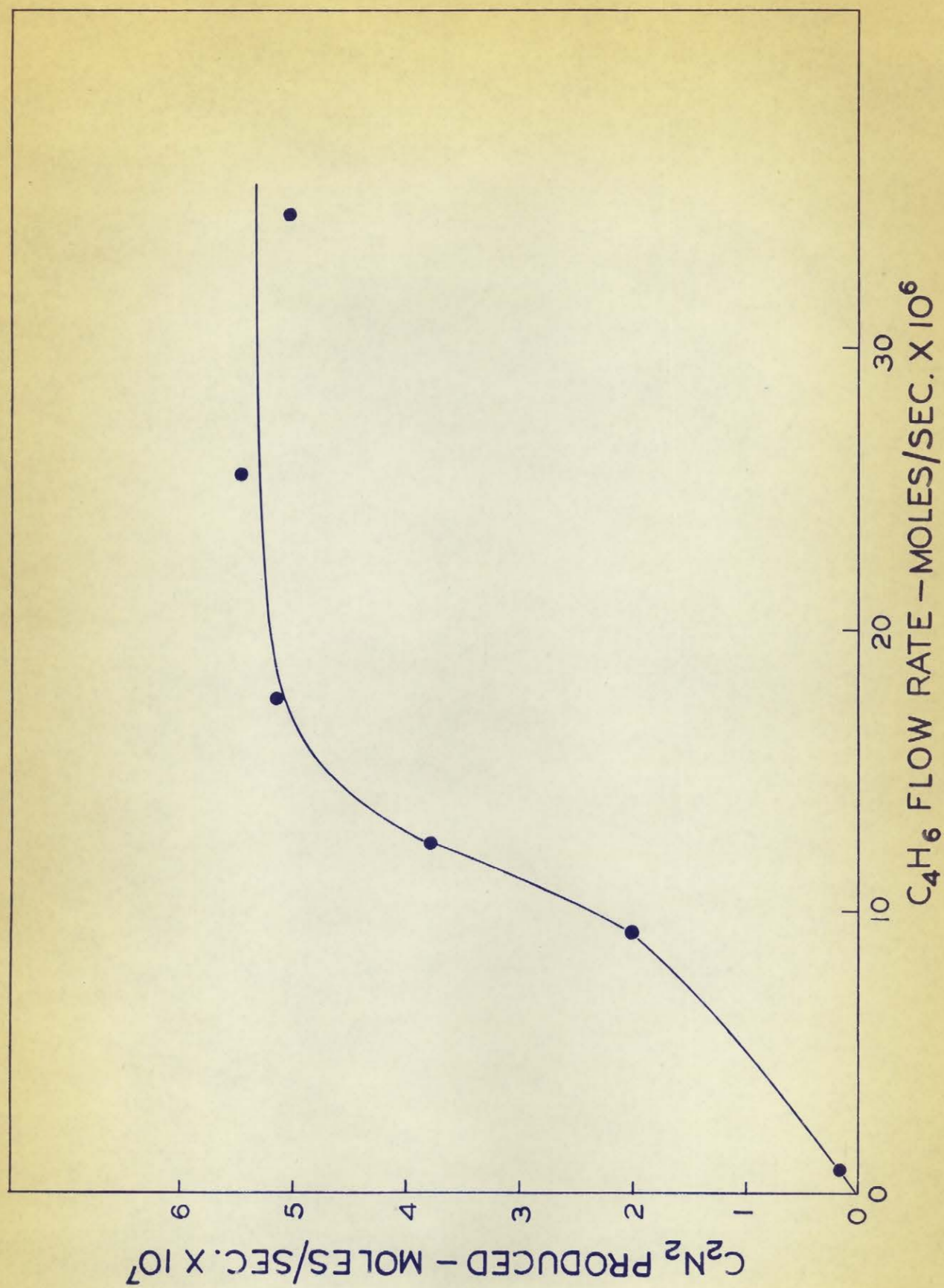
Analyses were made for cyanogen at temperatures in the neighbourhood of 169°C. The results are tabulated in Table XIV and plotted in Fig. 8. The yields of C_2N_2 increased more slowly with flow rate of hydrocarbon in the dimethylacetylene reaction than in the reaction with methylacetylene, at least in the low flow rate region. As the flow rate of dimethylacetylene was increased, production of cyanogen seemed to increase in rate until a maximum value was attained, after which a slow decrease in cyanogen production was indicated.

TABLE XIV
YIELDS OF C_2N_2 FROM THE REACTION OF ACTIVE
NITROGEN WITH DIMETHYLACETYLENE
Temperature . . . 169°C

C_4H_6 flow <u>moles/sec. $\times 10^6$</u>	C_2N_2 yield <u>moles/sec. $\times 10^7$</u>
0.827	0.15
9.20	2.00
12.43	3.78
17.53	5.16
25.5	5.48
34.7	5.02

FIGURE 8

YIELDS OF CYANOGEN AS A FUNCTION OF
DIMETHYLACETYLENE FLOW RATE



At all flow rates of dimethylacetylene, polymer production was so low that it was impracticable to obtain enough for analysis. At the end of a complete series of experiments a thin, narrow ridge of polymer remained at the entrance of the reaction vessel, and a thin, brown film of particles, almost microscopic in size, covered the lower portion of the first trap. There was no accumulation of amorphous solid, or of liquid, in the trap.

Condensable hydrocarbon products, identified by their vapour pressure in the low temperature still, were estimated for three flow rates of dimethylacetylene. The results of the analyses are recorded in Table XV. At the lowest flow rate of dimethylacetylene were found traces of mainly acetylene and ethane, while, with an intermediate flow rate, considerably more propylene was recovered, together with traces of acetylene, ethylene, and ethane. When the flow rate of reagent hydrocarbon was high the major products were C_3 and C_5 fractions, with smaller amounts of methane, acetylene, ethane and a trace of ethylene. Vapour pressure data indicated that the C_3 fraction might contain propylene, cyclopropane, and methylacetylene. The components of the C_5 fraction could not be identified separately.

Mass spectrometric analyses were made of non-condensable products corresponding to intermediate and high flow rates of dimethylacetylene. Methane was found only at the high flow rate of the reagent, as shown in Table XV. No molecular hydrogen was observed.

TABLE XV

HYDROCARBON PRODUCTS FROM THE REACTION OF
ACTIVE NITROGEN WITH DIMETHYLACETYLENE

Flow rates of C_4H_6 (micromoles/sec. $\times 10^6$)			
	1.053	5.96	19.90
Product Yields (micromoles/sec. $\times 10^6$)			
CH_4	trace	trace	2.5×10^{-1}
C_2H_2	trace	trace	1.83×10^{-1}
C_2H_4	trace	trace	trace
C_2H_6	trace	trace	8.4×10^{-2}
C_3H_6 (propylene)	trace	trace	2
C_3H_8	trace	trace	
C_5H_{10}	trace	trace	8
C_5H_{12}			

DISCUSSION

THE REACTION OF ACTIVE NITROGEN WITH ACETYLENE

It seems advisable to discuss the reaction of active nitrogen with acetylene before considering the similar reactions involving the other two alkynes. The study which has been made of the reaction with acetylene was intended to verify and extend, rather than dispute, the results which have been given by Versteeg (186). Using Versteeg's work as a basis, the present author hopes to clarify and amplify fact and theory concerning the reaction of active nitrogen with acetylene, and thereby to provide a sound basis for discussing the reactions with methylacetylene and dimethylacetylene.

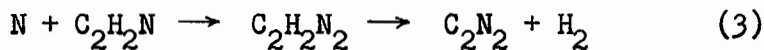
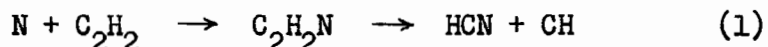
The reaction of acetylene stands in rather marked contrast with those of the two alkylated derivatives. The maximum yield of HCN was never more than half that which would correspond to maximum utilization of the available nitrogen. A satisfactory mechanism for the reaction must, of course, attempt to show the steps responsible for the formation of the main products, some of which (HCN, H_2) attain plateau values with increasing flow rate of hydrocarbon, while others pass through maximum values (C_2N_2 , CH_4). It should also indicate the part played by heterogeneous reactions, since surface reactions are probably important in polymer formation. The decrease of polymer yields with rising temperature, and the energetics of some of the intermediate reactions must also be considered.

In agreement with the assumptions made for several other recent

investigations of reactions involving active nitrogen (179 to 196), nitrogen atoms are postulated as the active species of nitrogen in the reaction being discussed.

Such atoms, in a $4S$ state, with three unpaired p electrons, should react very readily with the barrel-like sheath of four π orbitals which is conventionally assumed for the triple bond of acetylene.

The mechanism presented by Versteeg requires the following reactions:

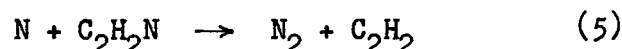


Some doubt about the validity of this suggested reaction mechanism must be entertained since the very important reaction (1) is not unequivocally exothermic, insofar as it depends strongly on a correct value of the heat of formation of the methynyl radical.*

If the heat of sublimation of graphite is more than six kcal./mole below the value of 170 kcal./mole, the primary reaction (1) would, in fact, be exothermic and acceptable. The limit on the yield of HCN may be explained

*Reaction (1) depends immediately on the heat of formation of CH, but this value is also strongly dependent on the heat of sublimation of carbon, which has not yet obtained universal acceptance at the value of 170 kcal./mole, which the majority of recent investigators support (198 to 206).

by assuming loss of active nitrogen by



and possibly consumption of active nitrogen by



(Recombination of N atoms in the presence of a third body may also occur.)

With increased flow rates of acetylene below the critical value, HCN formation rises faster than in direct proportion to the amount of reagent added, because N atoms are increasingly consumed by reaction (1) and the concentration of such atoms available for participation in reaction (5) is thereby reduced. The occurrence of reaction (6) in the presence of a third body, to remove a large portion of the energy which is evolved, would, of course, result in the production of stabilized HCN.

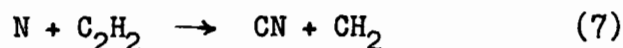
At large flow rates of acetylene the amount of HCN produced is limited by the amount of active nitrogen present. The competition between reactions (1) and (5), which consume $\text{C}_2\text{H}_2\text{N}$, determines the yield of HCN actually recovered.

Hydrogen, the second most important gaseous product recovered, is assumed to originate mainly from H atoms produced by reaction (6). Hydrogen atoms may recombine by the accepted three-body recombination process: H_2 may also be formed via intermediates formed from acetylene, by either of the mechanisms proposed by Geib and Steacie, and investigated by LeRoy (207 to 209).

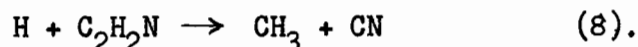
It is clear, by reference to the mechanism given here, that the amount of H_2 produced is limited by the concentration of N atoms, which

also determines the plateau yields of HCN.

There are reactions, other than (6), which might contribute to the production of CN radicals, but of these the only ones that seem probable are:

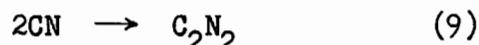


and

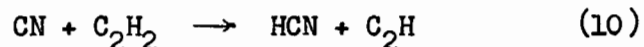


The extent of reaction (8), which is undoubtedly exothermic, must depend on the overlap of zones containing H atoms and $\text{C}_2\text{H}_2\text{N}$ complexes.

The most prominent reaction involving CN radicals is the formation of C_2N_2 . Little is known about the reaction



but its activation energy may be essentially zero (210). Data in Table IV and Fig. 9 show that for subcritical flow rates of acetylene the ratio $\text{C}_2\text{N}_2/\text{C}_2\text{H}_2$ appears to be essentially linear, but the range of flow rates used is too limited to specify with any precision the dependence of C_2N_2 on acetylene flow rate. For larger flow rates of acetylene C_2N_2 production drops and seems to level out. This behaviour may indicate that a reaction of CN with excess C_2H_2 , e.g.,

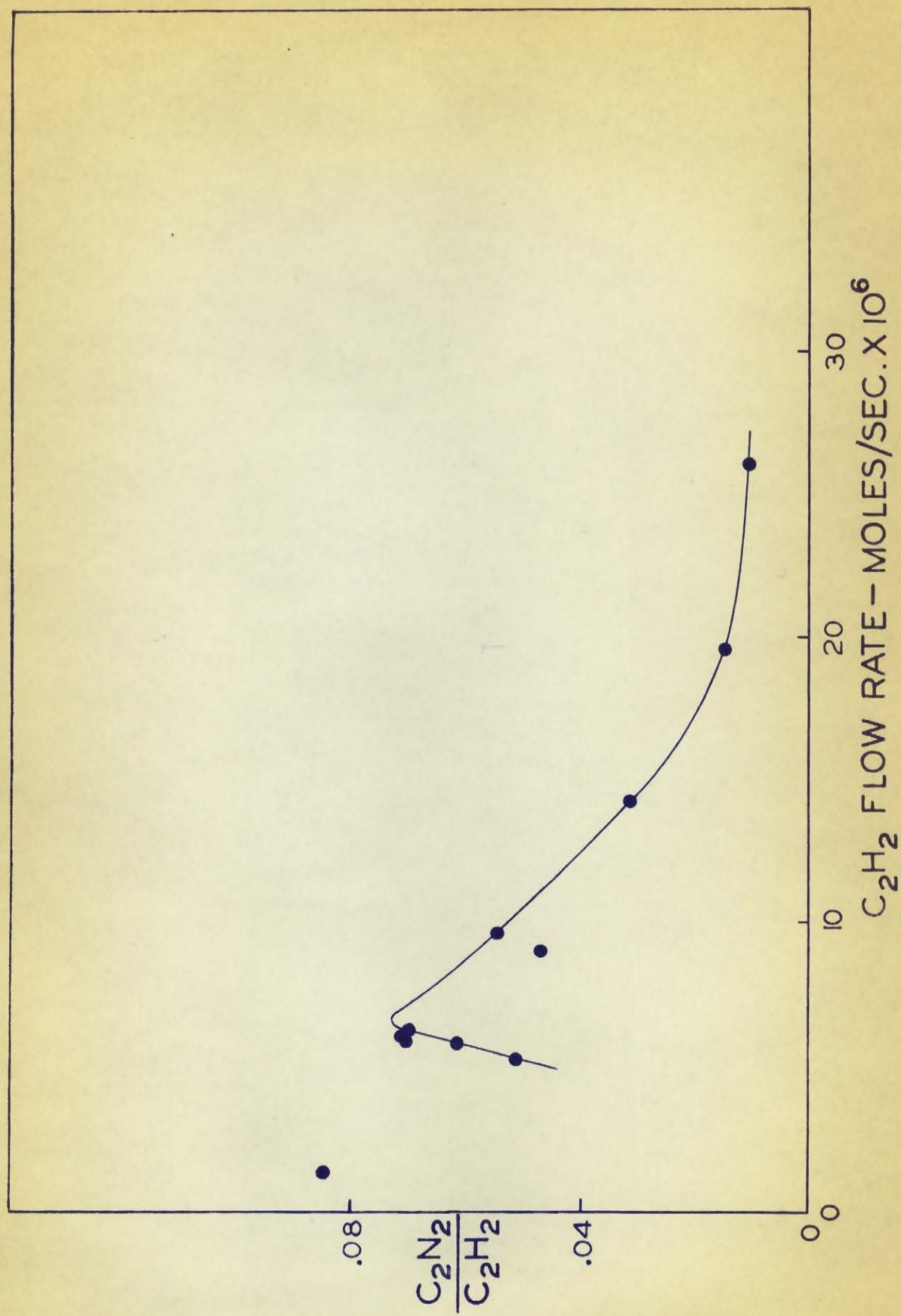


is beginning to compete successfully with reaction (9). The accompanying slow increase of HCN values may be attributable to reaction (10).

The production of C_2N_2 at high flow rates of acetylene may also drop because of the occurrence of reactions between CN radicals, or molecular cyanogen, and molecular or atomic hydrogen, respectively, to

FIGURE 9

THE RATIO C_2N_2/C_2H_2 AS A FUNCTION OF
ACETYLENE FLOW RATE



form HCN (210).

CN radicals or cyanogen may also be incorporated in polymer.

Methane may be derived from one-carbon radicals which are formed during the reaction. CH_x radicals have reaction (1) as their main source, but possible supplementary sources are



and reactions (7) and (8). In reaction (11), C_2H_2^* is assumed to be an electronically-excited product of reaction (5).

Reactions of CH_x with N atoms can occur, especially at subcritical flow rates of acetylene, under such conditions that not all available active nitrogen is consumed by reactions (1), (3), and (5) (182).

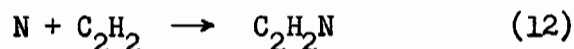
Hydrogenation of CH_x radicals by atomic hydrogen to yield methane as the ultimate product would be sufficiently exothermic that a third body might be required at each step (211).

The mechanisms and energies of activation for reactions of CH_x radicals with molecular hydrogen have not been, as yet, clearly determined (211). If such reactions do occur, the most likely products are CH_3 and CH_4 .

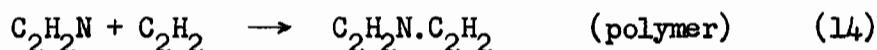
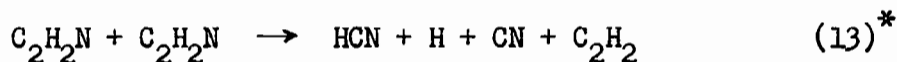
In view of the large number of reactions which may play a role in methane formation a quantitative formulation for the reactions in the flow system must be more complicated than the group of basic equations used in the mechanisms presented.

If, as seems highly probable (footnote, page 51), the energy of

sublimation of carbon is 170 kcal./mole, reaction (1) must be endothermic. An alternative mechanism can be suggested for the reaction of active nitrogen with acetylene which requires that the primary reaction be



and that the product, the complex $\text{C}_2\text{H}_2\text{N}$ be sufficiently stable to survive and undergo collisions and reactions with other reactive chemical species in the reaction zone. The other reactions required are reactions (5) and the following:



The greater-than-linear dependence of HCN yield on C_2H_2 flow is now explicable by the formation of HCN by the bimolecular process (13),** while the plateau yields are determined by the limited supply of available active nitrogen, as before, and its competitive consumption by reactions (5), (6), (7), (12).

The collision of two $\text{C}_2\text{H}_2\text{N}$ complexes may possibly lead, in some cases, to the formation of such radicals as CH, CH_2 , C_2H , C_2H_3 . Such species are likely present to only minor extents, and should quickly disappear to form the products of the reaction.

Reaction (13) is, in this scheme, the main source for H atoms and CN radicals. The reactions by which these species disappear, however, remain unaltered.

The discussion of the formation of CH_4 remains unaffected with

* See Appendix A

** See Appendix B

the use of the alternate reaction scheme.

In accordance with Versteeg, C_2H_2N complexes are assumed to diffuse to the wall of the reaction vessel and there polymerize to form surface polymer. At the wall C_2H_2N units can lose any excess energy which they may still retain from reaction (12), and can propagate the polymer network by as many as three centres of propagation. Such an explanation for polymer formation is consistent with its narrower and denser accumulation at the entrance of the reaction vessel at large flow rates of acetylene.

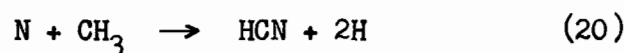
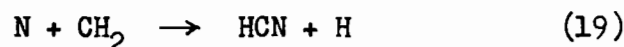
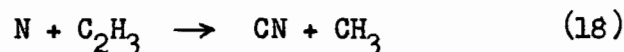
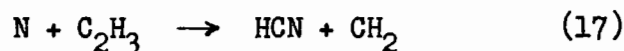
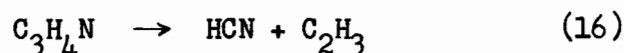
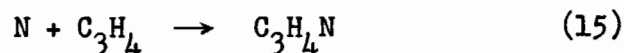
The polymer which is formed in the traps results, probably, from the occurrence of reaction (14) homogeneously. The species $C_2H_2N.C_2H_2$ might well exist long enough to reach the cold trap where loss of excess energy could result in rapid mutual polymerization, or polymerization with other molecules or reactive radicals, such as H, CH, CH_2 , CH_3 , and CN. The nitrogen content of such a polymer might be expected to be in the range observed by Versteeg (ca. 16%) for the material recovered from the traps, provided some CH_x fragments were added to the basic skeleton of $C_2H_2N.C_2H_2$.

THE REACTION OF ACTIVE NITROGEN WITH METHYLACETYLENE

From methylacetylene, as from acetylene, the main product is hydrogen cyanide. However, the yields of hydrogen cyanide obtained from methylacetylene do not exhibit a clear-cut induction relative to the flow rate of reagent, but rise almost linearly to a plateau region, which is almost twice as high as that found for acetylene (Figs. 3 and 5). The

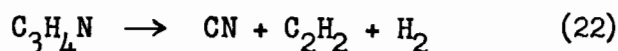
yield of hydrogen cyanide from methylacetylene, like that from acetylene, is appreciably sensitive to the temperature of reaction.

The following mechanism is suggested to explain the products formed in the reaction:



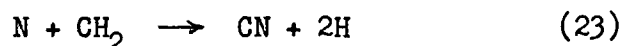
The product of reaction (15), $\text{C}_3\text{H}_4\text{N}$, is the three-carbon analogue of the acetylene complex, $\text{C}_2\text{H}_2\text{N}$, formed by reaction (1). The role of the methylacetylene complex must, however, be much less important than that of the acetylene complex, since the participation of $\text{C}_3\text{H}_4\text{N}$ complexes in reactions similar to reactions (5) and (13) would tend to emphasize a sigmoid dependence of HCN yield on flow rate of C_3H_4 , as well as to diminish the effective incorporation of N atoms into molecules of HCN. If the lifetime of $\text{C}_3\text{H}_4\text{N}$ were less than the time required for a collision (ca. 10^{-7} seconds), most $\text{C}_3\text{H}_4\text{N}$ complexes would disappear by reaction (16).

Other alternatives for reaction (16), namely, the reactions

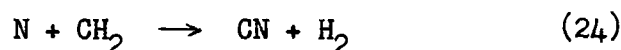


probably occur but to a lesser extent since the formation of C_2H_2 in large amounts should lead to recovery of more polymer than is experienced.

Considering that no molecular H_2 was recovered, reaction (17) may be more likely than reaction (18), since active nitrogen could release more hydrogen from its reaction with CH_3 than from its reaction with CH_2 , provided that the reactions



and



did not occur more readily than reaction (19).

H atoms, in the presence of hydrocarbon radicals and unsaturated hydrocarbons, should, of course, be consumed readily to form more fully hydrogenated products.

CN radicals are required for the formation of C_2N_2 , according to reaction (9), and could be supplied by reactions (18), (22), (23), and (24).

Table X shows that significant amounts of hydrocarbon products were recovered only at excess flow rates of methylacetylene. The failure to recover CH_4 from the reaction of methylene or methyl radicals with hydrogen may be explicable, at low C_3H_4 flow rates, by the consumption of the hydrocarbon radicals by reactions (19), (20), (23), and (24). With excess methylacetylene, CH_2 and CH_3 can disappear by addition to C_3H_4 to form C_4 hydrocarbons.

C_3H_6 was probably formed by the addition of hydrogen to excess

C_3H_4 . The small quantities of C_2H_2 which were found might have been formed according to reactions (21) and (22).

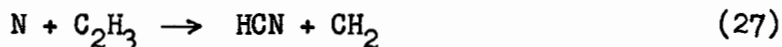
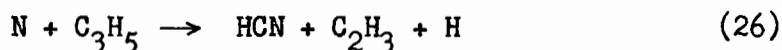
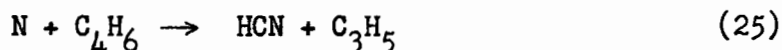
From Table IX it can be seen that the conversion of methylacetylene into polymer dropped steadily as the flow rate of methylacetylene was increased. Although more analyses might make possible a more detailed explanation of processes concerned with polymer formation, the conclusion is drawn from the present data that polymer here was formed from acetylene (cf. p. 57). Some polymer might also have been formed from C_3H_4N radicals which were sufficiently near to the wall of the reaction vessel to diffuse and be deposited there. The last-mentioned process might be especially important at low flow rates of methylacetylene, when the ratio, gram-atoms of hydrogen:gram-atoms of carbon, is the same as the ratio found in methylacetylene.

The failure to recover significant amounts of polymer from the reaction at higher temperatures is reflected in the increase in HCN yield. Since it does not seem plausible to explain the increased yield of HCN by assigning a greater activation energy to reactions (21), (22) than to reaction (16), it might be that this effect of temperature is due to a decrease in the stability, and hence the lifetime, of the complex C_2H_2N . In the reaction of active nitrogen with acetylene, the faster rise, at higher temperatures, of HCN yield with increasing C_2H_2 flow rate is not inconsistent with such an explanation.

THE REACTION OF ACTIVE NITROGEN WITH DIMETHYLACETYLENE

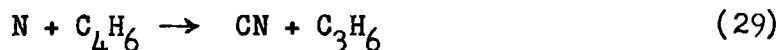
The salient observation for the reactions of active nitrogen with methyl- and dimethylacetylene is the similarity of HCN yields from the two reactions. As a function of increasing hydrocarbon flow rate, the yield of HCN rises for both reactions in the same way, without any clear-cut sigmoid inflection to maximal values which are essentially of the same magnitude (cf. Figs. 5 and 7).

For the reaction of dimethylacetylene with active nitrogen, more than three molecules of HCN are derived from one molecule of dimethylacetylene at very low flow rates of the reagent hydrocarbon (Table XI). By linear extrapolation it is easy to show a value of approximately four for the $\text{HCN}/\text{C}_4\text{H}_6$ ratio as the flow rate of dimethylacetylene approaches zero. The following reactions are proposed to explain the formation of products from the reaction:



With higher temperatures, the drop in HCN yield at large flow rates of dimethylacetylene might be due to loss of HCN by its addition to the considerable excess of C_4H_6 . (Such a product, presumably a nitrile, would have a vapour pressure similar to those of C_5 and C_6 hydrocarbons.)

The gradual rise of C_2N_2 yields up to rather large post-critical values of dimethylacetylene flow rates might mean that CN radicals are produced to an increasing extent by a reaction which is alternative to one of the early stages of reactions (25) to (28), e.g.,



The observed production of considerable amounts of C_3 hydrocarbon is not in disagreement with reaction (29). At high flow rates of dimethylacetylene, the fraction of available active nitrogen consumed by reactions (25) and (26) will be increased, as will be the yield of C_2N_2 derived from CN radicals formed by reaction (29).

CN radicals might also be derived from the occurrence of reactions (18), (23), (24).

Since hydrogen was not found by the mass-spectrometric analyses, it must be assumed that H and H_2 are consumed completely, probably in reactions involving hydrocarbon, and particularly unsaturated hydrocarbon species.

When excess dimethylacetylene is fed into the reaction vessel, the hydrocarbon radicals CH_2 , CH_3 , C_2H_3 , C_3H_5 must disappear by reactions not involving N atoms. CH_2 and CH_3 may react with H_2 , or with H atoms, which are present in the reaction space or are abstracted from C_4H_6 , to lead to the eventual formation of CH_4 (212). Traces of C_2H_2 probably result from the reaction of C_2H_3 with N atoms or with other C_2H_3 radicals (213).

The C_3 hydrocarbons which were recovered experimentally might have

been derived from the partial or complete hydrogenation of C_3H_5 . The sources of C_3H_5 for such reactions are reaction (25) and, possibly, two other exothermic reactions:



and



The C_5 hydrocarbons, recovered and identified tentatively from measurements of vapour pressure, were probably the products of the addition of CH_2 and CH_3 to C_4H_6 , or of C_2H_2 or C_2H_3 to C_3H_5 , followed by further saturation with atomic or molecular hydrogen.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The reaction of active nitrogen with acetylene has been reinvestigated. The low conversion of acetylene to hydrogen cyanide, found originally by Versteeg (186) has been verified.
2. The polymer, formed by the reaction of active nitrogen with acetylene, has been recovered and attempts have been made to characterize it. The physical and chemical properties of the polymer were consistent with the observations made by Versteeg.
3. If the heat of sublimation of carbon is as high as 170 kcal./mole, one of the main reactions proposed by Versteeg for the explanation of the reaction of active nitrogen with acetylene becomes thermodynamically endothermic. An alternative mechanism has been proposed, involving the participation of C_2H_2N complexes.
4. By working at very low flow rates of acetylene, the present author has found that the yield of hydrogen cyanide rises sigmoidally with increasing flow rate of acetylene. An explanation is suggested for this observation, involving the competitive interactions of C_2H_2N in reactions involving decomposition, polymerization, and effective recombination of nitrogen atoms.
5. The reaction of active nitrogen with methylacetylene has been investigated. Products which were recovered included hydrogen cyanide, cyanogen, polymer and condensable hydrocarbons.

6. From the reaction of active nitrogen with methylacetylene, the recovery of hydrogen cyanide did not show an inflection with increasing flow rate of hydrocarbon, but rose to a plateau yield which was approximately twice that recovered from the corresponding reaction of active nitrogen with acetylene. This higher recovery of hydrogen cyanide, together with a lower recovery of polymer, has been explained in terms of a greatly-decreased lifetime for the C_3H_4N complex. At a higher temperature the yields of hydrogen cyanide were generally higher.

7. At subcritical flow rates of methylacetylene essentially no hydrocarbons were recovered from the reaction of active nitrogen with methylacetylene. With post-critical flow rates of the alkyne appreciable amounts of unsaturated C_3 and C_4 hydrocarbons were recovered.

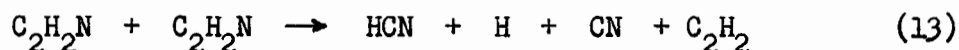
8. The products of the reactions of active nitrogen with dimethylacetylene have been collected and analyzed. Hydrogen cyanide, cyanogen, and condensable hydrocarbons have been recovered. Polymer was not present in significant amounts in the products. The mechanism proposed to explain this reaction is essentially an extension of the analogous mechanism for methylacetylene.

9. The yields of hydrogen cyanide from the reaction of active nitrogen with dimethylacetylene rose, without inflection, to essentially the same values as those obtained from the corresponding reaction with methylacetylene. At subcritical flow rates of hydrocarbons, yields of hydrogen cyanide from dimethylacetylene were less temperature-dependent than those from methylacetylene, and at post critical flow rates of dimethylacetylene yields of hydrogen cyanide were lower at higher temperatures.

10. Significant amounts of hydrocarbons were recovered only from the reaction of post-critical inputs of dimethylacetylene with active nitrogen. C_3 and C_5 hydrocarbons predominated, while C_2 hydrocarbons were much less pronounced.

APPENDIX A

Dr. J.L. Franklin, working at the National Bureau of Standards, U.S.A. (on leave from the Humble Oil Co.), has found, by mass spectrometric analyses, a species of mass 51 in the reaction products of N atoms with C_2H_2 .^{*} Dr. Franklin has suggested that this mass peak corresponds to the radical C_2HCN , formed by the reaction of CN radicals in the reaction mixture. Such an interpretation would tend to support the occurrence of reactions of the type suggested on page 56, i.e.,



It is interesting, however, that C_2HCN might be formed directly, by the reaction



The possibility of this reaction might serve to explain a long-standing difficulty in the mechanism of the N atom reaction with C_2H_2 , namely, the low conversion of C atoms from C_2H_2 into HCN, since the maximum HCN production corresponds to utilization of only about one half of the available nitrogen. The remaining N atoms might well enter the polymer through polymerization of the unsaturated species C_2HCN .

^{*}Private communication.

APPENDIX B

The straight-line portion of the plot of the ratio $\frac{\text{HCN}}{\text{C}_2\text{H}_2}$ against flow rate (Figure 4) can be explained quantitatively by using the alternative mechanism presented on p. 56.

For subcritical flow rates of C_2H_2 , the formation of HCN is assumed to be dependent on the interplay between formation of the complex $\text{C}_2\text{H}_2\text{N}$ (by reaction (12)) and its destruction by the competitive reactions (4), (13), (14). Under subcritical conditions the formation of HCN is limited by the pressure of C_2H_2 and given by

$$\begin{aligned} & (\text{Fraction of } \text{C}_2\text{H}_2\text{N} \text{ which forms HCN}) \times (\text{C}_2\text{H}_2) \\ &= \frac{\text{rate of reaction (13)}}{\text{sum of rates of reactions (4), (13), (14)}} \times (\text{C}_2\text{H}_2) \\ &= \frac{k_{13}K^2(\text{C}_2\text{H}_2)^2(\text{N})^2(\text{C}_2\text{H}_2)}{k_{13}K^2(\text{C}_2\text{H}_2)^2(\text{N})^2 + k_4K(\text{C}_2\text{H}_2)(\text{N}) + k_{14}K(\text{C}_2\text{H}_2)^2(\text{N})} \quad (32) \end{aligned}$$

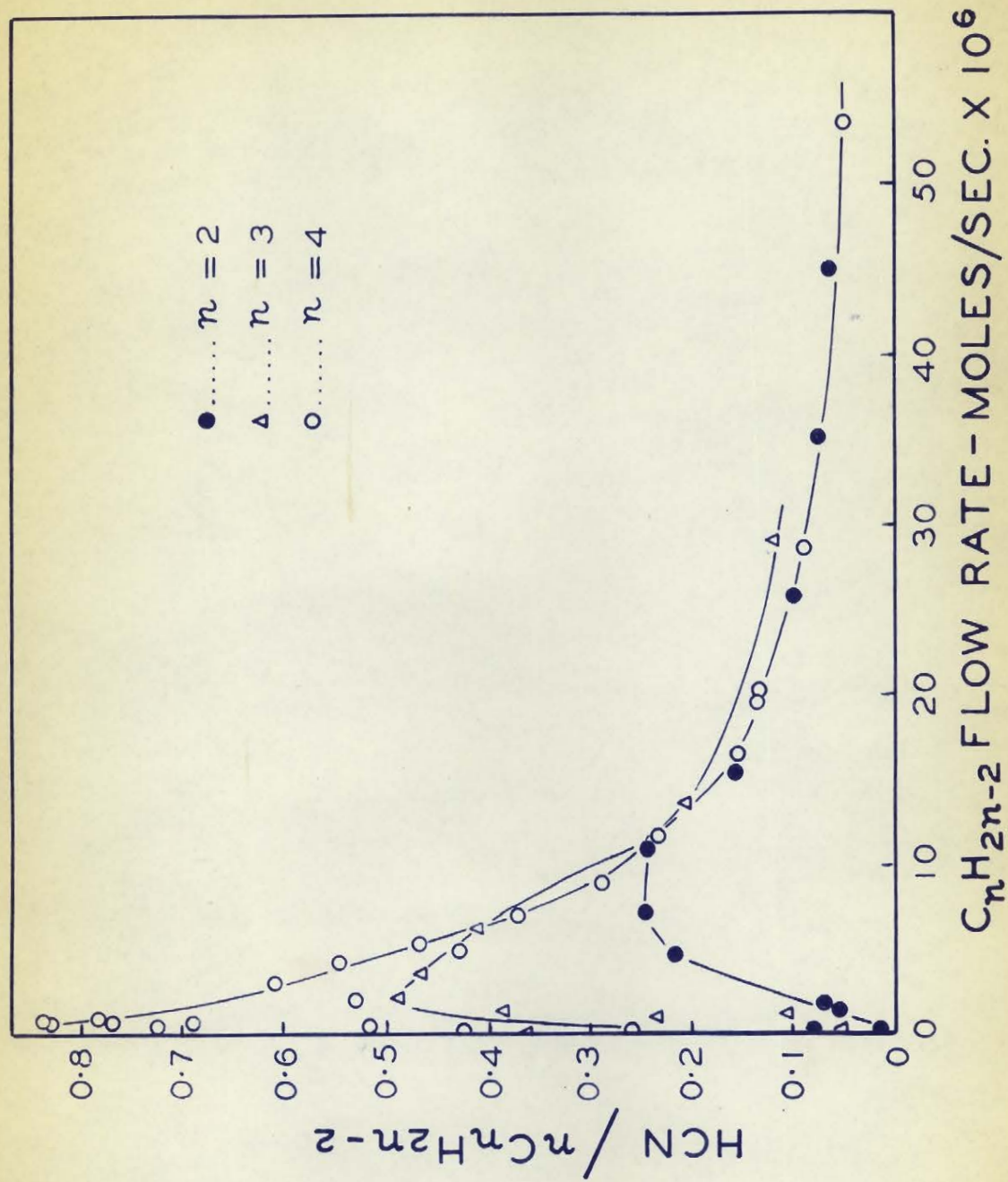
(Formation of $\text{C}_2\text{H}_2\text{N}$ is assumed to be very rapid and its concentration equal to $K(\text{C}_2\text{H}_2)(\text{N})$). At very low C_2H_2 input, polymer formation in the reaction vessel is very pronounced, and the middle term may well outweigh both of the other two terms in the denominator. With the retention of only the middle term, following division of expression (32) by (C_2H_2) , the ratio $\frac{\text{HCN}}{\text{C}_2\text{H}_2}$ can be shown to be proportional to (C_2H_2) .

At large post-critical flow rates of acetylene the rate of formation of hydrogen cyanide is determined by the finite concentration of nitrogen atoms present and is given by the expression

FIGURE 10

Plot of $\frac{\text{HCN}}{nC_{2n}H_{2n-2}}$

the fractional conversion of alkyne
into hydrogen cyanide,
as a function of $C_{2n}H_{2n-2}$ input.



(fraction of C_2H_2N which forms HCN) X (N atom concentration)

By setting up an equation based on this expression, analogous to equation (32), and by assuming that all N atoms form C_2H_2N , the rate of production of hydrogen cyanide can be shown to approach a plateau value.

Similar derivations can be made for the reactions of methylacetylene and of dimethylacetylene. It is, however, of interest to note that plots of the fractional yield of hydrogen cyanide/mole of hydrocarbon (cf. Fig. 10) do not show a clear-cut unambiguously linear portion at very low inputs of alkyne, as does the curve for $\frac{HCN}{2C_2H_2}$. This observation, together with the lack of inflexions in Figures 5 and 7, is explained by attributing much smaller lifetimes to the complexes C_3H_4N and C_4H_6N than to C_2H_2N .

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