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AN INVESTIGATION OF SOME REACTIONS OF ACTIVE NITROGEN

David R. Safrany

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AN INVESTIGATION OF SOME REACTIONS OF ACTIVE NITROGEN

by

David R. Safrany

A Thesis Submitted to the Faculty
of the Department of Chemistry
in Partial Fulfillment of the
Requirements for the Degree of
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Member

Member

Member

Member

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ABSTRACT

/ [redacted]

The reactions of active nitrogen have been studied in a fast-flow, low-pressure system using a mass spectrometer whose leak was located directly downstream from the reaction zone. Reactions of metastable $N_2(A^3\Sigma_u^+)$ molecules, produced by means of surface catalyzed excitation, were also studied.

The results of the excited molecule experiments indicated that, in general, $N_2(A^3\Sigma_u^+)$ molecules do not play a major role in the reactions of active nitrogen with inorganic and organic substances such as: O_2, O_3, N_2O, C_2H_2 and C_2H_4.

The reactions of N-atoms with hydrocarbons were studied along the lines of previous workers. It was found that, contrary to earlier work, HCN is not the only major nitrogen-containing product formed, but N_2 is also a substantial product. Under certain conditions, NH_3 and CH_3CN can also be major products. Ammonia added to the flame zone of the C_2H_2-active nitrogen reaction was found to react with CH radicals formed, yielding HCN.

In general, the following observations were made: [redacted]

(1) Alkanes, especially CH_4 and C_2H_6, react slowly with active nitrogen at room temperatures; the higher the alkane the greater the reaction rate;

(2) alkenes react much faster than alkanes, but slower than acetylene;

(3) some alkanes with weakly bound hydrogen atoms, <u>viz</u>, isobutane, react as rapidly as alkenes giving NH_3, as well as HCN, as a major product under conditions where complete consumption of N-atoms occurs;

(4) addition of HCl to the alkane reactions catalyzes the overall reaction and the rate then equals that of alkenes;

(5) under optimum conditions, greater conversion of N-atoms to HCN, as measured by NO titration, can be obtained from CH_4 than with any other hydrocarbon.

From these results a general degradation mechanism is proposed involving the attack of the hydrocarbon, in general, by a radical other than the N-atom as the initial step. The N-atoms rapidly attack the primary products producing new radicals and both HCN and N_2. The radicals then attack the hydrocarbons and the reaction proceeds, in many cases, over a chain-branching scheme.

This proposed reaction scheme, applied to C_2H_4 for demonstrative purposes, is as follows:

$H + C_2H_4 \rightarrow C_2H_3 + H_2$

$C_2H_3 + N \rightarrow NH + C_2H_2$

$NH \rightarrow NH_3$, or decomposed

$C_2H_2 + N \rightarrow CH\text{-}CN + H$ <u>initiation</u>

$\searrow HCN + CH$

$CH\text{-}CN + N \rightarrow HCN + CN$

$CN + N \rightarrow N_2 + C$

$C + C_2H_4 \rightarrow C_2H_2 + CH_2$

$CH_2 + N \rightarrow HCN + H$

$C_2H_2 + N \rightarrow CH\text{-}CN + H$ <u>propagation</u>

$CH\text{-}CN + N \rightarrow HCN + CN$

$CN + N \rightarrow N_2 + C$

Other reaction mechanisms involving similar parallel reactions have been considered but the above scheme seems most plausible to explain the observed results.

PART I

INTRODUCTION

A. Excited Molecules

1. Discovery of Surface Catalyzed Excitation (SCE) in this Laboratory

Since the early 1950's this laboratory has pursued a program of research devoted to understanding reactions of fundamental importance to processes that occur in the upper atmosphere. These investigations have dealt primarily with the photo- and radiation-chemistry of nitrogen and oxygen, and the reactions of nitrogen and oxygen atoms produced by discharge tube methods.

Rather recently (1959)(1) it was observed for the first time that metallic cobalt or nickel gave a red halo-like glow when exposed to mixtures of nitrogen and oxygen atoms at about 1 mm Hg pressure. Subsequent investigations found that many other metals gave glows similar to that obtained with Co or Ni and that the effect was a fairly general one; a very interesting luminosity was observed over a piece of Ni in a system that contained only O-atoms and O_2 molecules(2).

Spectroscopic analysis of the glows over Co and Ni in the mixed atom streams showed the presence of both the NO β- and the N_2 first positive-band systems, while the luminosity in the oxygen system was identified as the forbidden Herzberg band system. With appropriate filters it could be seen that the red N_2 first positive glow extended several cm from the surface of the metal while the blue NO β- and Herzberg-glows extended only a few mm from the surface. The glows were unaffected by magnetic fields and persisted after the discharges were turned off (until the atoms were pumped out of the system).

2. Mechanism Proposed for SCE

The N_2 first positive emission shows an extremely interesting anomalous intensity distribution of the vibrational bands; gas phase recombination of N-atoms gives rise primarily to the $v' = 12, 11, 10 \rightarrow v'' = 8, 7, 6$ transitions (discussed later in detail), while surface catalyzed recombination to the first positive level gives the strongest bands at $v' = 8, 7, 6 \rightarrow v'' = 4, 3, 2$. The following mechanism has been proposed$^{(1)}$ to explain this behavior: two N-atoms combine directly on the Co surface to give an $N_2(A^3\Sigma_u^+)$ molecule directly, in high ($v > 8$) vibrational levels:

$$N(^4S) + N(^4S) \xrightarrow{Co} \underset{v\,=\,\text{High}\,>\,8}{N_2(A^3\Sigma_u^+)} \quad ; \tag{1}$$

these molecules then diffuse into the gas phase and, through collisions, relax vibrationally to the crossing point of the $A^3\Sigma_u^+$ and the $B^3\Pi_g$ electronic level curves (see Fig. 1). Since a triplet-triplet crossing is involved, the probability for a radiationless transition is high and crossing occurs; this crossing is near the $v = 8$ level for the $B^3\Pi_g$ state, and radiation emitted should have primarily this amount of energy. This mechanism can be summarized as follows:

$$\underset{v\,=\,\text{high}}{N_2(A^3\Sigma_u^+)} + \text{collisions} \rightarrow \underset{v\,=\,\text{crossing region}}{N_2(A^3\Sigma_u^+)} \tag{2}$$

$$\underset{v\,=\,\text{crossing region}}{N_2(A^3\Sigma_u^+)} \rightarrow \underset{v\,=\,8,\,7,\,----}{N_2(B^3\Pi_g)} \tag{3}$$

$$\underset{v'\,=\,8,\,7,\,--}{N_2(B^3\Pi_g)} \rightarrow \underset{v''\,=\,4,\,3,\,----}{N_2(A^3\Sigma_u^+)} + h\nu \text{ (first positive system)} \quad . \tag{4}$$

3. SCE as a Tool for Study of Excited Molecules

Since the $N_2(A^3\Sigma_u^+)$ molecules diffused several cm into the gas phase, consistent with published values of their radiative lifetime(3), it might be possible to produce a stream of $N_2(A^3\Sigma_u^+)$ molecules free from N-atoms and to study the reactions of these highly excited molecules.

Calculations indicated that it should be possible to produce a jet of $N_2(A^3\Sigma_u^+)$ molecules if a sufficiently fast pumping system were employed, and early experiments confirmed this view. This unique jet of $N_2(A^3\Sigma_u^+)$ molecules made possible the first studies of excited N_2 molecules free from N-atoms; as far as is known there has been no study of this type to date.

B. Nitrogen Atoms

In the course of the investigation it became obvious that a thorough understanding of N-atom reactions is necessary in any study of excited nitrogen molecules. In addition, since O-atoms were necessary for the catalysis of excited molecules, it was important to know their effect on the reactions of active nitrogen with hydrocarbons; many interesting findings resulted from this investigation.

1. "Active" Nitrogen

When nitrogen is subjected to a strong momentary electrical discharge at low pressures (~ 1 mm Hg), a long-lived yellow luminescence is observed. In a flow system with a continuous discharge, this yellow emission can be observed downstream from this discharge and is called the Lewis-Rayleigh afterglow or simply the nitrogen afterglow. Under suitable conditions the luminescence can be made to persist for several hours(4).

It is known that the intensity of the afterglow is proportional to the square of the N-atom concentration(5) suggesting that the afterglow is a result of recombination of N-atoms. The intensity is found experimentally, by rapidly expanding the glowing gas, to vary inversely with the third power of the volume(5), suggesting a three-body recombination. The temperature dependence of the afterglow intensity has a negative coefficient, i.e., varies inversely with the temperature and is proportional to $T^{-0.64}$ (5).

The spectrum of the afterglow is complicated but the main feature is the N_2 first positive band system with strongest transitions from the $v' = 12, 11, 10 \rightarrow v'' = 8, 7, 6$ vibrational bands. It should be kept in mind that the spectrum of the discharge tube is different from that of the afterglow since the kinetic origins of the excited species responsible for light emission are different, i.e., excited molecules are formed directly in the discharge; the second positive band system ($C^3\Pi_u \rightarrow B^3\Pi_g$) is observed very strongly, while the afterglow is due to recombination of N-atoms.

2. Theories Proposed for Active Nitrogen

Many theories have been proposed to explain the properties of active nitrogen and the reactive species have included ground state $N(^4S)$ atoms(6), electronically excited molecules(7), ions(8), excited $N(^2P)$ atoms(9) and vibrationally excited $N_2(X^1\Sigma_g^+)$ ground state molecules(10) as the active species. Most of these theories involve a 3-body recombination of some sort to account for the long lifetime of the afterglow.

At present, the most widely accepted theory for the afterglow mechanism is that which was first proposed by Gaydon(11), and later expanded by Berkowitz, Chupka and Kistiakowsky(12). This theory suggests that ground-state nitrogen atoms can recombine along the $N_2(^5\Sigma_g^+)$ potential curve (refer to Fig. 1) in a 3-body collision and are practically in equilibrium with the loosely bound $N_2(^5\Sigma_g^+)$ molecules. The $^5\Sigma_g^+$ state is a metastable one and has no potential minimum or at best a very slight one. The $^5\Sigma_g^+$ curve crosses the $B^3\Pi_g$ curve at the v = 12 vibrational level and an inverse predissociation can occur; population of these levels near the crossing point leads to the observed strong

$$v' = 12,11,10, - - - - \rightarrow v'' = 8,7,6, - - - \text{ transitions.}$$

This behavior can be summarized by the following equations:

$$N(^4S) + N(^4S) + M \rightleftarrows N_2(^5\Sigma_g^+) + M \qquad (5)$$

$$\underset{\text{crossing region}}{N_2(^5\Sigma_g^+)} \rightarrow \underset{v = 12,\ 11,\ 10 - - -}{N_2(B^3\Pi_g)} \qquad (6)$$

$$\underset{v' = 12,11,10 - - -}{N_2(B^3\Pi_g)} \rightarrow \underset{v'' = 8,7,6 - - - -}{N_2(A^3\Sigma_u^+)} + h\nu \text{ (first positive system)} \qquad (7)$$

The highly complex nature of active nitrogen has made it difficult for any one theory to account for all of the observed phenomena associated with active nitrogen. One of the notable inadequacies of most of these theories is the inability to explain emission from the v' = 8, 6 vibrational levels found in the afterglow spectrum. The observance of enhanced emission from these levels, in the surface catalyzed formation of $N_2(A^3\Sigma_u^+)$, has suggested that emission from these lower levels of the $B^3\Pi_g$ state in the afterglow may possibly be due to recombination of N-atoms directly into the $A^3\Sigma_u^+$ state, probably in the gas phase but also possibly at the vessel walls(13,14).

3. Reactions of Active Nitrogen with Inorganic Substances

The reactions of active nitrogen with inorganic substances can be characterized as either fast, or slow.

Typically fast reactions are:

$$N + NO \rightarrow N_2 + O \quad ; \quad k = 2.2 \times 10^{-11} \ ^{(15)} \quad (cm^3/particle)/sec.$$

$$N + O_3 \rightarrow NO + O_2 \quad ; \quad k = 5.7 \times 10^{-13} \ ^{(16)} \quad "$$

$$N + NO_2 \begin{array}{l} \nearrow NO + NO \quad ; \quad k = 5 \times 10^{-13} \\ \rightarrow N_2O + O \quad ; \quad k = 3 \times 10^{-13} \ ^{(16,17,18)} \quad " \\ \searrow N_2 + 2O \quad ; \quad k = 2 \times 10^{-13} \end{array}$$

Typically slow reactions (including recombination) are:

$$N + O_2 \rightarrow NO + O \quad ; \quad k = 1 \times 10^{-16} \ ^{(18)} \quad "$$

$$N + O + M \rightarrow NO + M \; ; \quad k = 5 \times 10^{-33} \ ^{(19)} \quad (cm^3/particle)^2/sec.$$

$$N + N + M \rightarrow N_2 + M \; ; \quad k = 0.74 \times 10^{-32} \ ^{(20)} \quad "$$

4. Reaction of Active Nitrogen with Organic Substances

The reactions of active nitrogen with organic substances have been investigated thoroughly by Winkler and co-workers(21) who found that, generally, HCN was the major product of the reactions. The reactions at room temperature are very fast with unsaturated hydrocarbons while most alkanes react much more slowly or practically not at all, as is the case with methane(22). The reactions are accompanied by the persistent emission of the CN-red and violet band systems(23). The maximum amount of HCN formed from several of these hydrocarbons is approximately the same(24)* when an

---

*Ethylene, n-butane, but-2-ene and ethane at elevated temperatures in a spherical reaction vessel and ethylene and n-butane in an unheated cylindrical reaction vessel gave the same maximum yield of HCN.

excess of the hydrocarbon is added to active nitrogen, under conditions where complete consumption of N-atoms occurs, and the reaction of ethylene with active nitrogen has been suggested as a method for estimating the N-atom concentration in the afterglow(25,26).

5. The Concentration of Nitrogen Atoms in Active Nitrogen

Several methods have been used to measure the concentration of N-atoms in active nitrogen.

These have included:

(1) direct calorimetric measurement(5) of the heat of recombination of the atoms;

(2) direct measurement of mass-to-charge ratio 14(27) in the mass spectrometer;

(3) gas-phase titration with NO using a visual end point(28,29);

(4) titration by addition of excess ethylene(25,26), followed by volumetric determination of HCN frozen out in a cold trap;

(5) gas-phase titration with NO using a mass spectrometer(30) to measure the NO concentration (as used by the author in this laboratory);

(6) electron paramagnetic resonance spectroscopic methods(31).

The two most convenient methods are the NO gas-phase titration and the titration with ethylene. However, the two methods do not agree; the NO titration gives values approximately twice the C_2H_4 method. This discrepancy between the two methods has been claimed(32) to be due to the presence of excited N_2 molecules in the active nitrogen which presumably might decompose NO as follows:

$$N_2^* + NO \rightarrow N_2 + N + O \; ; \qquad (8)$$

thereby giving additional N-atoms, which lead to high values for the N-atom concentration.

C. Purpose of the Investigation

Although the quantitative aspects of the reactions of active nitrogen with a large number of different substances are quite well known, many unsolved fundamental problems still exist as to the mechanisms of these reactions. In addition, a major disagreement appears as to whether excited molecules, atoms, or both are the reactive species. It was therefore the purpose of this research to:

1. Observe the reactions of $N_2(A^3\Sigma_u^+)$ molecules;
2. clarify the reaction mechanisms of organic substances with active nitrogen; and
3. evaluate the reactive species in active nitrogen.

PART II

EXPERIMENTAL

A. Preparation of Materials

1. Cobalt Metal for Surface Catalysis

The cobalt used to catalyze the production of excited molecules (labeled 99.8%) was obtained from the A.D. McKay Co., and was obtained as 6-inch wide sheets. Two thicknesses were used, 0.010 inch and 0.025 inch. No special treatment was given the cobalt other than thorough grinding of the surface to remove grease, accumulated in the rolling process, and fingerprints.

2. Purification of Gases for Nitrogen Atom Experiments

The various hydrocarbons and inorganic gases used were obtainable commercially in a suitably pure form from the Matheson Company, East Rutherford, N.J., and were used directly from the tank with appropriate cold traps used where applicable. All of the gases used for this study except methylacetylene were found to exceed the minimum purity stated in the Matheson Handbook when analyzed with a mass spectrometer. If one percent impurity were taken as a hypothetical maximum limit for the least pure gas, then the concentration of impurity would be less than one part per thousand in the reaction system since at the very most the concentration of hydrocarbon in the system was about ten mole percent. This would occur under the worst conditions with the least pure gas; under most conditions no impurities were observed. Table I lists the gases used and their stated purities.

3. Purification of Gases for Excited Molecule Studies

In order to study the reactions of excited molecules it was necessary to use hydrocarbons of a very high degree of purity. A simple and very rapid adsorption-desorption method of purification was used. A large U-tube, both ends of which were connected to a vacuum system, was filled with anhydrous silica gel (20 mesh) and evacuated; the impure gas was then adsorbed on the silica gel while the U-tube was immersed in ice water to remove the heat of adsorption. After several liters of gas had been adsorbed the U-tube was heated mildly with a heat gun and the desorbed gas was collected in a storage bulb. After a little experience it became a simple matter to judge when to stop collecting the desorbed gas. With most gases only one treatment was required; however, for methylacetylene two were required since it contained approximately one-third dimethylacetylene. Using this method it was possible to prepare several liters (at STP) of high purity gases at one time. Mass spectrometric analysis showed the presence of undetectable amount of impurities; under the conditions of analysis the impurities could not be present in amounts greater than a few parts per ten thousand.

4. Preparation of Nitric Oxide

Nitric oxide was usually prepared by a series of simple trap-to-trap distillations from the commercially available NO, discarding the first and last fractions. Nitrogen was removed by pumping on the solid NO at liquid N_2 temperature. Mass spectrometric analysis showed only small amounts of N_2 impurity. At one point in the investigation, Matheson recalled all cylinders of nitric oxide due to an explosion involving this gas; during this period of unavailability NO was prepared by the action of $K_4Fe(CN)_6$, in dilute acetic acid, upon KNO_2 according to the following reaction(33):

$$K_4Fe(CN)_6 + KNO_2 + 2\ CH_3COOH \rightarrow NO + 2\ CH_3COOK + K_3Fe(CN)_6 + H_2O \qquad (9)$$

The evolved gas was rapidly collected by water displacement in a 5-liter flask with stopcocks on both ends. The NO was again freed from N_2 by pumping at 77°K and H_2O vapor was removed by "flashing" off the NO rapidly but allowing one or two cc of liquid to remain. Mass spectrometric analysis showed extremely pure NO with only minor amounts of N_2 and water vapor.

5. Preparation of Hydrogen Cyanide

HCN was prepared by the addition of dilute H_2SO_4 to a solution of NaCN. A few cc of the liquid HCN were then distilled into a cold trap cooled with dry ice. The solid HCN was then transferred to a vacuum system and pumped on at dry ice temperatures to remove N_2 and NO. The HCN was then rapidly heated to its boiling point and allowed to vaporize into a storage flask. This purified HCN was then condensed again and the distillation repeated. This removed most of the water vapor even though the vapor pressure of H_2O is relatively high at the boiling point of HCN (26°C). Mass spectrometric analysis showed only minor amounts of water vapor as impurity.

B. Apparatus

1. Vacuum System

The Wood-Bonhoeffer method was used for both the excited molecule and the nitrogen atom studies, and the apparatus used was the same for both except for minor differences. The very fast flow vacuum system was constructed using large diameter Pyrex brand glass pipe, except for the 6-inch cold trap and the 6-inch elbow from the trap to the diffusion pump which were Quick-fit brand glass pipe. The apparatus, which was quite heavy, was supported by properly fitted boards suspended on 2-inch iron pipes. The pumping system consisted of a CVC model MHG-900 Mercury diffusion pump with a rated pumping speed of approximately 1000 l/sec backed by two Beach-Russ model 100-D mechanical pumps rated at approximately 50 l/sec each. For this work the diffusion pump was not used. The total volume of the vacuum system was approximately 100 liters; using only one of the mechanical pumps, the system could be evacuated from atmospheric pressure to a few tens of microns in about one minute.

2. Spectrographs

Spectrograms were taken with any of three Hilger and Watts prism spectrographs. These were:

(1) A model E474 infra-red glass instrument with a range from 4000 A to 15,000 A and a dispersion of 45 A/mm at 5800 A;

(2) a model E498 medium quartz flat field instrument with a range from 2000 A to 10,000 A and a dispersion of 100 A/mm at 5800 A;

(3) a model E484 small quartz instrument with a range from 1600 A to 6000 A and a dispersion of 260 A/mm at 5800 A.

3. Photomultiplier

The light emitted by the excited molecules was measured with an RCA 7102 photomultiplier tube which has 10 electron multiplying stages. The spectral response of this phototube reaches a maximum in the red-infrared region; in order to reduce background noise, the tube had to be cooled with dry ice. The tube was operated at dynode-dynode potentials of about 70 volts; the photo-current was measured with a sensitive micro-ammeter (RCA model WV-84B). The dynode potentials were applied from a standard-design power supply.

4. D.C. Power Supply

A high-voltage condensed d.c. discharge was used for the production of nitrogen atoms. The power supply consisted of six high-voltage thyratron rectifiers whose output was used to charge either one, or more, 0.25 mfd capacitors. The capacitor was fired through the discharge tube approximately 30 times per second by means of a switch that rotated 300 times per minute and made 6 equally-spaced contacts per revolution. This particular power supply could provide up to 8000 volts at 250 ma.

5. A. C. Power Supply

An a.c. glow discharge was used for the production of oxygen atoms. The power supply was of a standard design consisting simply of a high-voltage transformer; the secondary voltage was simply applied to the discharge tube. A suitable limiting resistor or capacitor was connected in series with the primary windings of the transformer, either one of which could be used.

6. Pressure Measurements

Pressure measurements were made with a U-tube manometer containing Apiezon B oil (density = 0.86 gm/cm^3); oil levels were measured to within ± 0.005 cm (equivalent to ± 3 microns of mercury) with a standard Gaertner cathetometer. For rough measurements either an Alphatron type 520 vacuum gauge (National Research Corporation) or a CVC Pirani type gauge was used.

7. Mass Spectrometer

The mass spectrometer used for these investigations was a CEC model 21-130 instrument with an inlet system that was modified for this research. This modification is described in detail under Modifications to the Mass Spectrometer.

C. Experimental Arrangement

1. General Arrangement

The construction of the apparatus and the pumping system has already been described. Fig. 2 shows a pictorial layout of the various components.

Since both the mass spectrometer analyzer unit and the major components of the vacuum system were able to move independently of each other and since perfect alignment of the two units would be almost impossible to attain, a vacuum-tight flexible stainless steel bellows type coupling was used to join them. This was located well downstream from the reaction vessel so that no wall effects due to the coupling would interfere with the reactions that were under investigation. The reaction vessel consisted of a vertical length of 3-inch diameter Pyrex pipe located just above the mass spectrometer leak. The atom streams entered from a sidearm 50 cm above the leak while the reactant was added through 10 mm Pyrex tubing which could be raised or lowered in the reaction vessel by means of a 29/42 standard taper Teflon lead-through (Arthur F. Smith Co.). The Teflon gaskets in the system were used with either a fluorocarbon grease (Arthur F. Smith Co.) or with Kel-F grease (Minnesota Mining and Manufacturing Co.).

Discharge tubes for the production of N- and O-atoms were mounted on a nearby auxiliary vacuum system for convenience and connected to the main apparatus with 30-mm Pyrex tubing approximately 2 meters in length. The discharge tubes were coated with a solution of orthophosphoric acid to prevent wall recombination of the atoms.

This auxiliary vacuum system consisted of four 5-liter storage flasks with a standard-design arrangement of manifolds, cold traps, etc. This apparatus also contained the large U-tube, mentioned previously for purification of gases, and the various manometers used to monitor pressures.

2. Specific Arrangements

For both the nitrogen atom and the excited molecule experiments the same arrangement of major components of the vacuum system was used; only the reaction vessel section of the apparatus differed.

a. Nitrogen atom experiments. For these studies no access openings to the reaction vessel were required other than for a manometer and the reactant inlet tube (see Fig. 3a). The U-tube manometer was mounted on the auxiliary vacuum system and connected to the main apparatus with 10-mm Pyrex tubing.

b. Excited molecule experiments. For these experiments it was necessary to provide access openings to the reaction vessel. A 3-inch "Tee" was incorporated at right angles to the reaction vessel 15 cm above the mass spectrometer leak (see Fig. 3b). In addition, a pipe flange was substituted for the 29/42 ground glass joint used for the reactant inlet in the N-atom experiments.

This apparatus required openings for two manometers which were both mounted as described previously.

3. Modifications to the Mass Spectrometer

Since the mass spectrometer was to be used for routine laboratory analyses as well as these studies, a special inlet system was constructed which would allow both. This consisted of an aluminum valve in parallel with the mass spectrometer inlet system which also served as an adaptor for bolting the 3-inch Pyrex pipe to the analyzer unit. With the valve open the mass spectrometer was opened to the vacuum system; with the valve closed the instrument could be used for standard analyses. The valve consisted of a block which retracted into the valve body when the valve was opened, exposing the vacuum system to the mass spectrometer leak. The underside of this block was machined to accept a silicone rubber O-ring which was forced against the valve seat by the action of cams when the valve was closed. The entire valve was constructed of aluminum in order to prevent as much as possible wall recombination of the radicals in the system. For this reason, the leak capsule and the gold leak itself were replaced with aluminum components. The aluminum foil which served as the leak was attached to the capsule with Eastman 910 epoxy adhesive which has a vapor pressure of approximately 10^{-8} mm Hg (34); no background peaks were introduced due to the presence of the adhesive.

D. Experimental Procedure

1. Excited Molecule Studies

A primary objective of this work was to find a geometrical arrangement for the cobalt metal which would give an optimum value for the ratio of the number of excited molecules produced to the number of N-atoms remaining. Several glass nozzles were constructed (discussed later) which could be lowered into, or removed from, the apparatus with a length of stiff wire through the access opening provided for this purpose. See Fig. 3b.

After the nozzle containing the cobalt metal was positioned directly above the mass spectrometer leak, the system was evacuated for approximately 20 minutes; no other treatment was given the system, i.e., the walls of the reaction vessel were not poisoned with phosphoric acid. The valve to the mass spectrometer was opened and the flow rates of N_2 and O_2 were suitably adjusted to the desired values by varying the fore-pressures on capillary tubing through which the gases leaked into the system. It was not necessary to calibrate these "leaks" since the concentration of the added gas could be measured much more accurately as well as conveniently with the mass spectrometer.

When the N- and O-atom discharges were activated, a bright red jet of excited molecules would form in the nozzle. The reactant was leaked into the system through the inlet tube at a great enough distance downstream from the jet to prevent back diffusion to the metal surface. Generally, spectra were recorded with the discharges off and again with the discharges on; the entire spectrum or that of one component peak at a time could be observed.

The pressure drop across the nozzle could be measured with two manometers, one above and one below the nozzle.

2. Nitrogen-atom Studies

The general procedure used for these experiments was similar to that described previously for the excited molecule studies. Oxygen atoms were usually allowed to flow through the system overnight to burn off any adsorbed impurities which might have affected the results. In order to keep the system in this clean condition no wall poisoning was used in the reaction vessel. Again, as in the excited molecule experiments, the valve to the mass spectrometer was opened and N_2 was leaked into the system while its concentration was monitored with the mass spectrometer. The reactant was added from the inlet tube and the concentration of the several components of the reaction mixture again was determined when no N-atoms were present, and when the discharge was activated. For these experiments the O-atom discharge was not used; instead a known concentration of O-atoms was produced in the reaction system by adding NO to the stream of active nitrogen. The concentration of O-atoms was determined by simply shutting off the discharge and measuring the NO concentration, since one O-atom is produced, for each NO molecule consumed, by the very fast reaction:

$$N + NO \rightarrow N_2 + O \qquad (10)$$

Using this technique, the total concentration of N-plus O-atoms remained constant since one O-atom was produced for each N-atom destroyed. The pressure in the system was measured with the oil manometer.

3. Calibration of Mass Spectrometer

The relative mass spectral sensitivities of the gases used in these experiments were measured by adding a known forepressure of the gas to be calibrated to the inlet system of the instrument as measured with the micromanometer provided for this purpose. The spectrum was then scanned and compared with a N_2 sample whose sensitivity was always measured under identical conditions immediately prior to or immediately after that of the gas sample, i.e., with the same forepressure and the same emission current. Identical forepressures were used before the leak to eliminate possible errors in the pressure measurements due to inaccuracy of the micromanometer. By this method the sensitivity relative to N_2 was always determined; this relative sensitivity remained fairly constant for the several leaks used during the experiments, while the absolute sensitivity was found to vary from day to day, and even from experiment to experiment.

The spectral sensitivities of unidentified products formed in the reactions, or of those which were not available for calibration were estimated, based upon structural considerations. An error of a factor of possibly 3 could conceivably occur for these substances, but a much more reasonable estimate would be a 50% error. Table II lists the measured mass spectral sensitivities of the gases used in the investigations.

4. Determination of N-atom Concentration by NO Titration(28,29)

When NO is added to N-atoms the following extremely fast reaction occurs:

$$N + NO \rightarrow N_2 + O\,, \tag{10}$$

so that one NO molecule is consumed for each N-atom present. As the NO is added and N-atoms are consumed, the intensity of the yellow afterglow decreases until a blue glow is observed just before the end point. This corresponds to the reaction:

$$N + O + M \rightarrow NO^* + M \tag{11}$$

$$NO^* \rightarrow NO + h\nu \quad (\beta\text{-}, \gamma\text{ - and } \delta\text{ - bands}). \tag{12}$$

Exactly at the end point, the titration is colorless. As more NO is added and the end point is passed, the greenish-white so-called "air afterglow" is observed which corresponds to:

$$NO + O \rightarrow NO_2 + h\nu \quad \text{(greenish-white continuum).} \qquad (13)$$

This last reaction is slow and therefore does not interfere with the increase of NO concentration after the end-point is passed.

If the end-point is approached from the reverse direction, the transition from green to colorless is quite sharp: the NO concentration could be monitored with the mass spectrometer by looking at the NO peak; as the end-point was reached the NO concentration was reduced almost to zero. At this point the discharge was shut off and the NO concentration was measured; this was equal to the N-atom concentration.

Usually the titration was conducted using the more convenient visual end-point, since both-end points gave identical N-atom concentrations. NO was added to the active nitrogen from a storage flask at a flow rate such that the end-point was slightly passed; the NO was slowly pumped out of the flask (through a capillary) until the end point was reached; the discharge was then turned off and the NO concentration was measured.

5. Photomultiplier Measurements

In order to obtain an estimate for the concentration of excited molecules present in the jet, the total intensity of the emitted radiation was measured, with a photomultiplier tube. A 6-mm diameter brass tube a few cm long was taped perpendicularly to the light-sensitive face of the phototube. The entire tube was then covered with black electrician's tape so that light could enter only through the brass tube. The open end of the brass tube was directed toward the jet of light-emitting molecules and positioned as near as possible to the jet (until it touched the glass).

6. Spectrograms

The arrangement of the vacuum system was such that spectrographs could be pointed directly into the reaction zone. Standard procedures were used to develop the exposed plates, i.e., 4 minutes in Kodak D-19 developer, rinsing with water and fixing for 2 minutes in Kodak Rapid-Fix. D, N and Z type plates were used to observe the ultra-violet to red, red, and red-infrared regions of the spectrum, respectively.

PART III

RESULTS

A. Excited Molecules

1. Production of a Stream of Excited $N_2(A^3\Sigma_u^+)$ Molecules

Since different geometrical arrangements of the cobalt catalyst were to be investigated, a series of several glass nozzles was constructed in order to facilitate rapid removal and replacement of the cobalt. These consisted of a length of glass tubing, the outside diameter of which was slightly smaller than the glass pipe used for the vacuum system so that it would just fit snugly when placed inside the pipe. Fig. 4 shows a typical nozzle, containing cobalt, positioned in the vacuum system. One of the parameters to be varied in these experiments was the linear velocity through the nozzle. This was readily accomplished by simply reducing the diameter of the downstream end of the glass tubing, since the linear velocity through a nozzle, for a fixed volume rate of flow, is inversely proportional to the cross-sectional area.

As mentioned previously the surface catalyzed recombination of N-atoms presumably proceeds via the direct formation of $A^3\Sigma_u^+$ molecules in high vibrational levels. Since the radiative lifetime of the $N_2(A^3\Sigma_u^+)$ molecule is in the order of several millisec(3), considerable diffusion away from the surface of the cobalt can occur during this time interval at the pressures prevailing in the system (approximately 0.5 mm Hg). The $N_2(A^3\Sigma_u^+)$ molecules can then undergo stepwise vibrational deactivation during this time to the crossing-level of the $B^3\Pi_g$ and the $A^3\Sigma_u^+$ curves by collisions with other molecules. (Refer to Fig. 1.) Since the time required for this vibrational relaxation is less than or, as a maximum value, equal to the radiative lifetime of the $A^3\Sigma_u^+$ molecule, a radiationless transition to the $B^3\Pi_g$ state can occur. The $B^3\Pi_g$ state has a relatively short lifetime (10^{-8} sec)(35) and the observed N_2 first positive band system is emitted.

The linear velocity in a typical nozzle can be calculated as follows:

$$v = \frac{(\frac{V}{t})}{100 \times \Pi \times (\frac{d^2}{4})}$$

where v = the linear velocity in meters/sec,

$(\frac{V}{t})$= the volume rate of flow in cm^3/sec,

and

d = the diameter of the nozzle in cm.

The pumping speed of the mechanical pump (after losses) was approximately 40×10^3 cm^3/sec. Therefore, the linear velocity is:

$$v = \frac{40 \times 10^3 \frac{cm^3}{sec}}{100 \frac{cm}{m} 3.14 \times \frac{(2.54)^2}{4} cm^2} = 79 \text{ meters/sec}$$

when d = 2.54 cm .

Since the maximum time for emission of radiation is several millisec (approximately 10^{-2} sec), the excited molecules should be "swept" downstream for a distance of approximately 79 cm while emitting light.

In addition to being pumped downstream, the excited molecules also travel away from the surface in a perpendicular direction to the cobalt. Therefore, the width of the jet is determined by the distance traveled in this perpendicular direction and can be taken to a close approximation as equal to the diffusion distance, x, from the axis of the jet:*

$$x = \sqrt{2\,Dt}$$

$$= \sqrt{2 \times 260 \,\frac{cm^2}{sec} \times 10^{-2}\ sec}$$

$$= 2.3\ cm \quad ,$$

in a diffusion time of 10^{-2} sec. The excited molecules diffuse from both surfaces of the cobalt and the diameter of the jet is therefore twice this value, or 4.6 cm.

Experimentally, a jet approximately 20 cm in length and 5 cm in diameter was formed in early experiments. Figs. 5 and 6 show the effect of different nozzle diameters upon the streams of excited nitrogen molecules produced.

The cobalt was securely positioned in the nozzle by gently pressing the tightly fitting pieces of metal into the small diameter end; this press-fit was sufficient to prevent the metal from falling out of the nozzle when mounted vertically in the vacuum system.

In determining the optimum geometry for the cobalt in the nozzle,

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*It should be kept in mind that this calculation is an approximation since the jet has a finite diameter and diffusion is not simply from the axis of the nozzle.

two factors were considered. (1) Since the surface catalyzed recombination of N-atoms to excited molecules obviously is dependent upon the number of collisions with the cobalt, the surface of the metal should be as large as possible. (2) The surface should not be too large however, since the excited molecules that are formed can be deactivated by later collisions with the surface. In addition, the recombination of N-atoms to ground state molecules on the cobalt surface reduces the concentration of N-atoms available for catalysis to $N_2(A^3\Sigma_u^+)$ molecules. Since the heat of recombination of N-atoms is 225 kcal, the cobalt can easily become heated several hundred degrees because of this recombination. This heating of the cobalt leads to even further recombination of N-atoms to ground state molecules because of more efficient recombination on the hot surface.

With these considerations in mind the triangular arrangements such as that shown in Fig. 7 were found to give good streams of excited molecules; with this triangular arrangement reactant could be added directly into the center of the jet through glass tubing as shown in the drawing.

In these early experiments the jets contained N-atoms, as well as excited molecules (in addition to O-atoms), and therefore were not suitable for kinetic measurements. In order to completely eliminate N-atoms a much larger amount of cobalt was used (surface area approximately 100 cm^2 in contrast to 20 cm^2 for earlier experiments), without a nozzle. Under these conditions the length of the jet was quite short (5 to 10 cm) and the intensity was reduced by a factor of about 3. However, the stream consisted only of metastable molecules and O-atoms, the N-atoms being practically eliminated. This "clean" jet was used in efforts to detect the reactions of $N_2(A^3\Sigma_u^+)$ molecules.

Spectrograms of the red jet verified the light emission as due to the N_2 first positive band system, with the previously-mentioned(1) anomalous intensity distribution for the $v' = 8, 6$ levels.

2. Qualitative Observations of the Catalytic Activity of the Cobalt Surface

The concentration of excited molecules catalyzed by the cobalt was found to be highly dependent upon the condition of the surface. Although the cobalt received the same treatment for all the experiments (thorough grinding) three general types of behavior were noted.

1. When the cobalt was first exposed to the stream of N- and O-atoms only slight catalysis of excited molecules was observed and the intensity of the afterglow was reduced only slightly on passage through the nozzle. After a few minutes the catalytic efficiency increased to the extent that an intense jet of metastable molecules resulted. Under these conditions the surface of the cobalt remained bright and shiny with only a pale yellow coating of what supposedly was the metal oxide; however, some N-atoms were present in the jet.

2. On some occasions the cobalt was found to have extremely poor catalytic efficiency; in addition the nitrogen afterglow was completely quenched upon passing through the nozzle indicating recombination on the cobalt surface directly to ground state molecules. If the O-atom concentration was increased, the green air afterglow could be weakly observed downstream from the nozzle indicating formation of NO on the surface; also if an excess of NO over that required to titrate the N-atoms present was added to the N- and O-atom mixture before the nozzle, the bright green afterglow produced was completely quenched by the cobalt.

From these observations it is clear that the surface favored recombination to ground state molecules. When the surface was in this state, the cobalt became extremely hot in a few minutes and a dark blue oxide layer formed; in addition the already poor catalytic activity decreased even more. If the discharges were turned off and the surface allowed to cool, the catalytic efficiency for the formation of $N_2(A^3\Sigma_u^+)$ molecules was found to increase. After several of these alternate "off-on" treatments the formation of excited molecules would increase to a high enough concentration for kinetic studies. Although the concentration of excited molecules produced under these catalyst conditions was less than the maximum that could be obtained, the jet contained practically no N-atoms.

3. After several hours the catalytic activity of the cobalt would decrease greatly in either of the above cases; furthermore, the surface would no longer quench the nitrogen afterglow. Even though the cobalt surface was bright when this condition was reached, it was necessary to remove the cobalt from the system and grind the surface to restore catalytic activity.

The above observations are of a descriptive nature only and no explanation of the phenomena is given. Obviously a thorough investigation of the catalyst surface would be of interest as a subject for future investigation.

3. Behavior of Excited $N_2(A^3\Sigma_u^+)$ Molecules

A most striking observation was the resistance of the excited molecules to deactivation by collisions with other molecules or with surfaces. Early in the investigation several materials were placed directly into the jet of metastable molecules; these included glass, and aluminum, cobalt, silver, gold and platinum metals.

The jet could be deflected by the glass and the aluminum without becoming quenched and was only partially quenched by the metal surfaces.

A variety of gases was added to the jet in order to qualitatively observe any reaction. The jet was not quenched by O_2, O_3, CO_2, N_2O, CO, SO_2, H_2O vapor, CH_4, C_2H_2, C_2H_4, C_2H_6 or $CH_3C{\equiv}CH$. These visual observations were substantiated with the mass spectrometer for CH_4, C_2H_2, C_2H_4, C_2H_6 and $CH_3C{\equiv}CH$; no decomposition of these gases was observed.

The jet of $N_2(A^3\Sigma_u^+)$ molecules was found to be quenched somewhat by NH_3; however, no decomposition of NH_3 was detected, nor was H_2 observed as a decomposition product.

No definite results can be given for NO since the presence of O-atoms in the jet usually led to the light-emitting reaction:

$$NO + O \rightarrow NO_2 + h\nu \tag{13}$$

which interfered with any attempt to obtain a definitive result with this substance.

It should be pointed out that the above observations were made using a "clean" jet, i.e., almost free from N-atoms and no N_2 afterglow was observed below the jet under these conditions. It should also be mentioned that in early experiments the metastable species contained appreciable concentrations of N-atoms (yellow afterglow visible), and appeared to react; where, in reality, the N- and O-atoms present were the reactive species. A striking example of this could be seen by adding C_2H_4 to either a "dirty" jet or a "clean" jet; in the former the typical CN-bands were emitted while in the latter the jet remained unquenched and no light was emitted.

4. Estimation of the Concentration of $N_2(A^3\Sigma_u^+)$ Molecules in the Jet

Since the jet appeared to be unreactive towards most substances and even to NH_3, which seemed to quench the jet, it might be possible that the concentration of metastable molecules was too low for any reaction to be detectable with the mass spectrometer. Therefore, the light emitted by the metastable molecules was measured with an RCA 7102 infrared sensitive photomultiplier tube. The photocurrent produced by light entering the photomultiplier through the 6-mm brass tubing was 0.29 μ amp. The total distance from the center of the jet to the light-sensitive electrode of the phototube was 14.4 ± 1 cm and the jet was about 18 cm long and 5 cm wide. The tube was operated at dynode-dynode potentials of 70 volts; at this potential the tube had a median sensitivity of 0.06 amp/lumen, with maximum and minimum sensivities of 0.5 and 0.015 amp/lumen, respectively.

Using a mean energy of 1.5 ev per photon for the first positive bands emitted by the jet, it was calculated that between 6×10^{15} and 2×10^{17} $B^3\Pi_g$ molecules emitted light per second, with a median value of 5×10^{16} per second.* Therefore, at least this number of $N_2(A^3\Sigma_u^+)$ molecules should be formed in the jet per second, and possibly more. Since the flow rate of N_2 and O_2 was about 1×10^{20} particles per second, the concentration of metastable molecules should be about 0.05 percent of the overall gas mixture, i.e., about 10^{13} $N_2(A^3\Sigma_u^+)$ molecules per cm^3, or about one-third of a micron. Since the mass spectrometer could detect approximately 10^{12} particles entering the instrument per second, and the time available for reaction was about 0.01 sec, only very fast reactions, having

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*Appendix I gives this calculation in detail.

heats of activation of 2 to 3 kcal or less, could be expected to be detected.

It should be mentioned that the above estimates are probably too conservative and are taken as minimum values. With later jets, the time available for reaction may have been as much as 0.1 sec, and reactions having heats of activation as high as 4 kcal should have been detectable.

5. Attempts to Observe an Effect

Since the metastable molecules appeared in general to react much slower than anticipated, if at all, it might be that they were reacting rapidly with each other, perhaps by reactions of the following type:

$$N_2^* + N_2^* \rightarrow N_2 + N + N \qquad (14)$$

$$N_2^* + N_2^* \rightarrow N_3 + N \qquad (15)$$

$$N_3 + N \rightarrow 2\,N_2 \quad . \qquad (16)$$

If this were the case, then the concentration of metastable molecules should be greatest at the surface of the cobalt, on which they are produced, and rapidly decrease with increasing distance from the surface.

In order to detect any reaction that might have gone un-noticed, several reactant gases were mixed with the active nitrogen upstream from the cobalt catalyst; in this way the reactant gases would be exposed to the surface, and therefore to the highest possible concentration of metastable molecules. It should be kept in mind that one of the primary reasons for having a high velocity jet was to prevent back diffusion of reactant to the surface of the catalyst. These experiments defeated this purpose since surface reactions could now occur but the results proved extremely interesting.

Since the reactant gases were mixed with the active nitrogen upstream from the cobalt, only those gases could be added which did not react rapidly with N- and O-atoms. The gases used were CH_4, N_2O, CO_2, SO_2 and NH_3. The results were quite striking. CH_4, N_2O, CO_2 and SO_2 had no effect whatever upon the jet even though their concentrations were at least 10 times greater (approximately 10 mole percent) than that of the metastable molecules; the jet remained unquenched and the presence of these gases did not interfere with the catalytic activity of the cobalt, i.e., excited molecules were produced even though the stream of N- and O-atoms was mixed with a foreign gas that could be dissociated by a collision of the second kind with a metastable molecule.

In addition to these visual observations, no decomposition of any of these gases was detected with the mass spectrometer.

When NH_3 was mixed with the N- and O-atoms before the nozzle, no excited molecules were formed. This could either be due to poisoning of the surface of the cobalt by the NH_3 or by immediate reaction with the $N_2(A^3\Sigma_u^+)$ molecules as soon as they were formed. However, no NH_3 was destroyed (other than by O-atoms) and no H_2 was found as a product, indicating that no reaction occurred.

6. Attempts to Observe $A^3\Sigma_u^+$ Molecules in the Jet

Since the jet presumably contained a reasonable concentration of excited molecules which appeared to react more slowly than anticipated, if at all, an attempt was made to verify the presence of $A^3\Sigma_u^+$ molecules by a method other than light emission. After emitting the first positive bands the molecules should be in the $A^3\Sigma_u^+$ state. (Refer to Fig. 1.) This state is the upper level for the well-known Vegard-Kaplan transition $(A^3\Sigma_u^+)\rightarrow(X^1\Sigma_g^+)$ which, as already mentioned, has a radiative lifetime in the order of several milliseconds since it involves a change of spin, and therefore is metastable. It might be possible to apply a weak glow discharge directly below, or in the jet, and excite the $A^3\Sigma_u^+$ molecules to higher levels, especially the $B^3\Pi_g$ state.

If the $A^3\Sigma_u^+$ state molecules are excited in this manner, the light emitted subsequently by the $B^3\Pi_g$ molecules might have a significantly different vibrational distribution from that of the jet, in accordance with the Franck-Condon principle.

The experiment was conducted by photographing the spectrum of the jet of metastable molecules with the glow discharge turned on. The spectrum of the jet alone was then superimposed onto the spectrum of the glow discharge alone. If no effect occurred, the sum of these two spectra should be the same as that when the glow discharge was activated in the jet.

The spectrograms were found to be identical, and no conclusions can be reached from this experiment.

B. Nitrogen Atom Reactions

1. Quantitative Observations

a. Reaction of N-atoms with organic substances. The behavior of the reaction flames of unsaturated hydrocarbons, observed under the author's experimental conditions, i.e., low pressures and high pumping speeds, gave indications that possibly chain reactions, involving H-atoms and hydrocarbon radicals, were occurring when these substances were added to active nitrogen. If H-atoms reacted initially with the hydrocarbons to yield H_2 plus hydrocarbon radicals:

$$H + RH \rightarrow H_2 + R + 3\ \text{kcal}\ , \qquad (17)$$

these hydrocarbon radicals might then react rapidly with N-atoms forming HCN plus additional chain carriers, i.e., more H-atoms and hydrocarbon radicals:

$$R + N \rightarrow HCN + (H) + R' \ . \qquad (18)$$

This behavior could eventually lead to highly-branching reactions.

It is well known(36) that many hydrocarbons are also readily attacked by O-atoms (as well as H-atoms) forming hydrocarbon radicals by reactions such as:

$$RH + O \rightarrow OH + R + 1\ \text{kcal} \qquad (19)$$

$$RH + OH \rightarrow H_2O + R + 17\ \text{kcal}\ . \qquad (20)$$

N-atoms might then again readily attack these radicals giving HCN.

To test this hypothesis that N-atoms react readily with hydrocarbon radicals, varying amounts of O-atoms were added to the active nitrogen-hydrocarbon reactions in an attempt to catalyze the reaction between N-atoms and various hydrocarbons. The results of these experiments, showing the formation of HCN and H_2, are given in Figs. 8 to 22 and Tables VII to XV. CH_4 and C_2H_6 showed no effect.

In all of these experiments the concentration of O-atoms was varied by adding known amounts of NO to the N-atoms; in this way the sum of N- and O-atoms was always kept constant. The curves have all been normalized so that the N-atom concentration as determined by NO titration is taken as 100 div, and the reactant and product curves are directly comparable. Figs. 23 to 25 and Tables IV to VI show the differences in the formation of HCN, H_2 and other products when various hydrocarbons are added to active nitrogen with O-atoms absent. Under these conditions, the concentration of N-atoms in the active nitrogen was about 15 mole percent of the overall gas mixture.

b. Formation of NH_3 in the reactions of active nitrogen with unsaturated hydrocarbons. When the reactions of some hydrocarbons with active nitrogen was incomplete, i.e., when the concentration of N-atoms was large relative to the concentration of reacting hydrocarbon, NH_3 was always found as a substantial product, especially in the C_2H_4 reaction. The amount of NH_3 formed attained a maximum value with increasing quantities of hydrocarbon, and then decreased to practically zero concentration as N-atoms were completely consumed, and the reaction went to completion ("plateau" region). See Fig. 26 and Tables IV to VI. In addition, when the concentration of hydrocarbon (C_2H_4) was held constant, in this region of incomplete reaction, small concentrations of O-atoms catalyzed the formation of NH_3 to an extent approximately the same as HCN. See Figs. 27 to 29 and Tables VII to X.

Unfortunately, the regions of maximum interest for the formation of NH_3 were also subject to the largest errors due to wall contaminants, especially H_2; material balances were found to be consistently high in H_2. Therefore, the results must be taken as semi-quantitative, and indicative of a trend only.

c. HCl-catalyzed reactions of N-atoms with hydrocarbons. Since O-atoms were found to catalyze the reaction of hydrocarbons with N-atoms via production of hydrocarbon radicals, Cl-atoms might be even more efficient as a catalyst, since Cl-atoms react rapidly with hydrocarbons(37). HCl was added to the active nitrogen-hydrocarbon mixture and the results were quite striking. In contrast to the O-atom catalysis in which only a slight catalytic effect was observed, even the most stable saturated hydrocarbon molecules, CH_4 and C_2H_6, gave reaction flames at room temperatures; in addition, the effect seemed to be a general one inasmuch as HCl catalyzed the formation of HCN when several saturated hydrocarbons were added to active nitrogen. Tables XVI through XXII compare the products formed when several hydrocarbons were reacted with active nitrogen with, and without, HCl present. CN bands were also strongly emitted when alkanes were reacted with active nitrogen in the presence of HCl, making the flames visible to the eye.

2. Qualitative Observations

a. "Flashing" observed when C_2H_4 was added to active nitrogen.

The usual reaction of a small concentration of C_2H_4 with an excess of N-atoms led to a weakly cream-colored reaction in which N-atoms were not completely consumed (region of linear increase of HCN with added C_2H_4). In addition, the reaction did not appear to involve very rapid chain branching since no flame was observed, and the reaction was incomplete at the mass spectrometer leak (reaction time ~ 0.01 sec). In this region the CN radiation was weak relative to the region of excess hydrocarbon, i.e., flame region.

Under certain conditions, however, the reaction was observed to develop into a bright pulsating flame front about 50 cm downstream from the C_2H_4 inlet, when a small concentration of C_2H_4 was added to the active nitrogen stream. The flame front would pulsate a few times per second for about 2 sec and then rapidly sweep the 50 cm upstream to the C_2H_4 inlet; after a few seconds it would reappear downstream and the cycle would be repeated. With the passage of the flame front upstream, the nitrogen-atom afterglow was greatly reduced in intensity, indicating consumption of N-atoms. CN-bands were emitted strongly from the oscillating flame front making visual observation readily possible, and much less strongly from the body of the flame.

This behavior was described by Bayes(38) when CCl_4 was reacted with active nitrogen.* Bayes found that the flashing was not reproducible from day to day, and was evidently very dependent upon conditions. This non-reproducible behavior was also exhibited by the C_2H_4-active nitrogen flashing. Evidently conditions in the apparatus which promoted the flashing were destroyed eventually since the flashing ceased after a few hours of experimentation.

These C_2H_4 experiments were unique in that the flame front would sweep past the mass spectrometer leak during each cycle and any products formed could be observed during the passage of the flame. It was found that the rate of production of HCN increased by about one-third with each passage of the flame front indicating that chain-branching reactions might play an important role in the reactions of active nitrogen with hydrocarbons.

In order to see if H-atoms were involved in the flashing H_2 was added to the reaction mixture. The flashing stopped but no additional HCN

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*Flashing of this type was observed previously in this laboratory when N-atoms alone were flowing through the system; N-atoms probably attacked the grease used with the Teflon gaskets until the concentration of chain carriers became large enough for chain-branching reactions to occur.

was formed. When hydrogen atoms were added, not only did the flashing stop, but the HCN was found to increase to an extent similar to that observed during passage of a flame front past the mass spectrometer leak. These observations suggested that at least one of the chain carriers might possibly be H-atoms.

b. Addition of gases upstream from the active nitrogen-hydrocarbon flames. The intensity of the CN-bands emitted in several hydrocarbon reactions appeared to vary with the amount of HCN that could be produced when an excess of hydrocarbon was added to the active nitrogen. In addition, Bayes(38) claimed that NH_3 destroyed the species which initiated reactions leading to CN emission. NH_3, therefore, as well as CO_2 and N_2O were added to the reaction flame to see if quenching occurred or if HCN production were affected. A very interesting phenomenon was found. Both C_2H_4 and C_2H_2 gave strong flames when the pure hydrocarbon was added in concentrations such that all the N-atoms were consumed. When CO_2, N_2O and NH_3 were added to the C_2H_4 flame, no decomposition of these gases was observed and the rate of formation of HCN also remained unchanged. When CO_2 was added to C_2H_2, no effect was observed either; when N_2O was added, substantial consumption occurred, but no products could be observed. However, when NH_3 was added to the C_2H_2 flame, it was substantially decomposed. In addition, H_2 and HCN were formed to the same extent as the NH_3 that was consumed. This behavior was attributed to the CH radical, produced as follows:

$$C_2H_2 + N \rightarrow HCN + CH - 2 \text{ to } - 5 \text{ kcal} . \qquad (21)$$

This radical might then react with NH_3 by:

$$CH + NH_3 \rightarrow HCN + H_2 + H + 51 \text{ kcal} . \qquad (22)$$

If the CH radical were actually the radical involved in the reaction with NH_3, it should be possible to form HCN without N-atoms if CH radicals could be produced by some other method. It is well known(39) that the typical blue reaction observed when O-atoms react with many hydrocarbons is due to CH radicals. Therefore both C_2H_4 and C_2H_2 were reacted with O-atoms and NH_3 added; in both cases NH_3 was destroyed and HCN and H_2 were produced.

H-atoms were also reacted with C_2H_2 and NH_3 added; HCN was again formed but only to a minor extent. However, H-atoms form CH radicals from hydrocarbons only to a small extent(39); the blue CH emission was not observed but rather a green emission was seen, presumably due to C_2 radicals(39).

c. Reaction of HCN with active nitrogen(40). Since HCN is the common product formed when N-atoms react with many hydrocarbons, its stability toward N-atom attack was measured. HCN was added to N-atoms at room temperature and at a temperature of approximately 100°C. No decomposition could be measured with the mass spectrometer even though a slight cream-colored reaction was observed (but not a flame).

PART IV

DISCUSSION OF RESULTS

A. Review of Previous Work

Parts I, II and III of this report have been subdivided into two classifications: (1) Excited molecules and (2) N-atoms.

However, it has already been stated under RESULTS, that the most striking behavior of $N_2(A^3\Sigma_u^+)$ molecules was their stability, relative to fast N-atom reactions, toward reaction with other substances. These observations necessitated a new approach to elucidating the mechanisms of the reactions of active nitrogen, particularly with organics. Therefore, the majority of this research was directed towards better understanding the mechanisms of organic reactions, and following discussions deal primarily with the reactions of N-atoms.

The author feels that owing to this research a significant insight has been gained into the mechanisms of the reactions of organics with active nitrogen. Unfortunately, the unusually large amount of data obtained by others concerning the chemical reactions of these substances with active nitrogen makes discussion of the results of these experiments an extremely difficult task. Therefore, in order to present the author's views concerning these reactions in a clear, and yet concise, manner, following pages of text will be either double or single spaced. Double-spaced type will present the major features of the more important aspects of the research and is directed toward the casual reader. Single-spaced type is directed toward the more interested reader, those somewhat familiar with the literature in this field, and contains material that is less important to the overall understanding of the work, but yet should not merely be relegated to footnote importance.

1. Results of the Hydrocarbon Experiments by Winkler and Co-workers

A most comprehensive, classical investigation of the reactions of hydrocarbons with active nitrogen has been made by Winkler and co-workers, and his results constitute the basic knowledge in this field. Winkler reacted many different substances with active nitrogen including CH_4, C_2H_6, C_3H_8 and other saturated hydrocarbons, as well as many unsaturated hydrocarbons such as C_2H_4, C_3H_6, C_4H_8 and C_2H_2. The detailed results of these hydrocarbon experiments are given in many publications(21), and only the major features will be presented here.

These can be summarized briefly.

(1) Unsaturated hydrocarbons were found to react extremely rapidly with active nitrogen at room temperatures, forming HCN as the main product. Saturated hydrocarbons were found to react much more slowly, while CH_4 and C_2H_6 underwent appreciable reaction only at elevated temperatures. These saturated hydrocarbons again gave HCN as the main product. The only other nitrogen-containing products generally found were small amounts of NH_3 and traces of $(CN)_2$, although some workers(41), and the author, have found appreciable quantities of CH_3CN. In these reactions small amounts of saturated hydrocarbons, small to very appreciable amounts of unsaturated hydrocarbons, especially C_2H_4 and C_2H_2, and small amounts of polymers were generally found. The reaction with C_2H_2 displayed anomalous behavior and appreciable amounts of $(CN)_2$, and large amounts of a dark brown polymer containing 32% nitrogen were found. In addition, all of the hydrocarbon reactions were accompanied by the bright persistent emission of CN-bands.

(2) As increasing concentrations of hydrocarbon were added to the active nitrogen, the rate of formation of HCN was found to increase linearly until a sharp maximum, or "plateau" was reached. See for example Figs. 23 through 25.* When this plateau was reached, reaction was complete and no more formation of HCN occurred upon further addition of hydrocarbon. Also, the yellow nitrogen afterglow was fully quenched, indicating complete consumption of N-atoms. As given earlier, this maximum rate of production of HCN was found to be approximately the same for several hydrocarbons. In addition, good material balances, based upon carbon, generally were obtained in the plateau region, both by Winkler and the author. Winkler studied the reaction of C_2H_4 thoroughly(42,43) and this reaction is widely used for determining the concentration of N-atoms in active nitrogen as discussed below. This reaction was also studied in detail in this laboratory.

(3) A fixed maximum amount of only one nitrogen-containing product, HCN, is obtained from several different hydrocarbons(24), and this gives support to Winkler's postulate that this maximum production of HCN corresponds to the N-atoms present in the active nitrogen. The fact that only minor amounts of other nitrogeneous products are found also supports these views. Winkler's HCN method for determining the N-atom concentration in active nitrogen consists simply of adding a large amount of C_2H_4 to the active nitrogen, such that the hydrocarbon is present in a large enough excess so that complete consumption of N-atoms occurs. Under these conditions (termed the "plateau" region(42)), short, bright reaction flames are observed and reaction is complete in a few milliseconds. The HCN formed is then

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*These curves give the results of the author, but are similar to those obtained by Winkler.

frozen out in a cold trap and measured volumetrically by standard wet methods of analysis. The nitrogen content of the HCN is taken as a measure of the N-atoms in the active nitrogen. This method is based upon the condition that only HCN is produced from each N-atom present. The overall stoichiometry for ethylene would be:

$$C_2H_4 + 2\ N \rightarrow 2\ HCN + 2\ H\ (H_2) \quad . \tag{23}$$

It is clear that this method assumes that no reactions occur whereby N-atoms form products other than HCN. If competing reactions occurred, however, whose net result was the production of N_2, i.e., catalyzed recombination of N-atoms(44), then erroneous results would be obtained. Reaction (23) above would still occur giving the same stoichiometry, based upon carbon, but additional consumption of N-atoms could also occur via reactions whose only net result was the formation of N_2, such as:

$$C_2H_4 + N \rightarrow [C_2H_4N] \tag{24}$$

$$[C_2H_4N] + N \rightarrow N_2 + C_2H_4 \quad . \tag{25}$$

Nitrogen production would be difficult, if not impossible, to observe in a system containing initially large amounts of nitrogen. Each <u>carbon</u> atom, as opposed to each <u>nitrogen</u> atom, could still form HCN, and identical material balances, based upon carbon, would be obtained.

2. Winkler's Conclusions

a. Winkler's reaction mechanisms. From his experimental data, Winkler concluded the following general reaction mechanism(21). N-atoms attack the hydrocarbon directly and form a complex, by association, as follows:

$$RH + N \rightarrow [RHN] \quad . \tag{26}$$

This complex then rearranges, splitting off HCN, and giving fragments:

$$[RHN] \rightarrow HCN + \text{fragments} \quad . \tag{27}$$

These fragments, generally hydrocarbon radicals, can then react further to give more HCN plus additional hydrocarbon radicals and H-atoms. Most radical reactions of this type would be exothermic and could be expected to occur. In the case of C_2H_4, the reaction would be(21):

$$C_2H_4 + N \rightarrow [C_2H_4N] \rightarrow HCN + CH_3 + 62 \text{ kcal} \tag{28}$$

$$CH_3 + N \rightarrow HCN + 2H + 13 \text{ kcal} \quad . \tag{29}$$

It should be noted that, although the HCN formation is accounted for by this reaction mechanism, the mechanisms whereby unsaturated hydrocarbons, polymers, saturated hydrocarbons, NH_3 and other minor products are formed, are not adequately explained. The origin of the CN-bands emitted is also in doubt, although several secondary radical reactions have been suggested, which can lead to the formation of CN(21).

b. Discrepancy between N-atom concentrations determined from the maximum extent of HCN formation from hydrocarbons, and from titration with NO. When N-atom concentrations are determined by titration with NO, higher values are obtained than with the C_2H_4-HCN method(32). The possibility that reactions such as (24) and (25) above might occur with C_2H_4, whose net result would be production of N_2 instead of HCN, thereby giving low HCN production, was generally rejected by Winkler(45). Instead, a second reactive species in the active nitrogen, excited molecules, were postulated as being responsible for reactions which could decompose NO into N- and O-atoms(32), thereby giving higher N-atom concentrations when NO was used to titrate N-atoms. If this were the case, then the following reactions would occur when active nitrogen was titrated with NO. N-atoms would react as usual:

$$N + NO \rightarrow N_2 + O \quad . \tag{10}$$

However, more N-atoms would then be produced by collisions of the second kind with these excited molecules:

$$N_2^* + NO \rightarrow N_2 + N + O \quad . \tag{8}$$

These additional N-atoms would then react with more NO and give a high value for the N-atom concentration.

> Some experimental evidence for the presence of excited molecules in active nitrogen, capable of decomposing NO into N- and O-atoms has been accumulated, based partly upon the following results. First, Winkler added NH_3 upstream from the C_2H_4 reaction flame(46) with the intent to deactivate any excited molecules present. If however, N-atoms are consumed in a reaction with this NH_3, HCN production should decrease. No significant change was found; in fact a very slight <u>increase</u> was observed(46). The reason for this apparent paradox will be given later.
>
> Secondly, if NH_3 is added to active nitrogen <u>alone</u> (not to the C_2H_4 reaction flame), produced by a condensed discharge, i.e., containing a high concentration of N-atoms, a slight decomposition into N_2 and H_2 has been claimed to occur(43,23). This decomposition of NH_3 has been attributed(47) to reaction with excited molecules. This excited molecular species is though to possibly be the relatively long-lived metastable $N_2(A^3\Sigma_u^+)$ molecule(48), which obviously must be present in active nitrogen since it is the lower level of the transition responsible for the strong light emission of the afterglow.

B. New Evidence Due to Investigations in This Laboratory

1. Oscillating Flame-front Observed in the C_2H_4-Active Nitrogen Reaction

When alkenes are added to active nitrogen under normal laboratory conditions (pressure ~ 1 mm Hg, linear velocity ~ 5 meters per second and a reaction tube 2 cm in diameter) short reaction flames are obtained and it is difficult to make any semi-quantitative observations about their behavior. Under the conditions of the author's experiments, however, i.e., pressure ~ 0.25 mm Hg, linear velocity ~ 10 meters per second and reaction tube 6 cm in diameter, large flames about 6 cm in diameter and 10 to 20 cm in length were obtained making visual observation a simple matter. It was therefore possible, in a semi-quantitative manner, to simultaneously correlate the visually observed behavior of the reactions with the products detected with the mass spectrometer.

These observations for the reaction of C_2H_4 could be classified according to three conditions.

(1) When small quantities of C_2H_4 were added to the active nitrogen (N-atoms about 20 x C_2H_4), a pale, cream reaction occurred (not a flame) with weak CN radiation and the yellow nitrogen afterglow was not destroyed. These conditions of large excess of N-atoms over hydrocarbon will hereafter be called "non-flame" conditions. This reaction was relatively slow and the reaction showed no flame behavior, i.e., the reaction was obviously incomplete in the available reaction time and no indication of rapid chain-branching was observed. In addition, O-atoms were found to increase the rate of HCN production in this region.

(2) When a somewhat greater concentration of C_2H_4 was added to

to the active nitrogen (N-atoms about 5 x C_2H_4), the oscillating flame-front described under RESULTS would sometimes appear. Whenever the flame-front was upstream of the leak of the mass spectrometer, a large increase in HCN formation over the normal, non-flame reaction was noted. Obviously, the production of HCN occurred partly by the non-flame reaction and to a major extent via this flame reaction. This flame reaction also appeared to be responsible for the emission of CN-bands. In addition, the yellow nitrogen afterglow which was not destroyed by the non-flame reaction, was drastically reduced in intensity with each passage of the flame-front, indicating rapid consumption of N-atoms via this flame reaction. The velocity with which the flame-front would "sweep" upstream was such that rapid chain branching must have occurred. H-atoms added to the reaction mixture stabilized the flame upstream, thereby showing that the reaction might proceed via H-atoms.

(3) The typical short, stable reaction flame was observed only when large concentrations of C_2H_4 ($C_2H_4 > N$), sufficient to completely consume N-atoms, were added to the active nitrogen. Under these conditions (hereafter called "flame" conditions), O-atoms had no effect on the rate of production of HCN.

> The finding that O-atoms increased the rate of production of HCN under non-flame conditions, while no effect was observed under flame conditions, is readily explained. Under non-flame conditions, any hydrocarbon radicals produced, by the reaction of O-atoms with C_2H_4 as given earlier, result in an appreciable increase in the number of hydrocarbon radicals present in the system and these eventually produce HCN. As more C_2H_4 is added to the reaction, the number of radicals increases until the highly branching reaction predominates. Under these conditions the reaction becomes so rapid that it proceeds

to completion, and so many radicals are already produced in the reaction zone, that the addition of a relatively minor quantity of O-atoms, which provide a few additional radicals, has no effect.

The HCN formed goes through a maximum as the amount of oxygen atoms is increased and the N-atom concentration simultaneously decreased.* See Figs. 8 to 13. The addition of O-atoms was accomplished by adding a known amount of NO to the active nitrogen.

This increased production of HCN can be explained if O-atoms attacked C_2H_4 forming C_2H_3 or CH_2-radicals; these radicals could then react rapidly with N-atoms, giving HCN and other products by reactions such as the following:

$$C_2H_4 + O \rightarrow C_2H_3 + OH + 1\ \text{kcal} \qquad (30)$$

$$C_2H_4 + OH \rightarrow C_2H_3 + H_2O + 17\ \text{kcal} \qquad (31)$$

$$C_2H_3 + N \rightarrow HCN + \text{products} \qquad (32)$$

or

$$C_2H_4 + O \rightarrow CH_2O + CH_2 + 30\ \text{kcal} \qquad (33)$$

$$CH_2 + N \rightarrow HCN + H + 113\ \text{kcal} \qquad (34)$$

2. Formation of H_2 in the Reactions of Active Nitrogen with Hydrocarbons

Prior to this investigation, the formation of H_2 in the reactions of active nitrogen was generally not emphasized. However, the mass spectrometer used in the author's experiments, whose leak was located directly in the reaction vessel, detected quite appreciable (approximately 1→5 mole %)

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*The fact that several HCN molecules were produced, for each O-atom added, suggests that the formation of HCN probably proceeds via a chain mechanism.

concentrations of H_2, which was found to be an important product of all the hydrocarbon-active nitrogen reactions. See, for example, Tables IV to VI. In addition, reasonably good material balances were obtained for hydrogen under flame conditions.*

3. The General Role of Radicals and Branching Chain Reactions in the Reactions of Hydrocarbons with Active Nitrogen

The similarity in behavior of the reactions of several hydrocarbons with nitrogen atoms, especially the phenomenon of the oscillating flame-front, is typical of chain reactions and it appears that, contrary to previous views, chain reactions which may branch, involving hydrocarbon radicals and H-atoms play the major role in these reactions, and are responsible for the observed flame behavior under conditions where complete consumption of N-atoms occurs.

The original production of hydrocarbon-radicals that can initiate the reactions poses a problem. Obviously direct attack of most hydrocarbon molecules by an N-atom is considerably endothermic and cannot occur:

$$RH + N \rightarrow NH + R - 14 \text{ kcal} \quad . \qquad (35)$$

> The primary reason for postulating the formation of a complex which then rearranges(21), splitting off HCN directly, is the fact that most simple hydrocarbons, except possibly those with a weakly-bound tertiary hydrogen atom, would give rise to energetically impossible reactions if attacked by N-atoms in a simple abstraction reaction as follows:

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*Under non-flame conditions, material balances could not be obtained, but non-volatile polymers were formed which could not be detected with the mass spectrometer. These polymers accumulated on the walls of the reaction vessel and could readily be observed after several minutes.

$$RH + N \rightarrow NH + R - 14 \text{ kcal} \quad . \qquad (35)$$

Unfortunately the binding energy of the NH-radical is not very well known, but the two most widely-accepted values are 78(50) and 86(51) kcal. The binding energy of the first H-atom in simple hydrocarbons is approximately 100 kcal(49). Therefore this type reaction is endothermic by at least 14 kcal(49) and would not occur rapidly at room temperature.

An interesting consideration becomes apparent, however, when the heats of formation, of the species expected to be formed in these reactions, are examined. If, by some means, a hydrogen atom is removed from hydrocarbons (primarily those under consideration) giving hydrocarbon radicals with an odd number of H-atoms, several exothermic reactions with N-atoms become possible. For example:

$$C_2H_3 + N \rightarrow HCN + CH_2 + 61 \text{ kcal} \quad , \qquad (40)$$

could occur, since this reaction is exothermic. The analogous attack on C_2H_4 could not occur, since the reaction is endothermic:

$$C_2H_4 + N \rightarrow HCN + CH_2 + H - 37 \text{ kcal} \quad . \qquad (41)$$

Hydrocarbon radicals might be produced by reaction with metastable $N_2(A^3\Sigma_u^+)$ molecules in collisions of the second kind:

$$N_2(A^3\Sigma_u^+) + RH \rightarrow N_2(X^1\Sigma_g^+) + R + H + \sim 100 \text{ kcal} \quad . \qquad (36)$$

No indication was obtained, however, in the author's excited molecule studies, that $N_2(A^3\Sigma_u^+)$ molecules react rapidly enough with hydrocarbons to furnish large concentrations of hydrocarbon radicals.

Hydrocarbon radicals might be produced during the 3-body recombination of N-atoms via:

$$N + N + C_2H_4 \rightarrow N_2 + C_2H_3 + H + 125 \text{ kcal} \quad . \qquad (37)$$

It seems most likely that a few hydrogen atoms or other radicals, either present as impurities in the active nitrogen, or produced by a direct reaction of unsaturated hydrocarbons with N-atoms* are the initiators of chain reactions which produce additional hydrocarbon radicals. For example:

$$C_2H_4 + H \rightarrow H_2 + C_2H_3 + 3 \text{ kcal} \quad , \qquad (38)$$

can occur. The C_2H_3-radical thus formed, as opposed to the C_2H_4-molecule, can then undergo several exothermic reactions with N-atoms. If this were the case, the following chain process could occur:

$$C_2H_4 + H \rightarrow H_2 + C_2H_3 + 3 \text{ kcal} \qquad (38)$$

$$C_2H_3 + N \rightarrow HCN + CH_2 + 61 \text{ kcal} \qquad (40)$$

$$CH_2 + N \rightarrow HCN + H + 113 \text{ kcal} \quad . \qquad (34)$$

It can be seen that the overall stoichiometry would be the same as for Winkler's complex-rearrangement mechanism, namely:

$$C_2H_4 + N \rightarrow [C_2H_4N] \rightarrow HCN + CH_3 + 62 \text{ kcal} \qquad (28)$$

$$CH_3 + N \rightarrow HCN + 2H + 13 \text{ kcal} \qquad (29)$$

$$2H \rightarrow H_2 + 103 \text{ kcal} \quad . \qquad (42)$$

Even though this mechanism is compatible with the chain characteristics of the reactions, certain modifications are needed. In the following pages are discussed additional results which necessitate a considerable enlarge-

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*These reactions are discussed later. One such reaction might be, in the case of C_2H_4:

$$C_2H_2 + N \rightarrow NH_2 + C_2H_2 + 25 \text{ kcal} \quad . \qquad (39)$$

ment of this relatively simple radical reaction scheme.

4. The HCl-catalyzed Reaction of CH_4 with Active Nitrogen

The foregoing semi-quantitative experiments, and thermodynamic considerations, give indirect indications that hydrocarbon radicals formed prior to any reaction with N-atoms, might play major roles in hydrocarbon reactions with active nitrogen. If it were possible to enhance the production of large quantities of hydrocarbon radicals, prior to reaction with active nitrogen, additional pertinent information might be obtained concerning the role of radicals in these reactions.

It is well known that alkanes, and especially CH_4 and C_2H_6(22) react relatively slowly with active nitrogen at room temperatures. In an attempt to enhance the production of radicals, HCl was added to these alkane-active nitrogen mixtures. Not only did rapid reactions occur at room temperature and approximately 0.5 mm Hg pressure, but flames developed. The light emitted by the flame was due to CN bands, and indicated that complete reaction was occurring in less than 0.01 sec for C_2H_6. The CH_4 reaction was slightly slower than the C_2H_6 reaction and developed into a flame about 10 to 20 cm downstream from the CH_4 inlet (requiring about 0.02 sec for completion); when H-atoms were added, a flame developed immediately at the CH_4 inlet and the reaction rate then equaled that of the C_2H_6 reaction.

> It is well known(52) that, under certain conditions, mixtures of gaseous hydrocarbons or H_2, with Cl_2, explode when strongly irradiated with light. This is because Cl-atoms are produced and react rapidly with hydrocarbons forming hydrocarbon radicals and HCl, and are regenerated; the kinetic equilibrium(53) which exists between H-atoms, hydrocarbon radicals, Cl-atoms and HCl favors the rapid production of Cl-atoms via:

$$H + HCl \rightleftarrows H_2 + Cl + 1 \text{ kcal} \quad . \qquad (43)$$

Therefore, any radicals produced in these systems would be expected to give rise to further production of Cl-atoms via the above reactions. These Cl-atoms then produce additional H-atoms and hydrocarbon radicals, and rapidly-branching chain reactions leading to explosions occur.

Chlorine atoms were produced by adding HCl to the active nitrogen since Winkler found(54) that HCl reacted fairly rapidly with active nitrogen. Although the mechanism may be complicated, the overall result appears to be that one Cl-atom is produced and two N-atoms are recombined to N_2 in the process(54). No attempt is made by the author at this time to go into the detailed mechanism of the reaction. However, if the binding energy of NCl is comparable to that of HCl ($D_{NCl} \sim 100$ kcal), the following chain reaction might produce Cl-atoms and consume N-atoms:

$$N + HCl \rightarrow NCl + H \qquad (44)$$

$$N + NCl \rightarrow N_2 + Cl \qquad (45)$$

according to the proposed stoichiometry.

The obvious explanation, in the case of CH_4, is that CH_3-radicals were produced:

$$CH_4 + Cl \rightarrow HCl + CH_3 + 2 \text{ kcal} \quad . \qquad (46)$$

These CH_3-radicals then may be attacked by N-atoms and only the following reactions are energetically possible:

$$CH_3 + N \rightarrow HCN + 2H + 13 \text{ kcal} \qquad (29)$$

$$CH_3 + N \rightarrow HCN + H_2 + 116 \text{ kcal} \quad . \qquad (47)$$

Reaction (47), however, is spin forbidden and might not be expected to occur to as large an extent as (29). In addition, it was found that as a maximum, under optimum conditions of temperature, and CH_4 and HCl concentrations, as many as 65% of the N-atoms present, as measured by titration with NO, formed HCN. See Table XXIII. Since the formation of one Cl-atom requires the consumption of two N-atoms, and 1 N-atom is required to react with each CH_3 radical, only 33% HCN should have been produced. It is clear therefore that additional Cl-atoms must have been produced in a reaction other than the reaction of HCl with active nitrogen. Obviously, reaction (29) is producing H-atoms which then react rapidly with HCl:

$$H + HCl \rightarrow H_2 + Cl + 1 \text{ kcal} \quad . \qquad (43)$$

The fact that two H-atoms are produced for each HCN leads to subsequent formation of two additional Cl-atoms, and a branching reaction is therefore observed, as a flame. In addition, stoichiometric quantities of H_2 were found to support the above discussion. It should be noted that the HCl acts as a true catalyst, and no net consumption occurred in any of these experiments (see Tables XVI to XXII).

5. The HCl-catalyzed Reaction of C_2H_6 with Active Nitrogen

The HCl-catalyzed reaction of active nitrogen with C_2H_6 provided interesting results. Again a flame occurred, which was much shorter than the CH_4 flame. However, only 25% of the N-atoms present were converted to HCN. If only the following reactions occurred:

$$C_2H_6 + Cl \rightarrow HCl + C_2H_5 + 2 \text{ kcal} \qquad (48)$$

$$C_2H_5 + N \rightarrow HCN + CH_3 + H + 25 \text{ kcal} \qquad (49)$$

$$CH_3 + N \rightarrow HCN + 2H + 13 \text{ kcal} \quad , \qquad (29)$$

then the HCl-catalyzed reaction of C_2H_6 with active nitrogen should give the same, or even greater, conversion of N-atoms to HCN than the maximum from the CH_4 reaction (65%), since the additional CH_3-radical produced would again give HCN as shown earlier. The net result would be that each nitrogen atom present would eventually form HCN, as was approached in the reaction of CH_4 under optimum conditions. The fact that only 25% conversion was found provides direct evidence that some reaction, other than the above, must be occurring which consumes N-atoms forming N_2, i.e., catalyzed recombination to N_2.

6. The Disproportionation of Alkyl Radicals and Formation of N_2 in the HCl-catalyzed Reaction of Alkanes with Active Nitrogen

It is known that unsaturated hydrocarbons react much more rapidly with active nitrogen than saturated hydrocarbons(21). Even so, appreciable quantities of C_2H_4 and C_2H_2 are generally found as products in the reactions of saturated hydrocarbons with active nitrogen(21). It appears to the author (and was apparent to Winkler(21)) that the survival of large quantities of C_2H_4 and C_2H_2 in the reaction products is indicative that these unsaturated hydrocarbons are not only formed in these reactions, but are produced by a major reaction. Small quantities would be consumed, if only minor reactions were responsible for the formation of these species.

When a study is made of the possible mechanisms that can be written for the HCl-catalyzed reactions of alkanes, it becomes apparent that whenever hydrocarbons having two or more carbon atoms react with active nitrogen, exothermic reactions that produce unsaturated hydrocarbons become possible. Formation of alkenes can occur either by abstraction of an H-atom from alkyl radicals with simultaneous formation of the alkene:

$$C_2H_5 + N \rightarrow NH + C_2H_4 + 41\ \text{kcal} \quad , \qquad (50)$$

or by disproportionation of two alkyl radicals:

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 + 61\ \text{kcal} \quad . \qquad (51)$$

The latter reaction is well known and has a heat of activation of 0.8 kcal(55). In addition, alkenyl radicals can also undergo the same type reactions, leading to formation of an alkyne:*

$$C_2H_3 + N \rightarrow NH + C_2H_2 + 27\ \text{kcal} \qquad (52)$$

$$C_2H_3 + C_2H_3 \rightarrow C_2H_2 + C_2H_4 + 47\ \text{kcal} \quad . \qquad (53)$$

Methyl radicals, however, cannot react with N-atoms by H-atom abstraction:

$$CH_3 + N \rightarrow NH + CH_2 - 13\ \text{kcal} \quad , \qquad (54)$$

but can result in the formation of unsaturated hydrocarbons:

$$CH_3 + CH_3 \rightarrow CH_4 + CH_2 + 2\ \text{kcal} \qquad (55)$$

$$\rightarrow C_2H_4 + H_2 + 54\ \text{kcal} \qquad (56)$$

$$\rightarrow C_2H_2 + 2H_2 + 8\ \text{kcal} \quad . \qquad (57)$$

It is clear that nitrogen must be formed in subsequent reactions, and not

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*These reactions are energetically possible because each time the bond order is increased a large quantity of energy is released, since the binding energy of the carbon-carbon bond increases with bond order as follows(49):

C-C = 84 kcal ; C=C = 145 kcal ; and C≡C = 194 kcal ,

respectively.

in the primary stop. Therefore, the following mechanism is proposed for the HCl-catalyzed attack of C_2H_6 by N-atoms:

$$C_2H_6 + Cl \rightarrow C_2H_5 + HCl + 2\text{ kcal} \quad . \tag{48}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 + 61\text{ kcal} \quad . \tag{51}$$

$$C_2H_4 \xrightarrow{\text{N-atom reactions}} \text{products (including HCN and } N_2) \text{ .} \tag{58}$$

Winkler has argued(25) that the fact that alkanes yield unsaturated products with the same number of carbon atoms, is evidence that alkyl radicals are not the primary reactants (with N-atoms) in the reactions of alkanes since fragmentation into smaller radicals would then be expected, similar to that given by reaction (49). However, since the primary reaction of alkyl radicals appears to be the formation of an alkene by the disproportionation reaction:

$$C_nH_{2n+1} + C_nH_{2n+1} \rightarrow C_nH_{2n} + C_nH_{2n+2} \quad , \tag{59}$$

prior to any reaction with N-atoms, this argument would not be conclusive. In fact the production of unsaturated hydrocarbons in appreciable amounts, having the same number of carbon atoms as the saturated reactant, even lends support to the present views.

7. The General HCl-catalyzed Reactions of Alkanes with Active Nitrogen

Winkler(22,56) concluded that the reaction of CH_4 with active nitrogen proceeded via a concomitant H-atom attack but did not differentiate the role of H-atoms and N-atoms.

From these HCl-catalysis experiments, clear evidence is obtained why most simple alkanes react only at elevated temperatures. The formation of alkyl radicals in the absence of HCl occurs by attack of H-atoms:

$$RH + H \rightarrow H_2 + R + 2\ \text{kcal} \quad . \tag{17}$$

Reactions such as (17) are known to have heats of activation around 9 kcal(57), while the attack of CH_4 by an H-atom requires a heat of activation of about 11-13 kcal(57). The reactions of alkanes with N-atoms are slow at room temperatures because the slow, rate-determining step is the formation of alkyl radicals by reaction with H-atoms; the reaction of CH_4 is the slowest because this substance requires the largest heat of activation. Once alkyl radicals are produced, however, alkenes are formed, and further very fast radical reactions occur with these alkenes, all of them having heats of activation of a few kcal or less. In addition, when this alkane-active nitrogen mixture is heated and reaction has started, rapid chain branching can occur via H-atoms produced by the subsequent reactions of the alkenes that are formed. These H-atoms react to give additional alkyl radicals and flames are produced.

Considered from this viewpoint, it becomes clear why saturated hydrocarbons such as CH_4, C_2H_6, and C_3H_8 react so rapidly with N-atoms when HCl is added as a catalyst: the heat of activation for the slow, rate-determining step is reduced considerably by substituting Cl-atoms for the H-atoms.

8. The Reaction of Isobutane with Active Nitrogen

Simple alkanes react rapidly with active nitrogen only at elevated temperatures or, if HCl is added as a catalyst, at room temperatures. Isobutane, on the other hand, was found to react rapidly at room temperatures even without HCl catalysis.* This finding is readily explainable.

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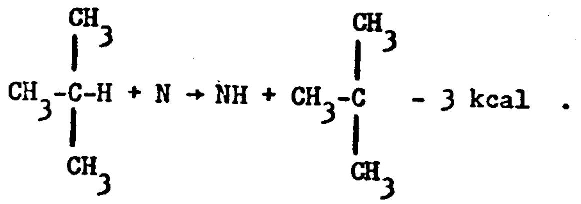
*Winkler studied the reactions of n-butane and isobutane(58) but made no mention of a noticeable difference in reaction rates or NH_3 formation.

Since the binding energy of the carbon-<u>tertiary</u>-hydrogen bond in isobutane is only 89 kcal(59) instead of about 100 kcal for primary H-atoms, the formation of alkyl radicals can occur for this substance by direct reaction with N-atoms <u>at room temperature</u>:



$$CH_3\text{-}\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}}\text{-}H + N \rightarrow NH + CH_3\text{-}\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}} - 3\ \text{kcal} \quad . \qquad (60)$$

These t-butyl radicals can then undergo disproportionation analogous to C_2H_5 radicals:

$$t\text{-}C_4H_9 + t\text{-}C_4H_9 \rightarrow C_4H_8 + C_4H_{10} + \sim 60\ \text{kcal} \quad . \qquad (61)$$

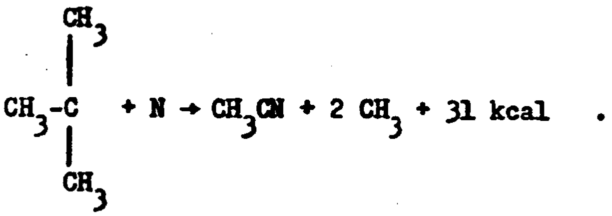
Evidence that t-butyl radicals are indeed formed in a direct reaction with N-atoms is given by the experimental finding of large quantities of NH_3 as a product of this reaction. See Table XX. If large quantities of NH radicals were produced by reaction (60), these would be expected to lead to eventual formation of NH_3.

If this is the case, alkanes having secondary H-atoms might be expected to lead to formation of smaller quantities of NH_3 since secondary H-atoms are bound intermediate between primary and tertiary H-atoms. Exactly this behavior was observed for n-butane and neo-pentane. See Tables <u>XIX</u> and <u>XXI</u>.

Another interesting finding is that considerable quantities of CH_3CN were found as a product of the isobutane reaction and for the n-butane reaction. This finding shows that not only do the proposed disproportionation reactions occur:

$$C_4H_9 + C_4H_9 \rightarrow C_4H_8 + C_4H_{10} + \sim 60\ \text{kcal} \quad , \qquad (61a)$$

but, for large alkyl radicals at least, direct reaction with N-atoms, leading to fragmentation, can also occur:



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} + N \rightarrow CH_3CN + 2\ CH_3 + 31\ \text{kcal} \quad . \qquad (62)$$

9. The Production of CH-radicals and Reaction with NH_3

A very interesting phenomenon was found in this laboratory when NH_3 was added upstream from the C_2H_2 reaction flame. NH_3 was found to be consumed with almost quantitative formation of HCN and H_2. This finding suggested that the following reaction, although spin forbidden and slightly endothermic, occurred to a fair extent:

$$C_2H_2 + N \rightarrow HCN + CH - 2 \text{ to } - 5\ \text{kcal} \quad , \qquad (21)$$

followed by:

$$CH + NH_3 \rightarrow HCN + H_2 + H + 51\ \text{kcal} \quad . \qquad (22)$$

CH-radicals are known to be present in many systems, especially in hydrocarbon reactions with O-atoms(39) (the blue Bunsen burner flame is due to the emission of CH-bands). Under favorable conditions, H-atoms also react with hydrocarbons, giving small amounts of CH-radicals(39). Therefore, CH-radicals were produced by reacting O- or H-atoms with C_2H_4 and C_2H_2; NH_3, added to these reactions, produced HCN in the <u>absence</u> of N-atoms. These findings indicate that, most likely, CH-radicals are the reactive species responsible for destruction of NH_3, the overall reaction leading to formation of HCN and H_2.

An estimate of the overall rate constant for the consumption of NH_3 or production of HCN when NH_3 is added to the C_2H_2-N-atom reaction flame was obtained as follows. The partial pressures of both HCN and NH_3 were about 1% of the total pressure, which was approximately 0.3 mm Hg. As will become apparent later, the partial pressure of CH should be about one-half that of HCN, or about 0.5% of the total pressure. Therefore:

$$P = 0.3 \text{ mm Hg} \sim 10^{16} \text{ particles/cm}^3$$

$$NH_3 \sim 10^{14} \text{ particles/cm}^3$$

$$HCN \sim 10^{14} \text{ particles/cm}^3$$

$$CH \sim 5 \times 10^{13} \text{ particles/cm}^3 \quad .$$

But: $$HCN \sim 10^{14} \text{ particles/cm}^3 = \frac{d(HCN)}{3 \times 10^{-2} \text{ sec}}$$

$$= 3 \times 10^{15} \text{ particles/cm}^3\text{-sec} \quad .$$

Therefore:

$$+\frac{d(HCN)}{dt} = k(CH)(NH_3)$$

$$3 \times 10^{15} = k \cdot 5 \times 10^{13} \cdot 10^{14}$$

$$k = 6 \times 10^{-13} \pm 1 \frac{\text{cm}^3}{\text{particles-sec}} \quad ,$$

approximately the same order of magnitude as the overall reaction of C_2H_4 with active nitrogen ($k = 1.6 \times 10^{-13} \frac{\text{cm}^3}{\text{particles-sec}}$)(61,62).

10. The Formation of NH_3 in the Reaction of C_2H_4 with Active Nitrogen*

Prior to this work, NH_3 was generally reported to be found only

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*The formation of NH_3 in the C_3H_6 reaction is more complicated, and is briefly discussed in Appendix II.

as a minor product(21) of the reactions of hydrocarbons with active nitrogen under conditions of complete reaction. Under non-flame conditions, however, NH_3 was found to be produced as a major product of the C_2H_4 reaction, being formed in quantities comparable to HCN as shown in Fig. 26 and Table V. As increasing concentrations of C_2H_4 were added to the active nitrogen, the rate of production of NH_3 increased and went through a maximum, eventually dropping to zero when flame conditions were reached. This result is similar to the semi-quantitative results recently reported by Winkler(62) for the reaction of C_2H_4 at 440°C although his results were not treated in any detail.

When small amounts of O-atoms were added to the C_2H_4 reaction under these non-flame conditions (with simultaneous decrease of N-atoms), a relatively large increase in NH_3 formation was found, the NH_3 production again going through a maximum, and dropping to zero as the O-atom concentration increased. See Figs. 27 to 29 and Tables VII to X. Since the addition of small amounts of O-atoms results in a relatively large increase in the formation of NH_3, the production must proceed by a chain mechanism.

In the non-flame region, where the C_2H_4 present is insufficien to completely consume N-atoms, hydrocarbon radicals and H-atoms are present in small concentrations (relative to the flame region). In this region NH_3 might be produced from reactions involving NH and NH_2 radicals in reactions such as the following:

$$NH + NH \rightarrow NH_2 + N + 2\ \text{kcal} \qquad (63)$$

$$NH + NH_2 \rightarrow NH_3 + N + 18\ \text{kcal}\ . \qquad (64)$$

It should be pointed out that these reactions are given only as examples since the mechanisms whereby NH_3 is produced from these nitrogen hydrides under these conditions where hydrocarbon radicals are present are not known and no definite reactions can be given as being responsible for NH_3 formation.

The relatively large increase in NH_3 production when small amounts of O-atoms were added under non-flame conditions probably is due to an increase in the number of radicals which can initiate chains. Additional C_2H_3 radicals could again be produced as previously given, via:

$$C_2H_4 + O \rightarrow C_2H_3 + OH + 1 \text{ kcal} \tag{30}$$

$$OH + C_2H_4 \rightarrow C_2H_3 + H_2O + 17 \text{ kcal} \quad . \tag{31}$$

These additional C_2H_3 radicals can then lead to formation of NH and NH_2 radicals by reactions such as:

$$C_2H_3 + N \rightarrow NH + C_2H_2 + 27 \text{ kcal}^{(37)} \tag{52}$$

$$NH + C_2H_3 \rightarrow NH_2 + C_2H_2 + 37 \text{ kcal} \quad . \tag{65}$$

NH_3 could then eventually be produced by subsequent reactions of NH and NH_2.

Under <u>flame</u> conditions, no NH_3 was found as a product. Winkler claimed(22) that the fact that only minor quantities of NH_3 are found, under conditions of complete consumption of N-atoms, is evidence against NH formation in these reactions since an accumulation of NH radicals would be expected to lead to formation of NH_3. Under these conditions, however, large concentrations of hydrocarbon radicals and H-atoms must be present in the reaction zone and therefore, several possibilities arise as to why no NH_3 is found under flame conditions. The NH and NH_2 radicals, as well as NH_3

itself, should readily react with some of the radicals present in the reaction flames. H-atoms are very likely to consume NH via:

$$H + NH \rightarrow H_2 + N + 17\ \text{kcal} \quad . \qquad (66)$$

The CH radical, as mentioned in the last section, was concluded to be the species responsible for consuming NH_3, when this substance was added to the C_2H_2-active nitrogen flame zone, giving HCN and H_2 via the reaction

$$CH + NH_3 \rightarrow HCN + H_2 + H + 51\ \text{kcal} \quad . \qquad (22)$$

This radical might conceivably also attack NH and NH_2 by:

$$CH + NH \rightarrow HCN + H + 140\ \text{kcal} \qquad (67)$$

$$CH + NH_2 \rightarrow HCN + 2H + 52\ \text{kcal} \ . \qquad (68)$$

In addition, the rate constant for the consumption of NH_3 by CH radicals was found to be about the same as that for the overall reaction of C_2H_4 with N-atoms and any CH radicals that might be produced in these reactions should consume at least part of any NH_3 that might be produced under flame conditions. Further, the possibility exists that under flame conditions a different chain mechanism exists that does not produce NH radicals (and therefore NH_3).

Winkler found(46) that the addition of NH_3 upstream from the C_2H_4 reaction flame leads to a slight increase in HCN production. This was attributed(63) to wall poisoning by the NH_3 against recombination of N-atoms, the slightly higher N-atom concentration giving slightly greater HCN production. However, the author's CH experiments make it appear more likely that the explanation for this behavior is that CH, or some similar radical such as C, CH_2, CH_3, etc. is producing HCN from the NH_3.

Summarizing the above discussion, it is obvious that the formation of NH_3 is complicated and involves many reactions of nitrogen hydrides, hydrocarbon radicals and H-atoms. However, two conclusions can be drawn concerning the mechanism whereby NH_3 is produced. (1) Under non-flame conditions, the concentration of radicals which can consume nitrogen hydrides is low and NH_3 formation occurs. (2) Under flame conditions, the concentration of radicals and H-atoms is relatively large and the many radical reactions that are energetically possible, such as those with CH reported in this work, can lead to consumption of nitrogen hydrides as well as NH_3 itself. The interreactions, however, of these nitrogen hydrides and radicals are not well enough known to allow any one unequivocal choice of mechanism at this time.

C. The Proposed Mechanisms for the Reactions of Hydrocarbons with Active Nitrogen

It is well known from combustion experiments that the oxidation reactions of even the most simple hydrocarbons are complicated and that there are a series of initiating steps that start the chain reactions. One of the outstanding features of these oxidations is the transition from reactions having limited chain lengths to reactions that appear to be highly branching, i.e., flame reactions(64). Analogous behavior seems to prevail in the reactions of hydrocarbons with active nitrogen. The discussion of these reaction mechanisms will primarily be concentrated on the reaction of C_2H_4 since the reaction of this substance with active nitrogen has been thoroughly investigated by Winkler and the mechanism proposed for this substance will be seen to be quite adequate to explain the reactions of other hydrocarbons.

The author's observations show that the reaction of C_2H_4 with active nitrogen can be classified into three categories, according to conditions:

A. "Initial" non-flame conditions where only a small quantity of hydrocarbon is added and the concentration of H-atoms and radicals is only minor ($N \gg C_2H_4$);

B. non-flame conditions where the radical concentration has increased to an extent that a reasonable extent of reaction occurs, but the reaction is still incomplete and ($N > C_2H_4$);

C. flame conditions where high radical concentrations prevail and reaction is complete ($C_2H_4 > N$).

It appears that even "pure" C_2H_4 reacts with "clean" active nitrogen, i.e., under initial non-flame conditions when only a small amount of hydrocarbon is added and only minor amounts of H- or C-atoms are present.

The fact that reaction occurs even under these conditions (condition A.) of low radical concentration suggests that a direct reaction with N-atoms such as the following occurs which can initiate further radical reactions:

$$\text{A.} \quad C_2H_4 + N \rightarrow C_2H_2 + NH_2 + 25 \text{ kcal.} \qquad (39)$$

This reaction has two features that are favorable to explain the behavior of the reaction under these "initial" non-flame conditions. First, the production of NH_3 under these conditions can be accounted for via the formation of NH_2 radicals and, as will be seen, as soon as C_2H_2 is formed, HCN can be produced by the reaction of this substance with N-atoms. This initial reaction, however, only appears to occur as an initiation step and no further discussion will be given to this reaction.

H- or O-atoms were found to enhance the reaction of N-atoms with C_2H_4 under non-flame conditions (condition B.). The only explanation for this behavior is that O- or H-atoms first attack C_2H_4 giving C_2H_3 and either OH or H_2:

$$C_2H_4 + O \rightarrow C_2H_3 + OH + 1\ \text{kcal} \tag{30}$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 + 3\ \text{kcal}\ . \tag{38}$$

Under non-flame conditions, these C_2H_3 radicals can then react with N-atoms as follows:

$$C_2H_3 + N \rightarrow NH + C_2H_2 + 27\ \text{kcal}\ . \tag{52}$$

This NH radical might eventually lead either to the observed NH_3 formation under these conditions or be consumed by atom and radical reactions as flame conditions are approached.

The author concludes that the primary formation of HCN occurs via C_2H_2, formed as a product in a prior reaction, such as (52) above. This C_2H_2 can react with N-atoms in <u>two</u> ways:

$$C_2H_2 + N \rightarrow HCN + CH - 2\ \text{to} - 5\ \text{kcal} \tag{21}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H + 2\text{-}7\ \text{kcal}\ . \tag{69}$$

Reaction (21) is spin forbidden and slightly endothermic but may still occur since the experimental findings are very well explained if it is assumed that the reaction occurs to a reasonable extent. Reaction (69) appears to satisfy the chain-branching behavior of the reactions under flame conditions since <u>two</u> new radicals are produced as opposed to <u>one</u> for reaction (21). In addition, the CN radiation observed under these flame conditions can also be readily explained by further reactions of the CH-CN radical.

The overall behavior of the reaction of C_2H_4 with active nitrogen suggests that the reaction proceeds via different parallel reactions depending upon conditions, i.e., under non-flame conditions a different reaction scheme appears to predominate than under flame conditions. A reaction scheme such as the following can be given for these non-flame conditions where a reasonable extent of reaction occurs but where not enough C_2H_4 is present to give complete consumption of N-atoms (condition B.):

B. a) $H + C_2H_4 \rightarrow H_2 + C_2H_3 + 3\ \text{kcal}$ (38)

b)
$$C_2H_3 + N \begin{array}{ll} \nearrow HCN + CH_2 + 61\ \text{kcal} & (40) \\ \rightarrow NH_2 + C_2H + 23\ \text{kcal} & (70) \\ \searrow NH + C_2H_2 + 27\ \text{kcal} & (52) \end{array}$$

c) $C_2H_2 + N \rightarrow HCN + CH - 2\ \text{to} - 5\ \text{kcal}$ (21)

d) $CH + C_2H_4 \rightarrow C_2H_3 + CH_2 + 16\ \text{kcal}$ (71)

e) $CH_2 + N \rightarrow HCN + H + 113\ \text{kcal}$ (34)

f) $C_2H_4 + H \rightarrow C_2H_3 + H_2 + 3\ \text{kcal}$ (38)

This scheme appears plausible to explain the behavior observed under non-flame conditions, since the radicals formed may react with themselves and reduce the concentration of chain carriers to an extent that rapid chain branching (and therefore, flames) do not occur.

Under flame conditions (condition C.), a different scheme, (with <u>C-atoms</u> as the chain carriers appears to occur:*

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*The kinetics of C-atom formation will be given later.

C. a) $C + C_2H_4 \rightarrow C_2H_2 + CH_2 + 45\ \mathrm{kcal}$ (72)

b) $C_2H_2 + N \rightarrow CH\text{-}CN + H + 2\text{-}7\ \mathrm{kcal}$ (69)

c) $CH\text{-}CN + N \rightarrow HCN + \underset{\searrow h\nu}{CN^*} + 98\ \mathrm{kcal}$ (73)

d) $CN + N \rightarrow N_2 + C + 38\ \mathrm{kcal}$ (74)

e) $CH_2 + N \rightarrow HCN + H + 113\ \mathrm{kcal}$ (34)

f) $C + C_2H_4 \rightarrow C_2H_2 + CH_2 + 45\ \mathrm{kcal}$. (72)

This scheme explains the flame behavior of the reactions under these conditions since the overall reaction is now seen to be highly branching. In addition, the relatively strong CN radiation observed under these conditions can also be explained by this reaction mechanism.

Evidence for a transition from one mechanism to another is given by the pulsating flame front observed with the C_2H_4 reaction and described earlier. It appears that the conditions under which this pulsation is observed are such that an extremely rapid transition from a reasonably fast chain reaction (but with limited chain length), to a branching chain reaction, occurs.

The major features of the limited chain length reaction observed under non-flame conditions are very well explained by scheme (B) while (C) adequately explains the extremely fast, pulsating flame that was obserbed to propagate through the C_2H_4-active nitrogen reaction at the transition region.

This transition from (B) to (C) would be expected to occur because, as increasing quantities of hydrocarbon are added to the active nitrogen, the reaction proceeds faster and the concentration of radicals increases.

When small amounts of hydrocarbon are present, the concentration of radicals is relatively small and only a limited amount of reaction can occur. At some critical point, however, certain radical reactions attain predominance and lead to the observed transition to a different mechanism. Different reactions consuming and producing radicals that occur under flame conditions might not occur under non-flame conditions. If this is the case, then a different chain mechanism with different chain carriers would occur under non-flame conditions than under flame conditions. It is seen that this transition from one mechanism to another would be expected to occur quite naturally. For example, the following might occur:

$$\mathrm{CH + CH \rightarrow CH_2 + C + 34\ kcal} \qquad (75)$$

$$\mathrm{CH + C_2H_3 \rightarrow C_2H_4 + C + 18\ kcal} \qquad (76)$$

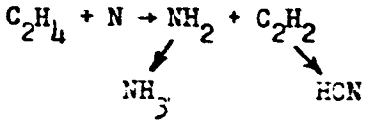
$$\mathrm{CH + H \rightarrow H_2 + C + 23\ kcal} \qquad (77)$$

Obviously, as soon as these conditions are reached, the transition to scheme (C) can occur. If the reaction is approached from the opposite direction, i.e., the amount of hydrocarbon is reduced, the flame reaction does not continue but the transition to the non-flame reaction occurs. This transition in the reverse direction can occur via reactions such as:

$$\mathrm{H + C_2H_4 \rightarrow H_2 + C_2H_3 + 3\ kcal} \qquad (38)$$

This C_2H_3, once formed, can then react according to scheme (B). The reaction of C_2H_4 with active nitrogen can now be given as:

A. "initial" non-flame conditions; $C_2H_4 << N$ (no radicals):



$$\mathrm{C_2H_4 + N \rightarrow \underset{\underset{NH_3}{\swarrow}}{NH_2} + \underset{\underset{HCN}{\searrow}}{C_2H_2}} \qquad (39)$$

B. "non-flame" conditions; $C_2H_4 < N$ (low radical concentration):

a) $H + C_2H_4 \rightarrow H_2 + C_2H_3$ (38)

b)

$$\begin{tikzcd}
 & HCN + CH_2 \quad (40) & \\
C_2H_3 + N \arrow[ur] \arrow[r] \arrow[dr] & NH_2 + C_2H \quad (70) & \\
 & NH + C_2H_2 \quad (52) \arrow[dr] & \\
 & & NH_3
\end{tikzcd}$$

c) $C_2H_2 + N \rightarrow HCN + CH$ (21)

d) $CH + C_2H_4 \rightarrow C_2H_3 + CH_2$ (71)

e) $CH_2 + N \rightarrow HCN + H$ (34)

f) $C_2H_4 + H \rightarrow H_2 + C_2H_3$ (38)

"transition region"

$CH + CH \rightarrow CH_2 + C$ (75)

$CH + H \rightarrow H_2 + C$ (77)

$CH + C_2H_3 \rightarrow C + C_2H_4$, etc. (76)

C. "flame" conditions; $C_2H_4 > N$ (high radical concentration):

a) $C + C_2H_4 \rightarrow C_2H_2 + CH_2$ (72)

b) $C_2H_2 + N \rightarrow CH\text{-}CN + H$ (69)

c)

$$\begin{tikzcd}
CH\text{-}CN + N \rightarrow HCN + CN^{*} \arrow[dr] & \\
 & h\nu
\end{tikzcd}$$

(73)

d) $CN + N \rightarrow N_2 + C$ (74)

e) $CH_2 + N \rightarrow HCN + H$ (34)

f) $C + C_2H_4 \rightarrow C_2H_2 + CH_2$ (72)

Since the reactions of C_2H_2 with active nitrogen are approximately thermally neutral, the above transition mechanism could occur if it is assumed that reaction (21)* which is slightly endothermic

$$C_2H_2 + N \rightarrow HCN + CH - 2 \text{ to } - 5 \text{ kcal} \quad , \qquad (21)$$

has practically no heat of activation while reaction (69) which is exothermic:

$$C_2H_2 + N \rightarrow CH\text{-}CN + H + 2\text{-}7 \text{ kcal} \quad , \qquad (69)$$

has a slight heat of activation. One objection that can be raised to scheme (C) is that no direct experimental evidence is available for the reactions of C-atoms with hydrocarbons. However, it is apparent to both Winkler and the author, despite differences in mechanisms assigned to the reactions, that the reactions of hydrocarbons with active nitrogen proceed via an initial degradation forming either HCN (Winkler) or C_2H_2 (the author). Except for this objection, this mechanism fulfills all the requirements needed to explain the experimental findings of both Winkler and the author, including the discrepancy obtained when attempts are made to determine N-atom concentrations by NO titration and by C_2H_4 titration. This latter discrepancy arises not because of reaction of NO with excited N_2 molecules, but because only a fraction of the N-atoms present are converted to HCN, the remainder form N_2 via reactions such as:

$$CN + N \rightarrow N_2 + C \quad . \qquad (74)$$

---

*Reaction (21) is also spin forbidden, but still appears likely. However, a similar parallel reaction which has not been considered may occur in an analogous manner.

At first it seemed that the reaction:

$$N + NH \rightarrow N_2 + H + 139\ \text{kcal} \quad , \qquad (78)$$

as applied under scheme (B) as follows might account for the formation of N_2 and therefore only incomplete conversion of N-atoms to HCN:

$$CH + C_2H_4 \rightarrow C_2H_3 + CH_2 + 16\ \text{kcal} \qquad (71)$$

$$C_2H_3 + N \rightarrow NH + C_2H_2 + 27\ \text{kcal} \qquad (52)$$

$$N + NH \rightarrow N_2 + H + 139\ \text{kcal} \qquad (78)$$

$$C_2H_2 + N \rightarrow HCN + CH - 2\ \text{to} - 5\ \text{kcal} \qquad (21)$$

$$CH_2 + N \rightarrow HCN + H + 113\ \text{kcal} \quad . \qquad (34)$$

This may indeed be partially the case but difficulties arise when NH_3 formation is considered. If N_2 formation occurred only by this reaction, it is difficult to understand why NH_3 is produced via NH radicals under non-flame conditions while N_2 is produced from this same radical under flame conditions.

The reactions of higher alkenes also appear to occur via similar mechanisms. In the case of each hydrocarbon studied, an abrupt transition from non-flame to flame conditions was observed, although the oscillating flame front itself was only observed by the author with C_2H_4. No attempt will be made to give mechanisms for the non-flame reactions of each of these higher alkenes, since the reactions obviously are complicated.

The reactions of C-atoms or CH radicals with C_2H_4 were previously written as follows:

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 + 45\ \text{kcal} \qquad (72)$$

$$CH + C_2H_4 \rightarrow C_2H_3 + CH_2 + 16\ \text{kcal} \quad . \qquad (71)$$

Because of the symmetry of the C_2H_4 molecule, these reactions can be looked upon as either abstraction of H_2 or an H-atom, or as detachment of CH_2. However, when the reactions of higher alkenes are considered, consistent stoichiometry is obtained if these reactions are postulated to occur by <u>detachment</u> of CH_2 rather than abstraction of H_2 or H.* It is clear that if this same detachment of CH_2 occurred with a higher alkene, the same species, i.e., C_2H_2 and C_2H_3, and the next lower alkene would always be formed, viz:

$$C + CH_3CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 + 106\text{ kcal} \tag{79}$$

$$CH + CH_3CH{=}CH_2 \rightarrow C_2H_3 + C_2H_4 + 77\text{ kcal} \tag{80}$$

$$C + C_4H_8 \rightarrow C_2H_2 + C_3H_6 + 94\text{ kcal} \tag{81}$$

$$CH + C_4H_8 \rightarrow C_2H_3 + C_3H_6 + 65\text{ kcal}\text{ , etc.} \tag{82}$$

This lower alkene could then be further degraded to the next lower alkene until eventually the lowest alkene, C_2H_4, is produced. It should be noticed that this degradation occurs prior to HCN formation and does not involve reactions with N-atoms. The C_2H_2, C_2H_3 and C_2H_4 produced could then react with N-atoms according to the scheme already proposed. It is because of this degradation to the <u>same</u> hydrocarbon products that several alkenes exhibit similar behavior in their reactions with active nitrogen. In addition, it becomes clear why appreciable quantities of C_2H_4 and C_2H_2 are found as products of the reactions. Also, several alkenes give approxi-

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*See Appendix III for a discussion of analogous CH_2 detachments in the reactions of O-atoms with alkenes.

mately the same conversion of N-atoms to HCN as C_2H_4 because HCN and N_2 are produced by the further reactions of either C_2H_2 or C_2H_3 with N-atoms, and not of the parent alkene. Approximately the same amount of N_2 is always produced by these reactions of C_2H_2 or C_2H_3 with N-atoms, the only difference being that higher alkenes are degraded to C_2H_3 or C_2H_2 prior to any reaction with N-atoms.

The reactions of alkanes exhibit behavior similar to those of the alkenes since they proceed via the initial production of large concentrations of alkyl radicals, produced by hydrogen atom attack, with subsequent formation of alkenes. The formation of these alkenes occurs by direct reaction of two alkyl radicals:

$$C_nH_{2n+2} + H \rightarrow H_2 + C_nH_{2n+1} + 3 \text{ kcal} \qquad (83)$$

$$C_nH_{2n+1} + C_nH_{2n+1} \rightarrow C_nH_{2n} + C_nH_{2n+2} + \sim 60 \text{ kcal} \qquad (59)$$

$$C_nH_{2n} \rightarrow \text{alkene reactions} . \qquad (84)$$

Abbreviated reaction mechanisms will be given for several hydrocarbons before any further discussion, in order to familiarize the reader with the general trend of the reaction mechanisms proposed to occur under flame conditions.

1. C_2H_4

$$C + CH_2{=}CH_2 \rightarrow C_2H_2 + CH_2 \qquad (72)$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \qquad (69)$$

$$CH\text{-}CN + N \rightarrow HCN + CN \qquad (73)$$

1st degradation

$$CN + N \rightarrow N_2 + C \qquad (74)$$

$$CH_2 + N \rightarrow HCN + H \qquad (34)$$

The overall stoichiometry for this mechanism is:

$$C_2H_4 + 4N \rightarrow 2HCN + N_2 + H_2 \qquad (85)$$

2. C_3H_6

$$C + CH_3\text{-}CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 \qquad (79)$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \qquad (69)$$

1st degradation

$$CH\text{-}CN + N \rightarrow HCN + CN \qquad (73)$$

$$CN + N \rightarrow N_2 + C \qquad (74)$$

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 \qquad (72)$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \qquad (69)$$

$$CH\text{-}CN + N \rightarrow HCN + CN \qquad (73)$$

2nd degradation

$$CN + N \rightarrow N_2 + C \qquad (74)$$

$$CH_2 + N \rightarrow HCN + H \qquad (34)$$

The net stoichiometry for this mechanism is given by:

$$C_3H_6 + 7N \rightarrow 3HCN + 2N_2 + \frac{3}{2} H_2 \qquad (86)$$

3. <u>but-1-ene</u>

$$C + CH_3\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow C_2H_2 + CH_3\text{-}CH{=}CH_2 \tag{87}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

<u>1st degradation</u>

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$C + CH_3\text{-}CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 \tag{79}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

2nd degradation

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 \tag{72}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

<u>3rd degradation</u>

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$CH_2 + N \rightarrow HCN + H \tag{34}$$

Overall:

$$C_4H_8 + 10N \rightarrow 4HCN + 3N_2 + 2H_2 \tag{88}$$

4. **but-2-ene**

$$C + CH_3\text{-}CH{=}CH\text{-}CH_3 \rightarrow C_2H_2 + CH_2{=}CH\text{-}CH_3 \tag{89}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

1st degradation

$$C + CH_3\text{-}CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 \tag{79}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

2nd degradation

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 \tag{72}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

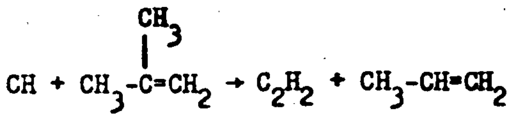
$$CH_2 + N \rightarrow HCN + H \tag{34}$$

3rd degradation

Overall:

$$C_4H_8 + 10N \rightarrow 4HCN + 3N_2 + 2H_2 \tag{88}$$

5. <u>iso-butylene</u>



$$CH + CH_3\text{-}\overset{\overset{\Large CH_3}{|}}{C}{=}CH_2 \rightarrow C_2H_2 + CH_3\text{-}CH{=}CH_2 \tag{90}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

<u>1st degradation</u>

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$C + CH_3\text{-}CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 \tag{79}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

<u>2nd degradation</u>

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 \tag{72}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \tag{69}$$

<u>3rd degradation</u>

$$CH\text{-}CN + N \rightarrow HCN + CN \tag{73}$$

$$CN + N \rightarrow N_2 + C \tag{74}$$

$$CH_2 + N \rightarrow HCN + H \tag{34}$$

Overall:

$$C_4H_8 + 10N \rightarrow 4HCN + 3N_2 + 2H_2 \tag{88}$$

It is seen that all three isobutenes lead to the same formation of HCN and consumption of N-atoms. This is because the C-atom attacks at the carbon-carbon <u>single</u> bond, detaching CH_2 and forming the next lower alkene.

6. <u>CH_4</u>

The reaction of CH_4 deserves special attention and will be discussed in detail later.

7. C_2H_6

$$2C_2H_6 + 2H \rightarrow 2C_2H_5 + 2H_2 \qquad (91)$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad (51)$$

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2 \qquad (72)$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H \qquad (69)$$

$$CH\text{-}CN + N \rightarrow HCN + CN \qquad \underline{\text{1st degradation}} \qquad (73)$$

$$CN + N \rightarrow N_2 + C \qquad (74)$$

$$CH_2 + N \rightarrow HCN + H \qquad (34)$$

Overall:

$$C_2H_6 + 4N \rightarrow 2HCN + N_2 + 2H_2 \qquad (92)$$

8. n-butane

$$2C_4H_{10} + 2H \rightarrow 2C_4H_9 + 2H_2 \qquad (93)$$

$$C_4H_9 + C_4H_9 \rightarrow C_4H_8 + C_4H_{10} \qquad (61a)$$

The C_4H_8 formed then reacts as given previously, according to the following net stoichiometry:

$$C_4H_8 + 10N \rightarrow 4HCN + 3N_2 + 2H_2 \quad . \qquad (88)$$

The overall stoichiometry for the n-butane reaction therefore is:

$$C_4H_{10} + 10N \rightarrow 4HCN + 3N_2 + 3H_2 \quad . \qquad (94)$$

It can be seen that the reason that alkanes give the same stoichiometry for formation of HCN and N_2 as alkenes is because alkyl radicals react rapidly with each other giving alkenes, prior to any reaction with N-atoms.

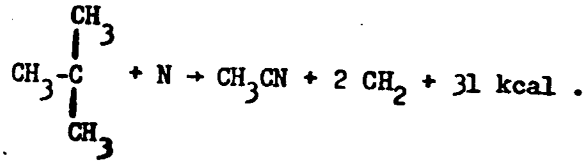
Most of the major features of the reactions of hydrocarbons with active nitrogen, i.e., approximately constant HCN formation, approximately constant N_2 formation, and the flame behavior of the reactions, can readily be explained without recourse to initial formation of a complex.

These reaction schemes are undoubtedly overly simplified and the overall reactions appear to be more complicated as is evidenced by the fact that HCN also may be produced by reactions that have not been considered. One such reaction:

$$CH + NH_3 \rightarrow HCN + H_2 + H + 51\ \text{kcal} \qquad (22)$$

was found by the author when NH_3 was added to the flame zone of the C_2H_2-active nitrogen reaction.

Another example is direct reaction of t-butyl radicals with N-atoms, leading to fragmentation:



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} + N \rightarrow CH_3CN + 2\ CH_2 + 31\ \text{kcal}\ . \qquad (62)$$

Other reactions undoubtedly occur.

D. The Approximate Constance of the Ratio: NO Consumed to Maximum HCN Obtainable from Hydrocarbons

The results of this study suggest that metastable $N_2(A^3\Sigma_u^+)$ molecules do not contribute appreciably to the chemical reactivity of active nitrogen. In addition, nitrogen can be produced by several reactions when hydrocarbons react with active nitrogen. Therefore, the overwhelming evidence makes it appear that the correct value for the N-atom concentration in active nitrogen corresponds to the consumption of NO and not the formation of HCN, when NO and C_2H_4 are used to measure N-atom concentrations, respectively. Winkler found that the ratio of NO consumed by N-atoms, to the maximum obtainable HCN from hydrocarbons, was approximately the same for several different hydrocarbons(24). In addition, the data of Winkler(65) show that the ratio is approximately temperature independent.

The temperature independence follows from the fact that all of the proposed radical reactions of alkenes would be expected to have heats of activation, of a few kcal or less. In addition, all of the degradation steps, regardless of the hydrocarbon, always consume 3 N-atoms, giving N_2 and HCN. The only net difference in the overall stoichiometry of hydrocarbon reactions would be the amount of hydrocarbon consumed, as was found experimentally. For every carbon atom present, one degradation step occurs with subsequent formation of N_2 and HCN via C_2H_2, the only difference being that the higher the hydrocarbon, the larger the number of degradation steps. Each degradation step consumes three N-atoms giving one N_2 molecule and one HCN molecule. The total number of HCN molecules produced is equal to the number of degradation steps, <u>plus one</u>. The additional one must be added because the degradation of alkenes by successive detachment of CH_2 groups eventually leads to formation of the lowest alkene, C_2H_4. Attack of C, or CH, on the lowest alkene, C_2H_4, again can lead to detachment of CH_2. However, one <u>additional</u> CH_2 radical is produced, which leads to formation of HCN from the last remaining carbon atom:

$$C + C_2H_4 \rightarrow C_2H_2 + \underline{CH_2} + 45 \text{ kcal} \qquad (72)$$

$$CH + C_2H_4 \rightarrow C_2H_3 + \underline{CH_2} + 16 \text{ kcal} \qquad (71)$$

$$\underline{CH_2} + N \rightarrow HCN + H + 113 \text{ kcal} \quad . \qquad (34)$$

In addition, it makes no difference how this last HCN-forming step occurs. Alternate to reaction (34), the CH_2-radical may first attack other species present such as the alkene molecule:

$$CH_2 + C_2H_4 \rightarrow CH_3 + C_2H_3 + \sim 0 \text{ kcal} \qquad (95)$$

$$CH_2 + C_3H_6 \rightarrow CH_3 + C_3H_5 + \sim 0 \text{ kcal} \text{ , etc.,} \qquad (96)$$

and the same overall stoichiometry results, since the CH_3-radical again can lead to formation of HCN:

$$CH_3 + N \rightarrow HCN + 2H + 13 \text{ kcal} \quad . \qquad (29)$$

From these considerations, the approximate constancy of the maximum amount of HCN available from several hydrocarbons is readily explained. It is obvious that 3 N-atoms are consumed, forming 1 N_2 and 1 HCN, from the C_2H_2 produced in each degradation step. In addition, an N-atom is also consumed in the degradation of C_2H_4 via formation of HCN from CH_2, in the last step, as shown above. Therefore, the general relationships involved are:

Number of N-atoms consumed = [3(No. of degradation steps)+1]

= [2(No. of carbon atoms-1)+(No. of carbon atoms)];

and

$$\text{Number of HCN molecules formed} = [\text{No. of degradation steps} + 1]$$

$$= \text{No. of carbon atoms}.$$

In the limiting case, where the number of carbon atoms is large and many degradation steps occur, the consumption of the last N-atom via CH_2 with formation of 1 HCN is negligible, compared with the consumption of N-atoms, and HCN production, via a large number of degradation steps. Therefore, it is seen that all alkenes would give the same ratio of N-atoms consumed to HCN formed and is equal to:

$$\frac{\text{No. of N-atoms consumed}}{\text{No. of HCN formed}} = \frac{3(\text{Number of degradation steps})}{(\text{Number of degradation steps})}$$

$$= \frac{2(\text{No. of carbon atoms}) + \text{Number of carbon atoms}}{\text{Number of carbon atoms}} = \frac{3}{1} \; ;$$

i.e., only one-third of the N-atoms consumed form HCN. Support for this view is given by the decreasing conversion of N-atoms to HCN with increasing size of the hydrocarbon in the author's HCl-catalysis experiments. C_2H_6 gave 25% conversion of N-atoms to HCN while neo-C_5H_{12} gave only 15%, under identical conditions. See Tables XVII to XXI.

The fact that the author generally found about 40 to 50% conversion of N-atoms to HCN with alkenes and approximately the same HCN from several hydrocarbons is fortuitous. With these lower alkenes, the limiting case cannot be applied, since the one extra N-atom consumed by CH_2, and subsequent HCN formation, accounts for an appreciable fraction of the overall reaction stoichiometry. The proposed reaction mechanism applied to the first three alkenes, C_2H_4, C_3H_6 and C_4H_8, would give ratios of NO consumed to HCN produced of: 4/2, 7/3 and 10/4, respectively. The ratios obtained experimentally in this laboratory for C_2H_4 and C_2H_6 were: 4/1.8 and 7/3.2. This is in excellent agreement with the proposed mechanism since polymer formation and the effect of side reactions (to be discussed later) are not included in the reaction mechanisms.

A number of alkanes, with the exception of CH_4, give the same conversion of N-atoms to HCN as alkenes, as was found by Winkler(24). This follows since the primary formation and reaction of alkyl radicals does not consume N-atoms or form HCN, but leads directly to formation of an alkene by the disproportionation reaction:

$$C_nH_{2n+1} + C_nH_{2n+1} \rightarrow C_nH_{2n} + C_nH_{2n+2} + \sim 60 \text{ kcal} \quad . \qquad (59)$$

It is these alkenes which then react with N-atoms according to the proposed degradation mechanisms.

E. The Formation of Polymers and Condensation Products in the Reactions of Hydrocarbons with Active Nitrogen

Under non-flame conditions hydrocarbons are almost completely consumed in the reactions with active nitrogen, even at the low pressures and short reaction times used in this study. It was found for C_2H_4 under non-flame conditions that 1/6 of the carbon that was consumed could not be accounted for in the products of the reaction.[*] See Fig. 24. The loss of carbon most likely occurs via diffusion to the walls of species stable toward

---

[*] In this non-flame region, in contrast to the flame region, no difficulties were encountered in the mechanical operations of obtaining material balances, i.e., only one volatile carbon-containing product was obtained, HCN; no products giving complex, overlapping spectra with interfering peaks and unknown mass spectral sensitivities were present.

attack by other radicals present in the reaction zones. One of these species may be the C_2H molecule, which is well known, and is readily observed in the radiation chemistry of C_2H_2(66). This molecule might be produced as one of the final stable degradation products of hydrocarbons, and reactions similar to the following, leading to formation of C_2H should occur to at least some extent:

$$C_2H_3 + N \rightarrow NH_2 + C_2H + 23\ \text{kcal} \tag{70}$$

$$C_2H_2 + H \rightarrow H_2 + C_2H + 3\ \text{kcal} \tag{97}$$

$$NH_2 + C_2H_2 \rightarrow NH_3 + C_2H + 4\ \text{kcal} \tag{98}$$

$$CH + C_2H_2 \rightarrow CH_2 + C_2H + 14\ \text{kcal}\ . \tag{99}$$

The extreme stability of the C_2H radical becomes apparent when its thermodynamic properties are examined. The C_2H radical has a binding energy of about 288 kcal and is seen to be a strongly-bound molecule, the carbon-carbon triple bond having a dissociation energy of about 194 kcal(49). An interesting consideration now becomes apparent. Any rupture of the C-H single bond leads to formation of the much more weakly-bound C_2 molecule (binding energy about 144 kcal(67)), with a subsequent energy deficit of 150 kcal:

$$\overset{194}{C\equiv}\,C\overset{100}{-H} \longrightarrow C\overset{144}{-}C + H$$

$$(194+100) - 144 = 150\ \text{kcal endothermic}\ .$$

In order for any reaction to occur, the binding energy of the products must overcome this very large energy deficit, and all reactions such as the following, which might occur with species present under non-flame conditions, with one exception, will be highly endothermic:

$$C_2H + H \rightarrow H_2 + C_2 - 41 \text{ kcal} \qquad (100)$$

$$C_2H + N \rightarrow NH + C_2 - 58 \text{ kcal} \qquad (101)$$

$$C_2H + CH \rightarrow CH_2 + C_2 - 30 \text{ kcal} \qquad (102)$$

$$C_2H + N \rightarrow CN + CH - 21 \text{ kcal} \quad . \qquad (103)$$

It is seen that even reaction (103), in which the very strongly-bound CN molecule is formed, is too endothermic to occur to any appreciable extent at low temperatures. The only reaction that might be expected to occur readily with species present in the reaction system (under non-flame conditions) is:

$$C_2H + N \rightarrow HCN + C + 18 \text{ kcal} \quad . \qquad (104)$$

From these thermochemical considerations, it appears highly likely that any C_2H radicals produced would diffuse to the walls of the reaction vessel where polymerization could occur. These low vapor pressure polymers would not be observable with the mass spectrometer, and could account for the carbon deficit in material balances under non-flame conditions. It can be seen that, according to the proposed mechanism, if polymer formation did not occur, each carbon atom would form HCN.

It should be recalled that the number of degradation steps undergone by alkenes is one less than the number of carbon atoms. If the proposed reaction mechanism for alkene reactions is correct, and polymer formation is due to competing reactions that lead to C_2H formation, then the amount of polymer formed (in the non-flame region) should increase as the number of degradation steps required to consume the alkene increases. It can be seen that the C_2H_4 reaction, in which 1/6 of the carbon (1/12 calculated as C_2H) was unaccounted for, proceeds via one degradation step, while the C_3H_6 reaction proceeds via two degradation steps. Therefore, for C_3H_6, 2 x 1/6 (or 1/3) of the carbon should form polymers, and be lost to the walls of the reaction vessel. Experimentally, almost exactly 1/3 of the carbon could not be accounted for in the C_3H_6 reaction under non-flame conditions, and presumably formed polymers as can be derived from Fig. 25. Further experimental confirmation is necessary, however, for this important result.

It should be emphasized that the above considerations apply only under non-flame conditions. Under flame conditions, good material balances were obtained for carbon and hydrogen. This finding is readily explainable. It was previously shown that energetically, reactions leading to rupture of the C-H bond in C_2H cannot occur with the simple radicals present in the systems under non-flame conditions. However, several abstraction reactions of C_2H such as the following are possible. For example:

$$C_2H + C_2H_4 \rightarrow C_2H_2 + C_2H_3 + 2\ \text{kcal} \qquad (105)$$

$$C_2H + C_2H_3 \rightarrow C_2H_2 + C_2H_2 + 49\ \text{kcal}\ , \qquad (106)$$

can all occur. In addition, under flame conditions, the hydrocarbons are present in large excess over N-atoms, making these reactions very likely.

In addition to polymer formation, leading to loss of non-volatile material to the vessel walls, a volatile product giving peaks at mass-to-charge ratios of 50, 51 and 52 was found by the author to be a common product of all the hydrocarbon reactions studied in this laboratory. These masses correspond to the formula C_4H_4 and are most likely due to vinylacetylene,  $H\text{-}C(H){=}C(H)\text{-}C{\equiv}C\text{-}H$, a product observed in pyrolysis reactions of acetylene(68).

Under the conditions used in the author's experiments, three body, or wall, recombination reactions would be unlikely. The formation of this substance must have occurred in two-body gas-phase reactions common to all the reactions, such as:

$$C_2H + C_2H_4 \rightarrow C_4H_4 + H - 3\ \text{kcal}^{*} \qquad (107)$$

$$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H - 5\ \text{kcal}\ . \qquad (108)$$

This product, common to all hydrocarbon reactions that were studied, strengthens the proposal that a common degradation mechanism occurs for at least the reactions of aliphatic hydrocarbons. Under flame conditions, the reactions of N-atoms appear to be actually secondary, serving only to produce radicals (and form HCN); the main reactions are those that occur between the several hydrocarbon radicals, C-atoms, and H-atoms present.

The only reactions that would be expected to exhibit anomalous behavior are those of C_2H_2, which will not be considered, and CH_4, which is discussed in Section H.

F. The Reaction of Acetylene with Active Nitrogen

It has already been mentioned briefly that the reaction of C_2H_2 with active nitrogen displayed anomalous behavior. Based upon the degrada-

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[*] These values for the heats of reaction are based upon the summation of bond energy values. The sum of the bond energies in the C_4H_4 molecule gives a binding energy of 822 kcal. However, this molecule is known to have a large amount of resonance energy (69); these reactions should easily be exothermic and reaction should occur quite readily.

tion mechanisms previously discussed, this behavior is to be expected since C_2H_2 obviously cannot be degraded to any lower hydrocarbon, as is the case for all the other hydrocarbons that were studied except CH_4, as will become apparent. The most striking feature is that the reaction of acetylene is extremely fast relative to alkene reactions, which in themselves are rapid. N-atoms were completely consumed when only a small amount of C_2H_2 was added to the active nitrogen ($C_2H_2 \sim 1/5$ of N, as opposed to 1/3 to 1/2 of N, for C_2H_4 and C_3H_6, respectively). See Figs. 23 to 25 and Tables IV to VI. In addition, only 10% conversion of N-atoms to HCN was obtained. Also, this reaction gave fairly large amounts of $(CN)_2$(70) and large quantities of a yellow-brown polymer (32% nitrogen(70) according to Winkler) which rapidly dirtied the walls of the reaction vessel. All other hydrocarbon reactions that were studied produced only traces of $(CN)_2$. After a thick layer of polymer had accumulated on the vessel walls, it appeared dark brown-black, and appeared to contain elemental carbon.

An outstanding feature of this reaction was the fact that NH_3 was destroyed when this substance was added to the reaction flame, as mentioned earlier. Therefore, it was concluded that CH, or some similar radical, was formed at least partly by the following reaction, which is spin forbidden and slightly endothermic:

$$C_2H_2 + N \rightarrow HCN + CH - 2 \text{ to } - 5 \text{ kcal} \qquad (21)$$

and NH_3 consumed by:

$$CH + NH_3 \rightarrow HCN + H_2 + H + 51 \text{ kcal} \quad . \qquad (22)$$

However, if the reaction of C_2H_2 involved only reaction (21) above, followed either by:

$$\mathrm{CH + N \rightarrow CN + H + 107\ kcal} \qquad (104)$$

or,

$$\mathrm{CH + N \rightarrow NH + C - 2\ or + 6\ kcal}\ , \qquad (110)$$

then at least 1/2 of the carbon in C_2H_2 should form HCN. In addition, the formation of nitrogenous polymers could not be explained if only these reactions occurred. Only 1/4 of the carbon in the reacted C_2H_2 formed HCN under <u>non-flame</u> conditions. Therefore, additional C_2H_2 molecules must have been consumed in another reaction, and one possible reaction scheme is:

$$\mathrm{C_2H_2 + N \rightarrow HCN + CH - 2\ to - 5\ kcal} \qquad (21)$$

$$\searrow \mathrm{CH\text{-}CN + H + 2\text{-}7\ kcal} \qquad (69)$$

$$\mathrm{CH + N \rightarrow CN + H + 107\ kcal} \qquad (109)$$

$$\mathrm{CH + N \rightarrow NH + C - 2\ or + 6\ kcal} \qquad (110)$$

$$\mathrm{CH\text{-}CN + N \rightarrow HCN + CN + 98\ kcal} \qquad (73)$$

$$\mathrm{C_2H_2 + H \rightarrow H_2 + C_2H + 3\ kcal} \qquad (97)$$

$$\mathrm{C_2H_2 + CH \rightarrow CH_2 + C_2H + 14\ kcal} \qquad (99)$$

$$\mathrm{CN + N \rightarrow N_2 + C + 38\ kcal} \qquad (74)$$

$$\mathrm{CH_2 + N \rightarrow HCN + H + 113\ kcal} \qquad (34)$$

$$\mathrm{NH + NH \rightarrow NH_2 + H + 2\ kcal} \qquad (63)$$

$$\mathrm{C_2H_2 + NH_2 \rightarrow NH_3 + C_2H + 4\ kcal} \qquad (98)$$

$$\mathrm{CH + NH_3 \rightarrow HCN + H_2 + H + 51\ kcal} \qquad (22)$$

$$\mathrm{C_2H \longrightarrow walls} \qquad (111)$$

$$\mathrm{C \longrightarrow walls} \qquad (112)$$

$$\mathrm{NH_2 \longrightarrow walls} \qquad (113)$$

(these radicals can undergo reactions on walls leading to nitrogenous polymers)

Reactions (111), (112) and (113) might account for the production of species that can eventually form nitrogenous polymers. The NH_2 and C_2H radicals formed in these reactions could diffuse to the walls of the reaction vessel and react, giving the polymers.*

> Earlier, it was mentioned that the only exothermic reaction C_2H could undergo with species present under non-flame conditions (low hydrocarbon concentrations), is:
>
> $$C_2H + N \rightarrow HCN + C + 18 \text{ kcal} \quad . \qquad (104)$$
>
> It was briefly stated that this reaction does not occur rapidly. The above finding, that only 1/4 of the available carbon forms HCN, is taken as evidence for this conclusion. Otherwise, at least 1/2 of the carbon present should form HCN if this reaction occurred to any appreciable extent.

In addition to only 1/4 of the carbon forming HCN under non-flame conditions, the remaining 3/4 of the carbon could not be accounted for. In the reactions of other hydrocarbons that were studied, the amount of polymer deposited on the walls under non-flame conditions was too small to be easily seen. However, in the C_2H_2 reaction, the walls rapidly became dirtied by the polymer, even under these non-flame conditions. Obviously, since a large amount of polymer was deposited on the walls, material balances could not be made for this reaction.

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*Winkler claimed that the formation of a polymer containing 32% nitrogen is direct evidence for the existence of a $[C_2H_2N]$ complex (35% N)(71). However, if the polymerization occurred at the walls of the reaction vessel via:

$$n\, C_2H + n\, NH_2 \rightarrow (C_2H \cdot NH_2)_n \quad , \qquad (114)$$

the polymer would contain 34% N, close to the 32% found by Winkler. Small amounts of carbon, produced by reaction (110) could bring the N-content down to the 32% found.

The most likely explanation for this anomalously large polymer formation is that much larger amounts of C_2H radicals were produced in this reaction than in the reactions of alkenes, and these diffused to the walls, where polymerization occurred. It would be expected that much larger quantities of C_2H should, and must be produced from C_2H_2 compared to alkenes. This is because higher hydrocarbons contain more hydrogen, and can form products other than polymers. In addition, H_2 was found to be produced in relatively large amounts in the C_2H_2 reaction, compared with HCN, ($H_2 \sim 1/3$ of HCN), showing that condensation must have occurred. Based upon these considerations, it can be seen that polymer formation would be expected, and polymers actually are found, experimentally, to be the major product. The formation of polymer can occur readily because almost any radical present in the reaction zone (except N-atoms or C-atoms can form C_2H directly by reaction with C_2H_2 via reactions such as (97), (99) and (98), above.

The formation of large amounts of polymer should also be considered from another point of view. Reactions such as the following can occur under flame conditions with other hydrocarbons:

$$C_2H + C_2H_4 \rightarrow C_2H_2 + C_2H_3 + 2 \text{ kcal} \qquad (105)$$

$$C_2H + C_2H_3 \rightarrow C_2H_2 + C_2H_2 + 49 \text{ kcal} \qquad (106)$$

$$C_2H + C_3H_6 \rightarrow C_2H_2 + C_3H_5 + 2 \text{ kcal} \quad , \qquad (116)$$

It can be seen however, that no net difference occurs in the C_2H_2 reaction:

$$C_2H + C_2H_2 \rightarrow C_2H_2 + C_2H + 0 \text{ kcal} \quad ; \qquad (115)$$

the C_2H radical is merely re-formed. Diffusion to the walls can occur and large amounts of polymer are produced. It now becomes apparent that for all hydrocarbons except C_2H_2, C_2H radicals can be consumed by these reactions, and the relatively low polymer yields, compared to C_2H_2, are readily explained. The C_2H radicals do not diffuse to the vessel walls as rapidly as with C_2H_2, because they are consumed to a large extent before they reach the walls.

The consumption of N-atoms cannot be accounted for by this mechanism. However, it is well known that small quantities of $(CN)_2$ added to active nitrogen, rapidly consume N-atoms(72), simultaneously forming a brown polymer on the walls. The fact that considerable $(CN)_2$ was found as a product of the C_2H_2 reaction, and that only this reaction, of all the reactions investigated gave a brown polymer makes it appear that the anomalously low HCN production obtained is due to the rapid consumption of N-atoms by $(CN)_2$, in a competing reaction. In addition, the C_2H_2 reaction was strongly pink in appearance, similar to the reaction of $(CN)_2$ with active nitrogen. No attempt was made to elucidate the mechanisms by which $(CN)_2$ is formed or N-atoms consumed, since this reaction poses a problem in itself, and no explanation is given at this time. See Appendix IV.

One other finding should be discussed. When O-atoms (NO) were added to the C_2H_2 reaction, under conditions where N-atoms were present in large excess over C_2H_2, an increase in the HCN production was found similar to that observed when O-atoms were added to C_2H_4. See Figs. 15 to 17. This is explained if C_2H radicals react rapidly with O-atoms as follows:

$$C_2H + O \rightarrow CO + CH + 48 \text{ kcal} \quad . \qquad (117)$$

This reaction is one of the few reactions of this type that C_2H

can undergo, and is energetically possible because CO is the strongest bound diatomic molecule known. The additional CH radicals produced could then form additional HCN by a chain mechanism such as:

$$C_2H + O \rightarrow CO + CH + 48 \text{ kcal} \qquad (117)$$

$$CH + C_2H_2 \rightarrow CH_2 + C_2H + 14 \text{ kcal} \qquad (99)$$

$$CH_2 + N \rightarrow HCN + H + 113 \text{ kcal} \qquad (34)$$

$$H + C_2H_2 \rightarrow H_2 + C_2H + 3 \text{ kcal} \qquad (97)$$

$$C_2H + O \rightarrow CO + CH + 48 \text{ kcal} \quad . \qquad (117)$$

It should be mentioned that no H_2O was found as a product when O-atoms were added to the C_2H_2 reaction. This finding supports the view that the reaction of C_2H actually occurs via (117) above. If the increased HCN production were instead due to a reaction of O-atoms with C_2H_2, rather than with C_2H, such as:

$$C_2H_2 + O \rightarrow OH + C_2H + 1 \text{ kcal} \quad ; \qquad (118)$$

much larger amounts of H_2O should have been produced than were observed, since an accumulation of OH radicals formed would be expected to lead to formation of H_2O by reactions such as:

$$C_2H_2 + OH \rightarrow H_2O + C_2H + 17 \text{ kcal} \quad . \qquad (119)$$

Also, under these non-flame conditions, all of the C_2H_2 is consumed by N-atoms, and reaction (118) is not very likely.

Based upon the above discussions, it can be seen that the reaction of C_2H_2 is complicated, and only a few of the possible reactions have been given here. Other possible competing reaction schemes can exist, but these are all hindered by a lack of sufficiently accurate thermodynamic data for the heats of formation of the species present in the reaction zone, and even more important, the heats of activation for the reactions that can occur between these species.

G. Side Reactions: The Reactions Responsible for the Formation of Minor Products and Radiation of CN-Bands

Only the major features of the reactions of hydrocarbons with active nitrogen have been discussed up to this section. The mechanisms proposed account very well for the production of N_2, HCN, C_2H_4, C_2H_2, NH_3, and condensation and polymerization products.

Winkler found varying amounts of minor products such as saturated hydrocarbons and higher alkenes and the author, as well as others(41), found CH_3CN as a product of some reactions.

Obviously the number of energetically possible reactions that can be written between species occurring in the reaction zones is large, and impossible to give here. It is to be expected, that depending on conditions, some reactions would be favored over others and lead to different product distributions.*

One additional point deserves mention. The CN radiation emitted in these reactions has been claimed to arise from at least two different kinetic origins(38). It is obvious that, in addition to the primary CN-producing reaction:

$$\begin{array}{l} \mathrm{CH\text{-}CN} + \mathrm{N} \rightarrow \mathrm{HCN} + \mathrm{CN}^{*} + 98\ \mathrm{kcal} \\ \qquad\qquad\qquad\qquad\qquad\quad \searrow \mathrm{CN} + h\nu \quad , \end{array} \tag{73}$$

---

*For example, Winkler generally found about 60% conversion of N-atoms to HCN (NO consumed/HCN produced ~ 1.7)(65), as opposed to the author's 45%.

reactions of other radicals can also lead to CN production. For example, reactions such as the following can occur:

$$CH + N \rightarrow CN^{**} + H + 107 \text{ kcal} \qquad (109)$$

$$CH_2 + N \rightarrow CN^{***} + H_2 + 96 \text{ kcal} . \qquad (120)$$

All of these reactions release enough energy to excite the CN radical to either the $A^2\Pi$ or $B^2\Sigma$ levels$^{(73)}$.

No further discussion of side reactions will be given.

H. Determination of N-atoms in Active Nitrogen by the Reaction of CH_4 with Active Nitrogen

The discrepancy between the values obtained for the concentration of N-atoms in active nitrogen by the HCN method and the NO titration heretofore has been claimed to possibly be due to the reaction of $N_2(A^3\Sigma_u^+)$ molecules with NO$^{(48)}$, as discussed earlier. It has been shown, however, that N_2 is formed in the reactions of hydrocarbons with active nitrogen. The author was able to obtain as high as 65% conversion of N-atoms (as measured by NO titration) to HCN using CH_4-HCl mixtures at an optimum temperature. All other hydrocarbons, even without HCl (which in itself consumes N-atoms giving N_2) gave only 40 to 50% conversion of N-atoms to HCN. Furthermore, the data of Gartaganis and Winkler$^{(56)}$ show that, although no details were given, under their experimental conditions (high temperatures), these authors also obtained higher yields of HCN with CH_4 than with C_2H_6. These findings show that the conversion of N-atoms to HCN with CH_4 is variable, and highly dependent upon conditions while the conversion of N-atoms to HCN with other hydrocarbons (that can form C_2H_2 readily during degradation) is almost constant. These results therefore discredit the HCN method for determining the concentration of N-atoms in active nitrogen, at least with hydrocarbons containing more than one carbon atom.

It might, however, be possible to obtain a nearly quantitative agreement between the two methods for titrating N-atoms if CH_4 is reacted with active nitrogen, in the presence of HCl at an optimum temperature. This is because, as mentioned earlier but not stressed from this point of view, under optimum conditions, the CH_3 radicals produced appear to undergo only one major reaction:

$$CH_4 + Cl \rightarrow CH_3 + HCl + 2\ \text{kcal} \qquad (46)$$

$$CH_3 + N \rightarrow HCN + 2H + 13\ \text{kcal} \quad ; \qquad (29)$$

From the previous discussions of the reactions of hydrocarbon radicals with active nitrogen, it immediately becomes clear why low HCN yields are obtained in the reactions of higher hydrocarbons, compared to the yield in the CH_4 reaction, under optimum conditions, thereby leading to the discrepancy between the HCN method for obtaining N-atom concentrations and the titration with NO. This is because of the peculiar bond forming properties of the carbon atom. C_2H_2 can be readily produced as soon as hydrocarbons containing two or more carbon atoms are present in a system.

Even the CH_4 reaction produces appreciable amounts of N_2 under suitable conditions. See Table XXIII. These are due to interfering reactions that lead to eventual formation of unsaturateds. For example, the following might occur:

$$CH_3 + CH_3 \rightarrow C_2H_4 + H_2 + 54\ \text{kcal} \qquad (56)$$

$$CH_3 + CH_3 \rightarrow C_2H_2 + 2H_2 + 8 \text{ kcal} \qquad (57)$$

As soon as C_2H_4 or C_2H_2 is formed, many more of the previously discussed radical reactions become possible and formation of N_2, as well as HCN occurs. However, as given earlier, under optimum conditions, these degradation reactions leading to N_2 formation instead of HCN, can be relatively minor since, even though a considerable number of N-atoms present form N_2 in the reaction with HCl giving Cl-atoms, as much as 65% conversion of N-atoms to HCN was found in the CH_4-active nitrogen-HCl reaction. Under the conditions of these experiments, about 1/3 of the N-atoms should have formed N_2 by reaction with HCl. If reactions leading to N_2 formation, rather than HCN, were important under these conditions much less conversion would have been observed. On the other hand alkenes, and all higher alkanes, both of which can undergo reactions leading to N_2 formation via C_2H_2, all gave much lower HCN formation. See Tables XVII to XXII.

From these considerations it can be seen that it is futile to try to obtain quantitative conversion of N-atoms to HCN with any hydrocarbon except CH_4, and perhaps the methyl halides, i.e., CH_3Cl, CH_2Cl_2 and $CHCl_3$.

In conclusion, it appears that attempts to obtain agreement between the NO-titration and HCN formation in the CH_4 reaction would only be of theoretical, and not practical, importance, since the NO-titration is very easily and conveniently performed, especially when a mass spectrometer is used to measure the NO concentration.

I. The Failure of $N_2(A^3\Sigma_u^+)$ Molecules to React

No indication was obtained that $N_2(A^3\Sigma_u^+)$ molecules react with any of a large number of substances that were introduced into the jet of these molecules, as described under RESULTS. See p. 27. The fact that the jet was entirely unaffected when large excesses of several "chosen" foreign gases were added, shows that no energy was lost by the excited molecules and that fast reactions ($k > \sim 10^{-13}$ cm^3/particle-sec) could not have occurred.*

At the beginning of this investigation, it was anticipated that $N_2(A^3\Sigma_u^+)$ molecules would react extremely rapidly with other substances, perhaps with each collision. Under the conditions of these experiments, the $N_2(A^3\Sigma_u^+)$ molecules are estimated to have survived at least 50 to 100 collisions with foreign gases without having reacted. It should be pointed out that these $N_2(A^3\Sigma_u^+)$ molecules, in the jet, are similar to those responsible for the yellow light emission of active nitrogen, except that slightly lower vibrational levels are populated (v=8,7,... vs v=11,10,...). These results therefore provide additional evidence that these metastable $N_2(A^3\Sigma_u^+)$ molecules are highly unlikely to be the species responsible for the decomposition of NO, during titration of active nitrogen with that substance since the reaction of N-atoms with NO appears to be much faster than

---

*Indirect evidence that excited molecules (with a few quanta of vibrational energy, as are formed in the afterglow) do not react rapidly with NO, has been obtained by adding ^{15}NO to active nitrogen(74). If only the atom reaction occurred:

$$^{14}N + ^{15}NO \rightarrow ^{15}N^{14}N + O \quad , \qquad (121)$$

then only the $^{15}N^{14}N$ molecules having mass 29 should be found as a product. If excited molecules reacted, in a collision of the second kind:

$$^{14}N_2^* + ^{15}NO \rightarrow ^{14}N_2 + ^{15}N + O \quad , \qquad (122)$$

then these ^{15}N-atoms should react with additional ^{15}NO and give $^{15}N_2$, having a mass of 30. These experiments found that practically no $^{15}N_2$ was produced, and the conclusion reached was that the reaction of excited molecules with NO occurs only to a negligible extent.

the reaction with $N_2(A^3\Sigma_u^+)$ molecules, if they react at all.

Also, the concentration of $N_2(A^3\Sigma_u^+)$ molecules in the active nitrogen would have to be very high, in order to explain the results obtained. Under the conditions used in this laboratory, less than 50% conversion of N-atoms to HCN, as measured by NO titration was found when hydrocarbons were reacted with active nitrogen. If the amount of HCN produced in the reactions of hydrocarbons corresponds to the N-atom concentration in the active nitrogen, and the discrepancy between the two titration methods is due to production of high concentrations of additional N-atoms via:

$$N_2(A^3\Sigma_u^+) + NO \rightarrow N_2(X^1\Sigma_g^+) + N + O \quad , \qquad (123)$$

then obviously the concentration of these excited molecules in the active nitrogen must be at least 50% of the N-atom concentration, in order to explain the less than 50% conversion of N-atoms to HCN found in this laboratory. Obviously, the concentration of $N_2(A^3\Sigma_u^+)$ molecules cannot be this high if the presently-accepted mechanism for the light emission by active nitrogen is considered. It therefore appears that metastable $N_2(A^3\Sigma_u^+)$ molecules can play only minor roles in the reactions of active nitrogen.

NH_3 was found to slowly quench the jet. However, no decomposition of NH_3 was detectable, nor were any products observed. Therefore, it appears, that the slight decomposition of NH_3, and formation of H_2 that has been observed by others when NH_3 is added to active nitrogen, cannot be due to the presence of $N_2(A^3\Sigma_u^+)$ molecules. It should be mentioned that, in this laboratory, no destruction of NH_3 or production of H_2 was observed when NH_3 was added to active nitrogen as found by others(43,23). As mentioned above, even when NH_3 was added to a stream of metastable molecules, which was free of N-atoms and contained a higher concentration of $N_2(A^3\Sigma_u^+)$ molecules than could be produced by other workers, working under these conditions, no consumption of NH_3 or formation of H_2 was observed. It is therefore suggested that the consumption of NH_3 found by other workers may possibly be due to the production of small concentrations of CH, or other similar radicals, produced when hydrocarbon greases, used in the apparatus, are attacked by active nitrogen. It has already been shown that a radical, most likely CH, attacks NH_3 and forms HCN and H_2. Supporting these views is the fact that decomposition of NH_3 is only observed when active nitrogen is produced by a condensed discharge; active nitrogen produced by a microwave discharge shows no ability to consume NH_3(43,32,26). If small concentrations of CH radicals, produced from greases in a reaction with active nitrogen, instead of metastable $N_2(A^3\Sigma_u^+)$ molecules, were responsible for the consumption of NH_3, then the above results are readily explained. Active nitrogen produced by a condensed discharge contains large concentrations of N-atoms (approx. 10-50%). In addition, greases are inadvertently admitted to the reaction system, during handling of the electrodes used in the construction of the discharge tubes, and through the use of stopcocks, lubricated with hydrocarbon, or other greases. Active nitrogen produced by a microwave discharge, on the other hand, contains only about 1% N-atoms. Also, experiments performed using microwave energy as the means for producing N-atoms, are usually constructed with cleanliness a prime consideration, i.e., with no electrodes and a minimum of stopcocks. Therefore, it can be seen that CH radicals are much more likely to be produced in a system where a condensed discharge is used to activate the nitrogen. Not only are the systems inherently less clean, but larger N-atom concentrations are available to react with the greases. It is clearly obvious that much greater concentrations of CH radicals are likely to be produced in the system using a condensed discharge as the means for activating the nitrogen.

An interesting finding deserves comment. In this laboratory, not even active nitrogen produced by a condensed discharge (N-atoms ~ 15%), in a relatively "dirty" system (large glassware, several stopcocks, and several gaskets lubricated with relatively large quantities of greases), showed any reaction with NH_3. This could very well be due to the low pressures and short reaction times available in the author's experiments. In these short reaction times, only a slight reaction could have occurred with the relatively stable greases used for stopcock lubricants, and only minor concentrations of CH radicals could have been produced. Also, since only minor concentrations of CH radicals could be present, only a minor reaction could occur with NH_3 since the rate of NH_3 consumption is proportional to the CH concentration. It should also be re-stated here that the overall rate of consumption of NH_3 by CH radicals, was found to be approximately the same as the rate, claimed by others, for the reaction which decomposes NH_3 when this substance is added to active nitrogen produced by a condensed discharge ($k \sim 10^{-13}$ (cm^3/particle)/sec)(61).

The hypothesis that has been proposed to explain this behavior, i.e., active nitrogen of microwave origin produces only small concentrations of metastable $N_2(A^3\Sigma_u^+)$ molecules capable of decomposing NH_3, appears unreasonable in view of the experimental evidence for CH radicals. It is possible, however, that a second excited species may be responsible for destruction of NH_3(75). However, if this is the case, and if another species were present in reasonable concentrations, and reacted at the rates given by others for the decomposition of NH_3(48), decomposition of this substance should have been observed by the author. As mentioned above, no decomposition was observed, and it is concluded that the active nitrogen produced in the author's experiments contained only N-atoms as the reactive species.

PART V

CONCLUSIONS

Prior to this work, the reactions of simple hydrocarbons with active nitrogen were believed by some workers to occur via a relatively simple mechanism that involved initial formation of a complex, which then rearranged, splitting off HCN directly, and giving fragments:

$$RH + N \rightarrow [RHN] \rightarrow HCN + \text{fragments} \quad .$$

The role of radicals was given only secondary importance in these reactions, the primary step being formation of the above complex. In addition, the constant amount of HCN obtained from several different hydrocarbons, both alkenes and alkanes, was thought to correspond to the concentration of N-atoms in the active nitrogen. It may be seen that the establishment of the nitrogen atom concentration is important in testing the validity of the above reaction mechanism. However, in determining the N-atom concentration by hydrocarbon titration, and by NO titration, a serious discrepancy is observed. This discrepancy was believed to be due to the presence of a second reactive species in the active nitrogen, $N_2(A^3\Sigma_u^+)$ molecules, which reacted with NO, dissociating this substance into N- and O-atoms, by collisions of the second kind:

$$N_2(A^3\Sigma_u^+) + NO \rightarrow N_2(X^1\Sigma_g^+) + N + O \quad .$$

The additional N-atoms thus produced would then lead to the high values obtained for the N-atom concentration, characteristic of the NO titration procedure.

Contrary to these views, the author has shown by direct experimental evidence that, compared with N-atoms, $N_2(A^3\Sigma_u^+)$ molecules react slowly with a large number of molecules, if at all, and therefore are not the species responsible for the observed discrepancy. To further support this conclusion, it was also shown that the above discrepancy between the two titration methods for estimating the concentration of N-atoms in active nitrogen is due to the formation of N_2, in large amounts, in the reactions of hydrocarbons with active nitrogen.

In this study, it is concluded that radicals play the <u>major</u> role in the mechanisms of the reactions of hydrocarbons with active nitrogen. The mechanisms of several of these reactions appear to be similar and have been concluded to be as follows. Under what is called "flame conditions," a radical, most likely the C-atom, is formed in small concentrations by any of several reactions, and initiates highly branching chain reactions involving the interactions of several hydrocarbon radicals, nitrogen hydride radicals and H-atoms. The reactions are highly complex and proceed via a series of successive degradations, each degradation step consuming three N-atoms and forming one N_2 and one HCN molecule. Although, according to this mechanism, several hydrocarbons give yields of HCN proportional to the number of carbon atoms, more N-atoms are consumed as the number of carbon atoms increases, and the net production of HCN per N-atom consumed is approximately the same for different hydrocarbons. It is because of this constant stoichiometry of each degradation step that several hydrocarbons give the same yield of HCN, and not, as previously believed, because the amount of HCN produced corresponds to the concentration of N-atoms in the active nitrogen. The mechanism proposed for the reaction of alkenes is as follows:

(1) **Radicals are formed initially by any of several reactions.**

(2) Degradation occurs by a chain mechanism with C-atoms as the primary chain carrier:

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H$$

$$CH\text{-}CN + N \rightarrow HCN + CN$$

$$CN + N \rightarrow N_2 + C$$

$$CH_2 + N \rightarrow HCN + H \quad .$$

C_3H_6 undergoes <u>two</u> degradations, C_4H_8 <u>three</u>, etc:

$$C + C_3H_6 \rightarrow C_2H_2 + C_2H_4$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H$$

$$CH\text{-}CN + N \rightarrow HCN + CN$$

$$CN + N \rightarrow N_2 + C$$

$$C + C_2H_4 \rightarrow C_2H_2 + CH_2$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H$$

$$CH\text{-}CN + N \rightarrow HCN + CN$$

$$CN + N \rightarrow N_2 + C$$

$$CH_2 + N \rightarrow HCN + H \quad .$$

Alkanes react by initial formation of alkyl radicals. These alkyl radicals then react with each other, giving alkenes <u>prior</u> to any reactions with N-atoms:

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \quad .$$

The alkenes formed then react according to the proposed degradation mechanism. It can at once be seen that the reason alkanes give the same stoichiometry as alkenes, for HCN formation, is because alkyl radicals react with themselves, prior to any reaction with N-atoms.

In addition, the extremely fast rate of the alkene reactions at room temperatures is due to chain-branching steps. Also, certain minor features of the reactions can now be explained. These minor features include the formation of saturated products, polymers, condensation products, NH_3 and the radiation of CN-bands. These minor products are all due to the many possible reactions that can occur between the species present in the reaction zones. It was also found that ammonia added to the C_2H_2-active nitrogen flame reaction resulted in a net consumption of ammonia, with formation of HCN, due to the reaction of CH-radicals with the ammonia.

It was also found that the reaction could be promoted between active nitrogen and several alkanes (which react only slowly at room temperatures) by adding HCl as a catalyst which promotes the formation of radicals. The rates of the reactions were increased to an extent that flames developed and reaction time was of the order of a few milliseconds.

APPENDIX I

Calculation of the Number of Photons Emitted per Second by the Jet of $N_2(A^3\Sigma_u^+)$ Molecules

At dynode-dynode potentials of 70 volts, E = 840 volts and the tube sensitivity, according to RCA data sheets for the type 7102 phototube, is given as follows:

max. at 840 volts = 0.5 amp/lumen
min. at 840 volts = 0.015 amp/lumen
median at 840 volts = 0.06 amp/lumen .

The measured photocurrent obtained was: 0.29 μ/amp. Therefore, the energy striking the tube face (median value) is:

$$\frac{0.29 \times 10^{-6} \text{ amp}}{0.06 \text{ amp/lumen}} = 4.84 \times 10^{-6} \text{ lumen} \times 1.5 \times 10^{-3} \frac{\text{watt}}{\text{lumen}} \times \frac{10^7 \text{ ergs}}{\text{watt sec}}$$

$$= 7.25 \times 10^{-2} \text{ ergs/sec} .$$

However, this amount of energy is only a fraction of the total emitted by the jet since the radiation is emitted uniformly in all directions. The amount detected by the phototube is that fraction of the area of the surface of a sphere, whose radius is equal to the distance from the point emitting light to the light-sensitive element of the phototube, intersected by the areas of the phototube light element at that distance.

This fraction is therefore equal to:

$$\text{fraction of E detected} = \frac{\text{surfaces area of sphere intersected by phototube}}{\text{surface area of sphere over which light is emitted}}$$

$$= \frac{\text{Area of brass tube}}{\text{Area of surface of sphere}}$$

The diameter of the brass tube used to direct the light to the phototube was 1/4 inch, while the radius of the sphere of radiation, R, is equal to:

R = radius of reaction vessel + length of brass tube + distance from brass tube to inside of reaction vessel + distance from tube face to light-sensitive element

$$= 3.8 + 7.6 + 1.0 + 2.0 = 14.4 \text{ cm} .$$

Therefore, the fraction of energy detected is equal to:

$$\text{fraction of E detected} = \frac{\pi r^2}{4\pi R^2} = \frac{(1/8 \times 2.54)^2}{4\cdot(14.4)^2} = 1.22 \times 10^{-4} .$$

In addition, the jet has length and width and if the phototube were moved along the axis of the jet (or perpendicular to the axis) additional light would be detected by the phototube, the fraction again being determined by the area of the sphere of radiation intersected by the phototube. This is equivalent to saying that light is also emitted over several spheres of radiation and again, only a fraction is detected at any one fixed position of the phototube. If the jet is considered as a cylinder of length 18 cm and diameter 5 cm, this fraction is equal to:

$$\text{fraction of E detected} = \frac{\text{Area of brass tube}}{\text{longitudinal area of jet}} = \frac{0.318}{18 \times 5} = 3.54 \times 10^{-3} .$$

Therefore, the total amount of radiation emitted by the jet is equal to the amount detected by the phototube multiplied by the reciprocals of these functions:

$$E_{total} = E_{detected} \times \frac{1}{1.22 \times 10^{-4}} \times \frac{1}{3.54 \times 10^{-3}}$$

$$= 7.25 \times 10^{-2} \text{ erg/sec} \times \frac{1}{1.22 \times 10^{-4}} \times \frac{1}{3.54 \times 10^{-3}}$$

$= 1.68 \times 10^5$ ergs/sec .

Assuming a mean energy of 1.5 eV for the light emitted, the number of $B^3\Pi_g$ molecules radiating is about:

$$n_{\text{radiating}} = \frac{1.68 \times 10^5 \text{ erg/sec}}{1.5 \times 1.6 \times 10^{-12} \text{ erg}} = 7.0 \times 10^{16}/\text{sec} \quad .$$

Assuming an error of ± 1 cm for the measurement of the distance from the jet to the phototube element, and assuming less optimistic values for the length and diameter of the jet (10 x 4 cm), maximum and minimum values for the number of molecules radiating can be calculated. These values are 6×10^{15} and 2×10^{17}/sec, respectively, with an average value, calculated using median tube characteristics, of 5×10^{16}/sec.

APPENDIX II

The Increased Rate of Production of NH_3 and HCN when O-atoms are Added to the C_3H_6 Reaction

As discussed in the text, NH_3 is produced in large quantities in the C_2H_4 reaction, in the non-flame region, when small amounts of hydrocarbons are added to the active nitrogen. When O-atoms are added in this region, the rate of production of both NH_3 and HCN are increased considerably. See Figs. 8 to 11 and Tables V and VII to X.

In the C_3H_6 reaction, very little NH_3 is produced under non-flame conditions, and in addition, when O-atoms are added, only a slight increase of NH_3 and HCN production is observed, and this increase occurs only when substantial amounts of C_3H_6 have reacted (appreciable concentrations of C_3H_6 present). See Figs. 18 to 22 and Tables VI and XI to XV.

Evidently, the formation of both NH_3 and HCN requires that C_2H_3, C_2H_4 or both these species be present in the reaction zone. If the reaction of C_3H_6 occurs via the proposed degradation mechanism for hydrocarbon reactions with active nitrogen, (see p. 75), then the explanation for this behavior becomes clear. In the C_2H_4 reaction, relatively large quantities of C_2H_3 and C_2H_4 are present even when small quantities of C_2H_4 are added to the active nitrogen. The degradation of C_3H_6 leads to formation of C_2H_4 via:

$$C + CH_3\text{-}CH{=}CH_2 \rightarrow C_2H_2 + C_2H_4 \; .$$

In the C_3H_6 reaction, however, C_2H_3 and C_2H_4 are only intermediates, and only minor quantities of these species are formed at small C_3H_6 concentrations. The concentrations of C_2H_3 and C_2H_4 increase to an extent large enough to form NH_3, only when quantities of C_3H_6 great enough to lead to considerable reaction, are added. As soon as the concentration of these intermediates becomes appreciable, increased NH_3 formation can occur.

However, the amount of NH_3 produced is less than that formed in the C_2H_4 reaction. This is because, as soon as the concentration of radicals leading to NH_3 formation becomes appreciable, the concentration of other radicals, that consume these nitrogen hydrides, also increases and less NH_3 production occurs.

This proposal also explains why O-atoms have practically no effect when they are added to the C_3H_6 reaction. At low concentrations of C_3H_6, only minor increases of NH_3 and HCN production are observed because only small concentrations of C_2H_3 and C_2H_4 are present. As the amount of C_3H_6 added becomes larger, these species are formed in the reaction zone, and the effect of adding O-atoms is to increase the production of C_2H_3 radicals from the C_2H_4. Nitrogen hydrides can then be formed, in the same reactions that produce these radicals in the C_2H_4 reaction, as discussed in the text, and increased NH_3 and HCN are observed.

APPENDIX III

The Detachment of CH_2 from Alkenes by O-atoms

The detachment of CH_2 by radicals was postulated for several reasons which will become apparent. However, it should be mentioned here that a similar detachment of CH_2 from C_2H_4 by O-atoms was found by Avramenko and Kolesnikova(76). These workers studied the reactions of O-atoms, produced by an electrical discharge, with ethylene and propylene, and concluded that the primary reaction of C_2H_4 was:

$$O + C_2H_4 \rightarrow CH_2O + CH_2 \quad .$$

Radicals such as CH or C-atoms should have properties similar to O-atoms and, as was proposed prior to any knowledge of the above work, might react by the analogous reaction:

$$C + C_2H_4 \rightarrow CH_2{\cdot}C + CH_2 \; .$$

However, others, notably Cvetanovic(76), have questioned the validity of the above detachment of CH_2 as the primary reaction, claiming that the presence of O_2 molecules might have interfered with the kinetic analysis of the data. These other workers produced O-atoms by the mercury photosensitized decomposition of N_2O and arrived at the conclusion that the primary reaction was direct addition of an O-atom to the double bond, giving an energy-rich intermediate which could then undergo additional reactions, especially rearrangement and splitting into CH_3 and CHO:

$$O + C_2H_4 \rightarrow [C_2H_4O]$$

$$[C_2H_4O] \rightarrow HCO + CH_3 \; .$$

It immediately is apparent that this reaction mechanism parallels that given by Winkler for the reaction of N-atoms with C_2H_4:

$$N + C_2H_4 \rightarrow [C_2H_4N]$$

$$[C_2H_4N] \rightarrow HCN + CH_3 \quad .$$

Avramenko and Kolesnikova found that an O-atom also detached CH_2 from propylene, again giving CH_2O:

$$O + CH_3CH{=}CH_2 \rightarrow CH_2O + C_2H_4$$

or: $$O + CH_3{-}CH{=}CH_2 \rightarrow CH_2O + C_2H_2 + H_2 \quad .$$

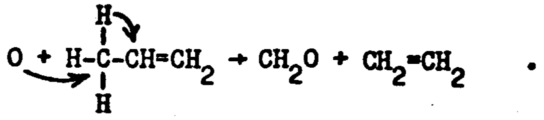
The conclusions reached as the result of experiments in this laboratory lead to the view that the degradation of alkenes proceeds via successive detachments of CH_2 by C-atoms, analogous to the detachment of CH_2 by O-atoms:

$$C + CH_3{-}CH{=}CH_2 \rightarrow CH_2{\cdot}C + C_2H_4 \quad .$$

In the case of C_2H_4, it makes no difference which CH_2 is detached. For propylene, the question arises as to which carbon atom is detached since identical products would be formed whether attack occurred at the methyl carbon or at the methylene carbon. The attack of an O-atom or a C-atom would be expected to occur most likely at the double bond, i.e., the methylene group. However, surprisingly, the above authors found that the attack of butadiene by an O-atom occurred at the carbon-carbon single bond as follows:

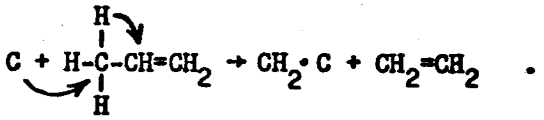
$$O + CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CHO + CH_2 \quad .$$

They therefore concluded that O-atoms preferentially detached CH_2 from the methyl group in propylene, with simultaneous migration of a hydrogen atom to the adjacent doubly-bonded carbon atom, as follows:



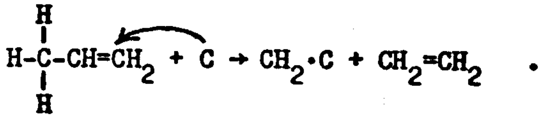
$$O + H-\overset{H}{\underset{H}{C}}-CH{=}CH_2 \rightarrow CH_2O + CH_2{=}CH_2 \quad .$$

If C-atoms reacted analogously and attacked the CH_3 group, the following reaction would occur:



$$C + H-\overset{H}{\underset{H}{C}}-CH{=}CH_2 \rightarrow CH_2{\cdot}C + CH_2{=}CH_2 \quad .$$

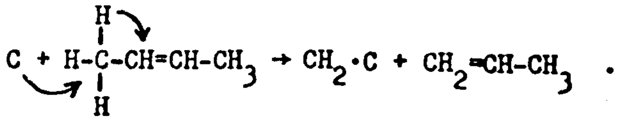
If C-atoms attacked propylene at the double bond, then the following would occur:



$$H-\overset{H}{\underset{H}{C}}-CH{=}CH_2 + C \rightarrow CH_2{\cdot}C + CH_2{=}CH_2 \quad .$$

It is seen that the net result is the same; CH_2 is detached with simultaneous migration of an H-atom to the adjacent carbon atom.

In addition to the above considerations, Winkler found that but-2-ene reacted rapidly with N-atoms, giving the same yield of HCN as C_2H_4. If the degradation of alkenes actually occurs via CH_2 detachment by C-atoms as mentioned in the text, then the only possible attack of this substance that could lead to formation of the next lower alkene, propylene, must be at one of the methyl groups as follows:



$$C + H-\overset{H}{\underset{H}{C}}-CH{=}CH-CH_3 \rightarrow CH_2{\cdot}C + CH_2{=}CH-CH_3 \quad .$$

This mechanism of attack would then be consistent with the above authors' conclusions that attack of alkenes by O-atoms occurs at least as readily on carbon-carbon single bonds as on double bonds. Also, it is difficult to see how C-atoms might attack the but-2-ene molecule in any other way, and lead to stoichiometry consistent with the observed experimental findings both by Winkler, and in this laboratory.

APPENDIX IV

The Formation of $(CN)_2$ in the Reaction of C_2H_2 with Active Nitrogen

No attempt was made to elucidate the mechanisms by which $(CN)_2$ is formed or N-atoms consumed in this reaction. However, these reactions are extremely fast and must be of a chain nature. The initial formation of $(CN)_2$ could occur via reactions such as the following.

$$C_2H_2 + N \rightarrow HCN + CH - 2 \text{ to } - 5 \text{ kcal}$$

$$CH + N \rightarrow CN + H + 107 \text{ kcal}$$

$$C_2H_2 + N \rightarrow CH\text{-}CN + H + 2\text{-}7 \text{ kcal}$$

$$CH\text{-}CN + N \rightarrow HCN + CN + 98 \text{ kcal} \ .$$

Small amounts of $(CN)_2$ might then be produced from these CN radicals.

The following chain process could then lead to N_2 formation:*

$$N + (CN)_2 \rightarrow NCN + CN - 6 \text{ kcal} \qquad (1)$$

$$N + NCN \rightarrow N_2 + CN + 112 \text{ kcal} \ , \qquad (2)$$

and rapid consumption of N-atoms might occur. Again, the question of whether these reactions can occur is hindered by the lack of sufficiently accurate thermodynamic data for the heats of formation of the species involved. Reaction (1) might be expected to be exothermic because of the resonance stabilization of the doubly-bonded NCN molecule(38).

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*This reaction scheme has been suggested by Bayes(38).

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Table I. Gases used in the investigation and their stated impurities (Matheson Handbook).

Gas	Stated Impurities (mole percent)		Comments
N_2 (prepurified)	O_2	20 ppm (max)	
	H_2	20 ppm (max)	
NO	CO_2	0.37	purified by trap-to-trap distillation
	H_2O	0.02	
HCl	inerts	0.2	
	CO_2	0.5	
HCN			prepared in laboratory
C_2H_2	CO_2	0.04	
	O_2	0.04	(volume percent)
	N_2	0.14	
	moisture	0.12	
C_2H_4 (c.p. grade)	C_3H_6	0.05	
	C_3H_8	0.07	
	C_4H_{10}'s	0.01	
	C_4H_8's	0.07	
	C_2H_6	0.08	
C_3H_6 (research grade)	C_3H_8	0.26	
	C_2H_6	nil	
	CO_2	0.04	
CH_4 (c.p. grade)	C_2H_6	0.06	
	CO_2	0.01	
	N_2	0.6	
	C_3H_8	0.01	
C_2H_6 (research grade)	---		

Table I. (Continued)

Gas	Stated Impurities (mole percent)		Comments
C_3H_8 (c.p. grade)	small amounts of iso-C_4H_{10} and C_2H_6; sulfur content 0.005 weight % max		
n-C_4H_{10} (c.p. grade)	iso-C_4H_{10} 2,2-dimethylpropane moisture ~ 100 ppm sulfur content less than 0.005 weight %		
iso-C_4H_{10} (c.p.) grade	n-C_4H_{10} sulfur content less than 0.005 weight %		
neo-C_5H_{12} (c.p. grade)	small amounts of n-C_4H_{10} and iso-C_5H_{12}		
cyclopropane	N_2		
	O_2		
	C_3H_7Cl	traces	
	unsaturates	traces	
methyl-acetylene	aldehydes	none	found to contain 33% dimethylacetylene
	dimethylacetylene	0.1	
	dimethyl ether	0.1	
	H_2O	trace	
	O_2	trace	
	N_2	remainder	
NH_3	moisture	< 50 ppm by weight	
	residue after free evaporation	0.002% by weight	
	oil	3-5 ppm	
CO_2 (Bone Dry grade)	N_2 and O_2	0.05%	
	oil content less than 5 ppm		
	dew point -30°F		
N_2O	air		

Table II. Measured mass-spectral sensitivities of the gases used in this investigation, relative to $N_2 = 1$.

	Mass-Spectral Sensitivity	
Substance	(parent peak)	(most-sensitive peak)
N_2	1	
HCN	1.12	
NO	1.02	
H_2	0.69	
NH_3	0.70	
C_2H_2	1.54	
C_2H_4	0.96	
C_3H_6	0.50	0.79 (41)
CH_4	0.89	
C_2H_6	0.30	
C_3H_8	0.121	1.03 (29)
n-C_4H_{10}	0.128	1.13 (43)
iso-C_4H_{10}		1.48 (43)
neo-C_5H_{12}	---	1.32 (57)
cyclopropane	0.72	

Table III. Approximate binding energies of the species present in the reaction zones.

Species	Binding Energy* (kcal)	(eV)
CH	80	3.46
CH_2	194	8.40
CH_3	293	12.7
CH_4	394	17.1
C_2H_6	672	29.1
C_2H_5	574	24.8
C_2H_4	537	23.2
C_2H_3	439	19.0
C_2H_2	388	16.8
C_2H	288-291	12.5-12.6
C_2	144	6.24
C_3H_6	819	35.4
C_3H_5	721	31.2
C_4H_4	822	35.6
CN	187	8.10
$(CN)_2$	493	21.4
HCN	306	13.3
NH	86 (78)	3.38-3.72
NH_2	174	7.5
NH_3	278	12.0
H_2	103	4.46
HCl	102	4.42
N_2	225	9.76
CO	256	11.1
CH-CN	390-395	17.0
H_2O	218	9.45
OH	101	4.38

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*The values in parentheses have been included as alternative possible binding energies, but have not been used in the text. Even if some of these values should be correct, the discussion is not affected.

Table IV. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_2 with active nitrogen; O-atoms absent. N-atoms = 100 div. Pressure = 0.264 mm Hg.

C_2H_2 reacted (div)	NH_3 (div)	HCN (div)	H_2 (div)
2.16	2.88	1.35	0.803
6.84	0.32	3.13	1.34
12.6	0.08	5.93	2.30
18.9	0.06	9.79	2.78
23.4	0	10.0	3.69
18.6	0	10.1	3.05
23.0	0	12.0	4.06

Table V. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_4 with active nitrogen; O-atoms absent. N-atoms = 100 div. Pressure = 0.241 mm Hg.

C_2H_4 reacted (div)	NH_3 (div)	HCN (div)	H_2 (div)
1.84	5.95	2.36	0.333
4.71	7.96	6.51	0.666
8.35	10.0	13.5	1.27
16.5	9.50	24.9	2.26
19.8	6.16	34.6	3.60
23.2	1.72	43.6	4.73
27.0	0.43	45.0	4.86
24.6	0	44.6	5.60
28.7	0	46.0	4.54

Table VI. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 with active nitrogen; O-atoms absent. N-atoms = 100 div. Pressure = 0.283 mm Hg.

C_3H_6 reacted (div)	NH_3 (div)	HCN (div)	H_2 (div)
1.20	2.25	1.99	0.175
1.80	2.07	3.33	0.262
2.40	1.41	4.57	0.436
3.00	1.41	5.92	0.524
4.20	1.13	8.12	0.697
5.51	1.22	11.1	1.05
7.19	1.50	14.5	1.22
9.34	2.26	17.4	1.66
11.8	2.26	20.9	1.75
12.1	1.88	23.6	2.01
15.8	1.41	28.6	2.62
18.7	0.75	34.4	2.70
20.5	0.38	39.4	3.50
25.8	0.28	44.0	3.67
24.4	0	46.4	3.84

Table VII. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_4 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.216 mm Hg.

C_2H_4 added = 3.40 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	2.94	2.40	Not measured in this experiment
0.053	4.25	2.56	
0.74	4.92	2.98	
2.43	6.12	3.32	
7.56	5.28	3.04	
15.7	1.31	2.38	
26.2	0	1.94	
38.7	0	1.73	
77.3	0	1.10	

Table VIII. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_4 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.213 mm Hg.

C_2H_4 added = 6.90 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	6.88	6.16	1.82
0.04	7.85	6.20	1.82
0.48	8.05	6.40	1.93
2.04	9.73	7.32	2.53
3.92	11.0	7.40	3.14
8.36	11.3	6.97	3.75
14.1	9.85	5.64	3.64
25.6	4.96	4.28	3.54

Table IX. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_4 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.238 mm Hg.

C_2H_4 added = 9.85 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	8.93	7.45	2.04
0.21	9.53	8.32	2.24
0.99	10.4	9.05	2.92
2.84	12.6	9.93	3.32
7.28	14.7	9.77	4.68
18.9	14.0	8.00	5.56
35.8	7.52	5.88	5.64
50.4	3.10	4.64	5.84
70.0	0	2.97	6.16

Table X. Formation of HCN, H_2 and NH_3 in the reaction of C_2H_4 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.246 mm Hg.

C_2H_4 added = 16.5 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	11.8	18.5	5.20
0.08	9.05	15.1	4.60
0.77	9.05	15.5	5.04
1.80	9.05	16.1	5.72
3.12	9.25	15.2	6.05
5.64	9.68	14.5	6.56
9.40	10.8	13.1	7.85
16.2	11.0	11.2	9.85
32.5	6.24	7.00	11.8
54.5	0.90	2.68	14.0

Table XI. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.158 mm Hg.

C_3H_6 added = 1.08 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	3.32	2.06	0.308
0.03	3.22	1.95	0.370
0.16	3.04	1.95	0.246
0.52	2.94	1.84	0.246
1.21	2.86	1.75	0.246
2.41	2.57	1.60	0.308
4.92	1.54	1.48	0.246
9.65	0.28	1.34	0.246
15.2	0.05	1.25	0.185
22.0	0	1.16	0.185
42.8	0	0.990	0.246
65.2	0	0.584	0.185

Table XII. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.166 mm Hg.

C_3H_6 added = 3.27 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	2.40	6.20	0.92
0.1	2.18	6.24	0.805
0.24	2.57	5.96	0.92
0.92	3.05	5.92	0.92
1.92	4.30	5.45	0.92
4.08	5.19	5.00	0.688
6.69	6.10	4.24	0.688
13.0	2.18	3.42	0.688
22.6	0.44	2.77	0.688
32.9	0.13	2.28	0.576
39.8	0.13	1.79	0.576
61.2	0	1.19	0.688

Table XIII. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.220 mm Hg.

C_3H_6 added = 7.70 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	1.81	15.4	2.30
0.1	2.12	15.4	2.20
0.74	2.36	15.1	2.30
2.11	2.83	16.1	2.50
5.92	6.08	13.7	2.60
10.5	9.07	12.2	2.50
16.4	9.50	10.0	2.50
27.8	8.09	8.40	2.20
61.6	6.19	3.96	2.80

Table XIV. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.220 mm Hg.

C_3H_6 added = 26.5 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	1.25	40.8	7.16
0.1	1.03	39.5	6.76
0.63	0.89	40.0	7.29
1.95	0.996	40.4	6.69
5.00	0.951	38.8	8.09
14.0	0.907	35.4	7.69
29.2	0.605	25.4	9.69
61.2	0.302	13.9	9.29

Table XV. Formation of HCN, H_2 and NH_3 in the reaction of C_3H_6 when NO is added to active nitrogen; N-plus O-atoms constant and = 100 div. Pressure = 0.231 mm Hg.

C_3H_6 added = 54.8 div

O-atoms (div)	NH_3 (div)	HCN (div)	H_2 (div)
0	0.302	59.2	10.3
0.1	0.412	58.4	8.96
1.28	0.275	60.0	9.92
4.36	0.248	60.5	9.80
10.3	0.183	58.0	11.2
18.9	0.092	59.2	10.0
32.2	0.183	46.0	11.5
74.0	0.183	22.2	10.6

Table XVI. The reaction of CH_4 with active nitrogen at room temperature.

CH_4 added = 108 div

active nitrogen only
N-atoms = 100 div

CH_4 reacted (div)	undetectable
Products (div)	
HCN	0.1
H_2	0.1
NH_3	1.2

active nitrogen plus HCl
N-atoms = 100 div; HCl = 94 div

CH_4 reacted (div) (reaction incomplete, see Table XXIII)	5.26
HCl reacted (div)	0
Products (div)	
HCN	3.78
H_2	3.06
polymer (mass 49→53)	0.8

Table XVII. The reaction of C_2H_6 with active nitrogen at room temperature.

C_2H_6 added = 109 div

active nitrogen only N-atoms = 100 div		active nitrogen plus HCl N-atoms = 100 div; HCl = 94 div	
C_2H_6 reacted (div)	undetectable	C_2H_6 reacted (div)	13.9
		HCl reacted (div)	0
Products (div)		Products (div)	
HCN	0.8	HCN	25.2
H_2	0.7	H_2	26.7
NH_3	2.4	CH_4	1.7

Table XVIII. The reaction of C_3H_8 with active nitrogen at room temperature.

C_3H_8 added = 108 div

active nitrogen only
N-atoms = 100 div

C_3H_8 reacted (div)	1.58
Products (div)	
HCN	4.19
H_2	1.09
NH_3	4

active nitrogen plus HCl
N-atoms = 100 div; HCl = 94 div

C_3H_8 reacted (div)	11.0
HCl reacted (div)	0
Products (div)	
HCN	24.4
H_2	23.6
CH_4	0.7

Considerable quantities of several unidentified products; appear to be:

CH_3CN

C_2H_2

C_2H_4

Table XIX. The reaction of n-C_4H_{10} with active nitrogen at room temperature.

n-C_4H_{10} added = 107 div

active nitrogen only N-atoms = 100 div		active nitrogen plus HCl N-atoms = 100 div; HCl = 94 div	
n-C_4H_{10} reacted (div)	7.06	n-C_4H_{10} reacted (div)	7.05
		HCl reacted (div)	0
Products (div)		Products (div)	
HCN	13.2	HCN	19.6
H_2	5.16	H_2	20.5
NH_3	7.77	CH_4	0.3
		CH_3CN	2.62

considerable quantities of several unidentified products; appear to be:

C_2H_2

C_2H_4

Table XX. The reaction of iso-C_4H_{10} with active nitrogen at room temperature.

iso-C_4H_{10} added = 94 div

active nitrogen only N-atoms = 100 div		active nitrogen plus HCl N-atoms = 100 div; HCl = 94 div	
iso-C_4H_{10} reacted (div)	16.0	iso-C_4H_{10} reacted (div)	6.65
		HCl reacted (div)	0
Products (div)		Products (div)	
HCN	31.0	HCN	19.5
H_2	21.4	H_2	20.6
CH_3CN	9.95	CH_3CN	4.88
NH_3	5.26	CH_4	0.2

considerable quantities of several unidentified products; appear to be:

C_2H_2

C_2H_4

Table XXI. The reaction of neo-C_5H_{12} with active nitrogen at room temperature.

neo-C_5H_{12} added = 94 div

active nitrogen only N-atoms = 100 div		active nitrogen plus HCl N-atoms = 100 div; HCl = 94 div	
neo-C_5H_{12} reacted (div)	2.12	neo-C_5H_{12} reacted (div)	5.31
		HCl reacted (div)	0
Products (div)		Products (div)	
HCN	7.12	HCN	15.5
H_2	2.04	H_2	18.8
CH_3CN	2.34	CH_3CN	5.16
		CH_4	0.2
		considerable quantities of several unidentified products; appear to be:	
		C_2H_2	
		C_2H_4	

Table XXII. The reaction of cyclopropane with active nitrogen at room temperature.

cyclopropane added = 104 div

active nitrogen only

N-atoms = 100 div

cyclopropane reacted (div)	----
Products (div)	
HCN	2.72
H_2	0.8
NH_3	3.82
polymer (mass 51,52)	0.3

active nitrogen plus HCl

N-atoms = 100 div; HCl = 94 div

cyclopropane reacted (div)	---
HCl reacted (div)	0
Products (div)	
HCN	7.07
H_2	
polymer (mass 49→52)	0.9

considerable quantities of several unidentified products; appear to be:

C_2H_2

C_2H_4

C_3H_6

Table XXIII. The reaction of CH_4 with active nitrogen. Approximate variation of HCN production with concentration of CH_4 and HCl.

N-atoms = 100 div

pressure 0.5 mm Hg

CH_4 added (div)	HCN formed (div)	HCl added (div)	conditions
443	4.5	0	room temp.
448	4.7	0	room temp.
455	10.3	300	room temp.
443	10.3	150	room temp.
440	13.1	300	room temp.
1420	31.0	300	> 100°C
475	31.4	300	room temp.
180	40.9	150	> 100°C
444	46.2	150	> 100°C
412	64	400	> 100°C

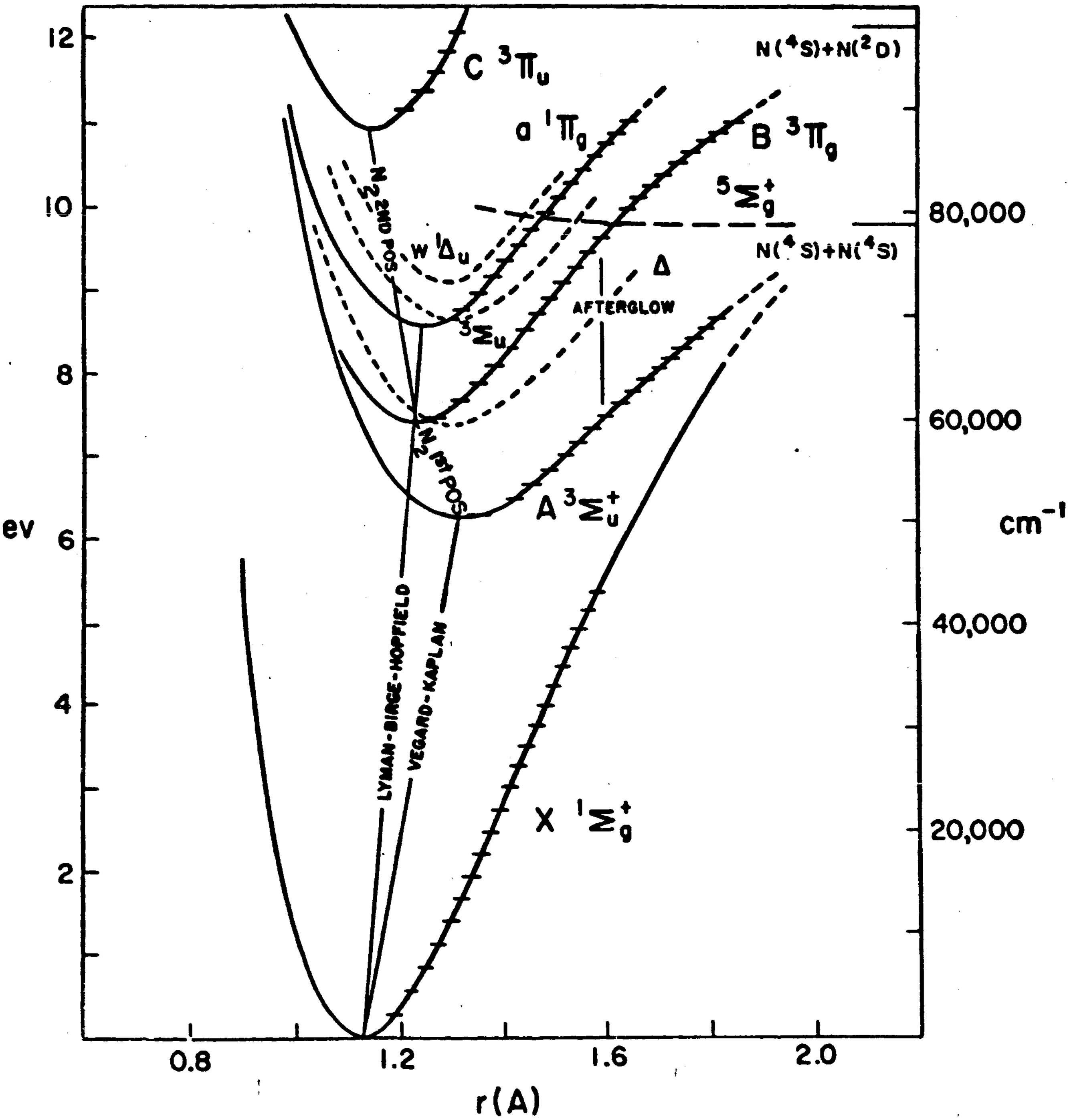


FIG. 1. Potential curves of the nitrogen molecule.

(From: U. H. Kurzweg and H. P. Broida, J. Molecular Spectrosc. 3, 388 (1959).)

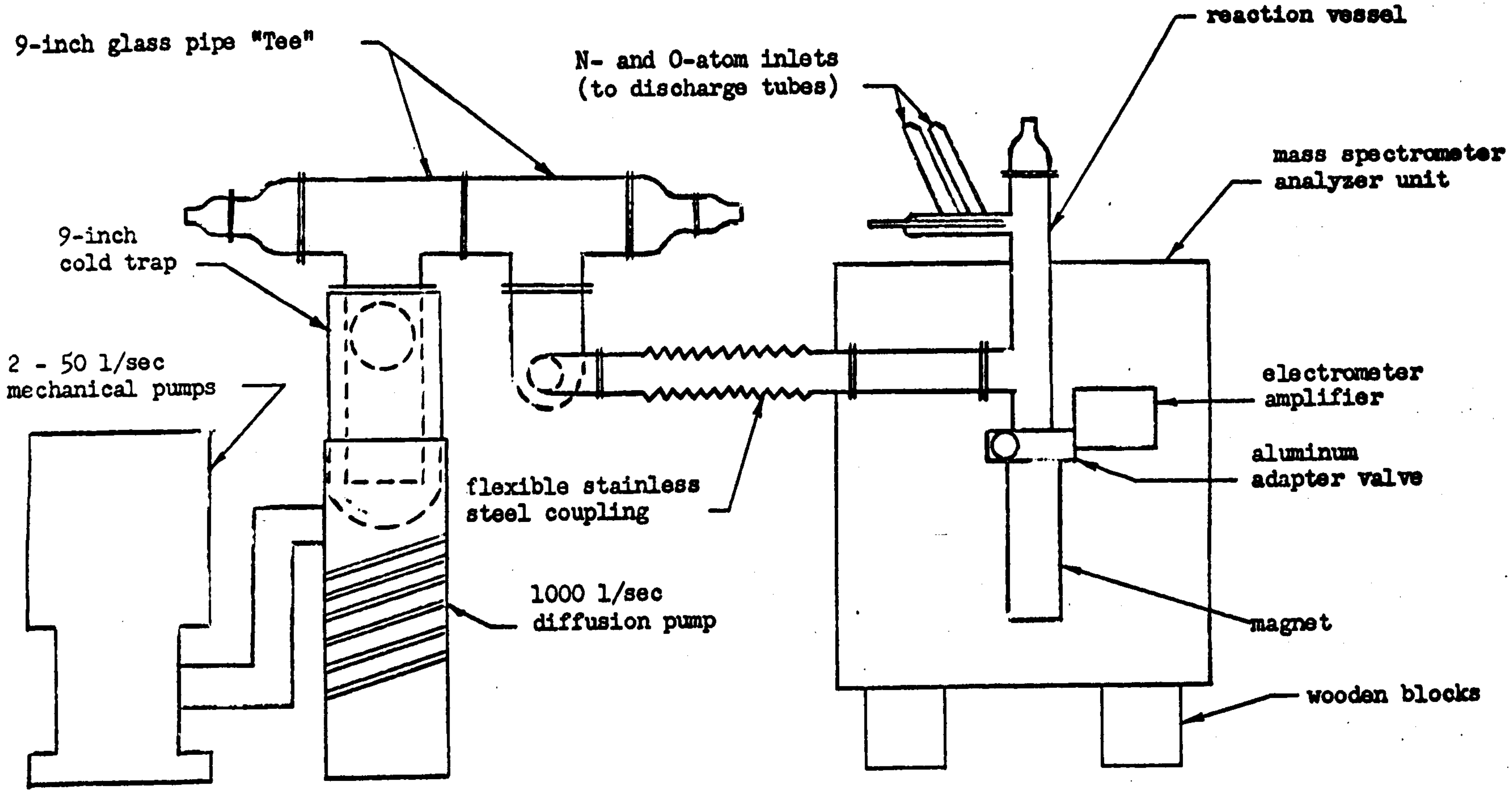
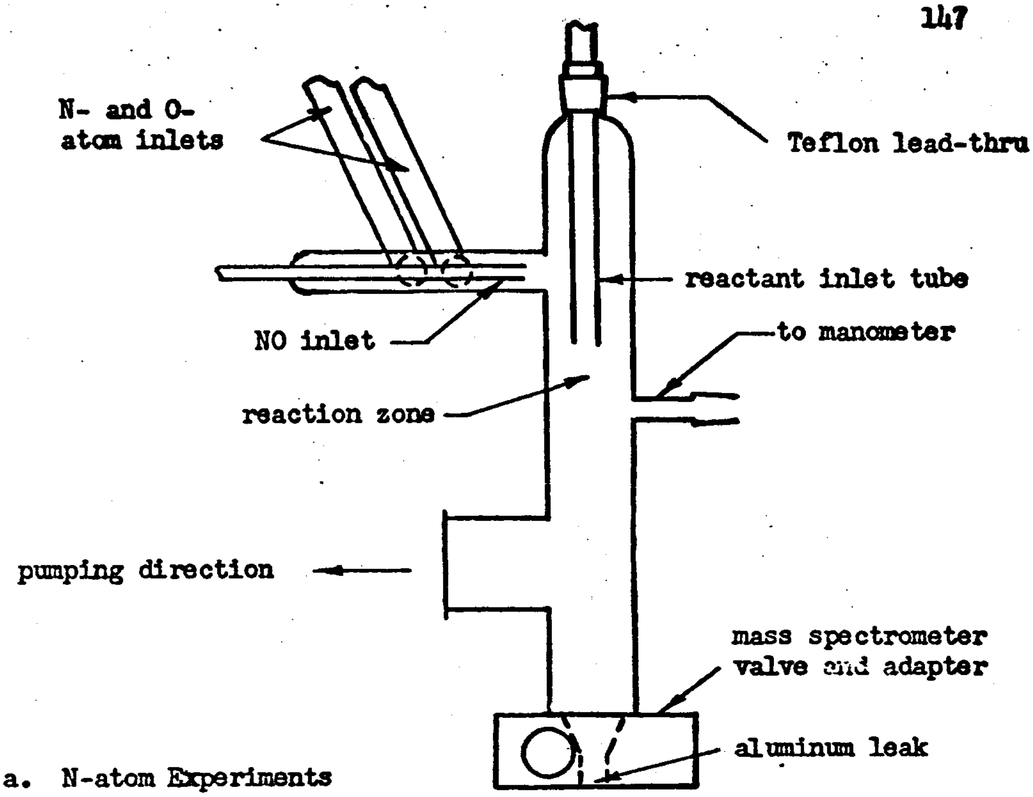
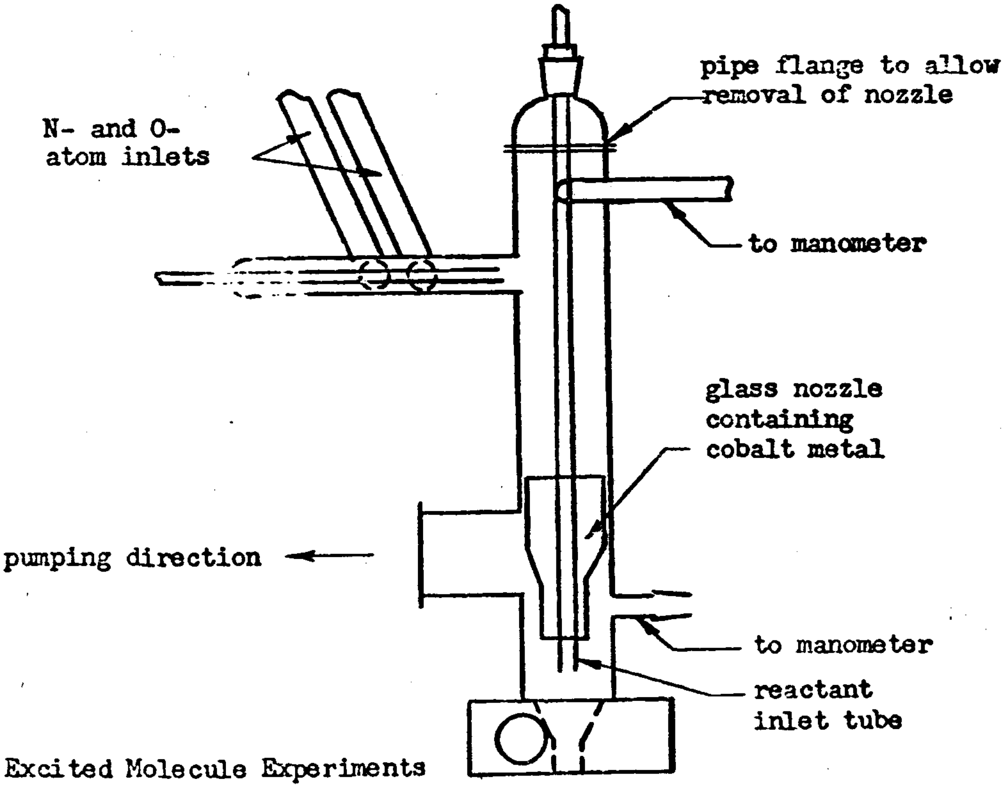


Fig. 2. Pictorial layout of the various components of the vacuum system.



a. N-atom Experiments



b. Excited Molecule Experiments

Fig. 3. Design of reaction vessels.

Direction of Flow

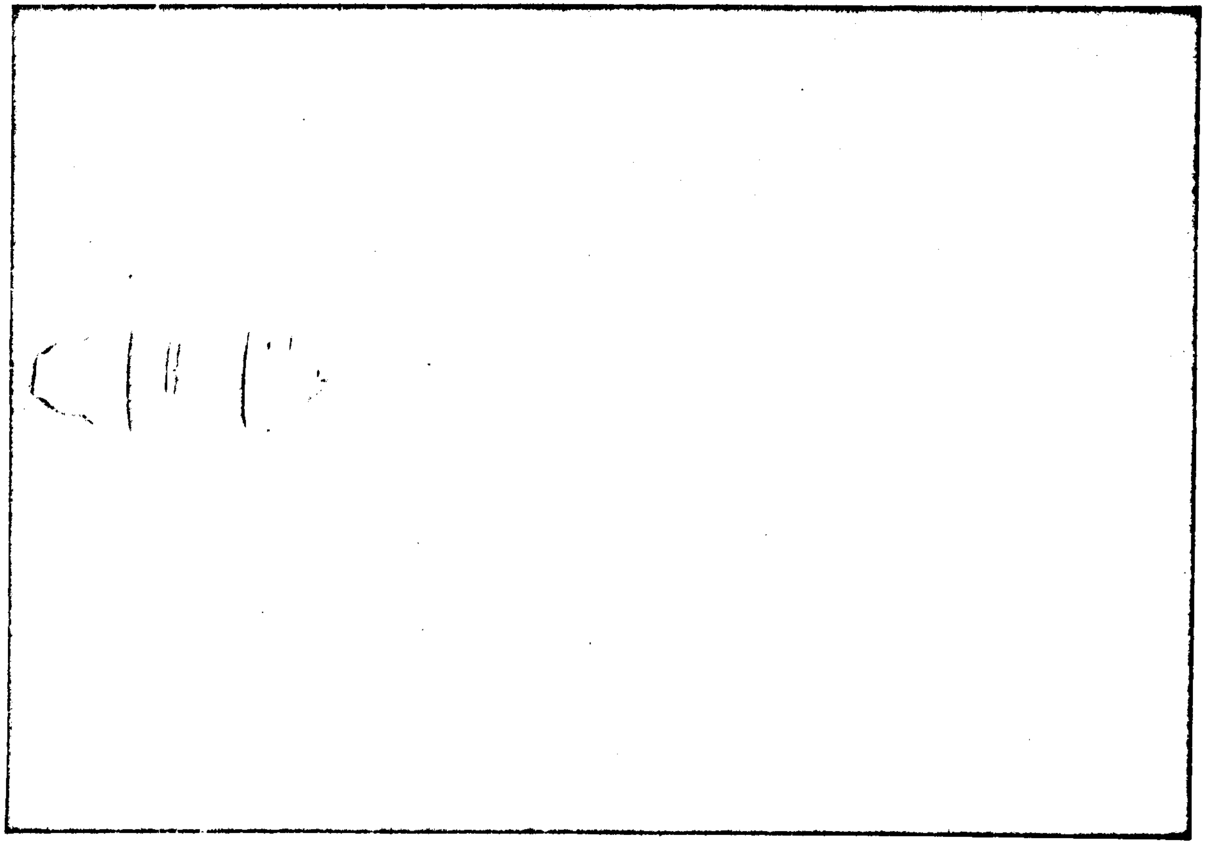
→

Glass nozzle positioned inside vacuum system

Triangular arrangement of cobalt catalyst in nozzle

Stream of excited molecules, emitting first positive band system of N_2; distance ~ 15 cm, equiv. to 0.01 sec

Fig. 4. Photograph showing triangular arrangement of cobalt metal in nozzle, and position of nozzle in vacuum system. Nozzle dia. 1-1/4 inch.



Direction of Flow $\longrightarrow$

Active nitrogen stream with O-atoms

Cobalt catalyst in nozzle

Stream of excited molecules, emitting first positive band system of N_2; distance ~ 40 cm, equiv. to 0.01 sec

Fig. 5. Photograph showing effect of linear velocity through nozzle (nozzle diameter) upon length of jet of $N_2(A^3\Sigma_u^+)$ molecules. Nozzle dia. ~ 3/8 inch.

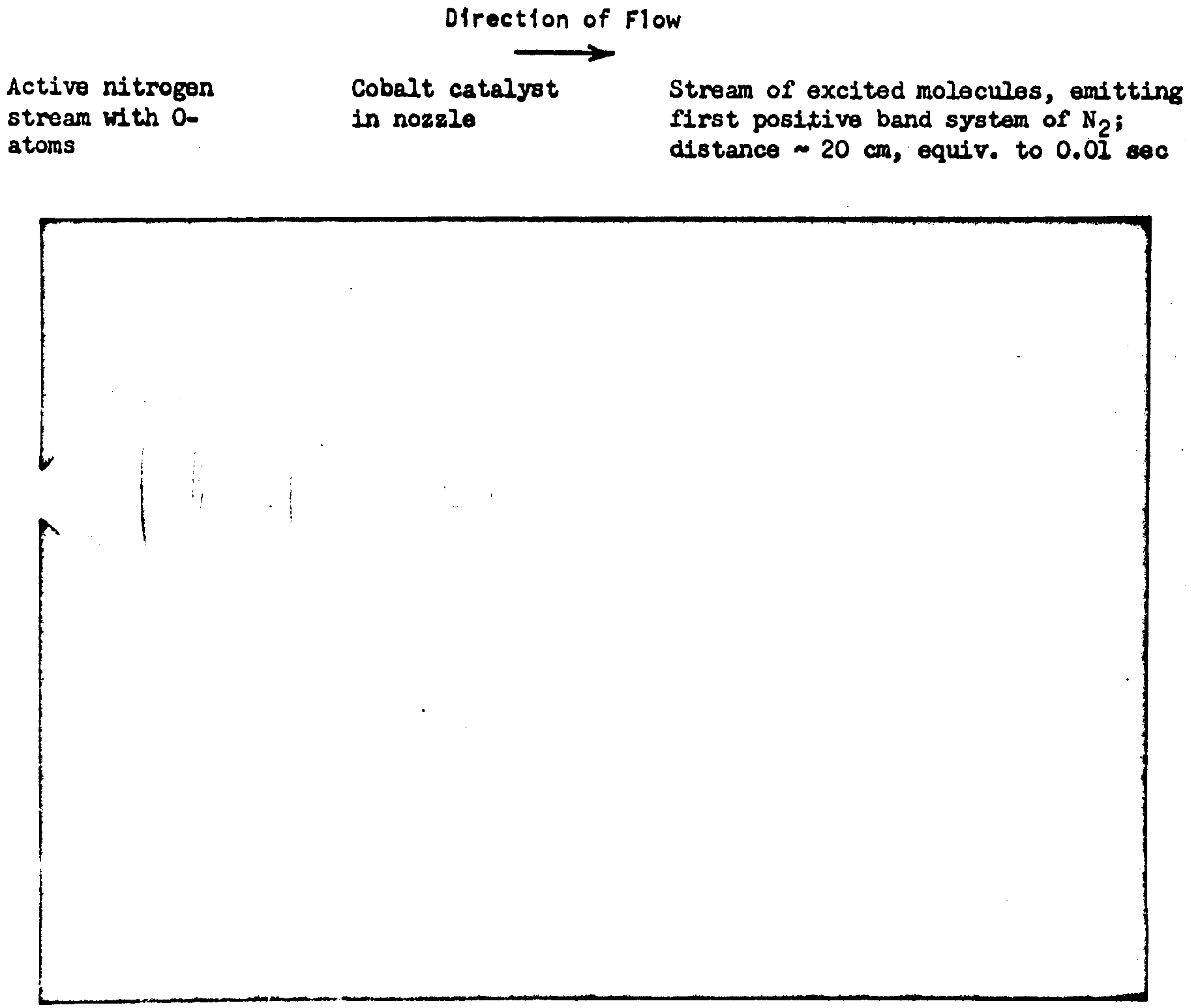


Fig. 6. Photograph showing effect of linear velocity through nozzle (nozzle diameter) upon length of jet of $N_2(A^3\Sigma_u^+)$ molecules. Nozzle dia. ~ 1 inch.

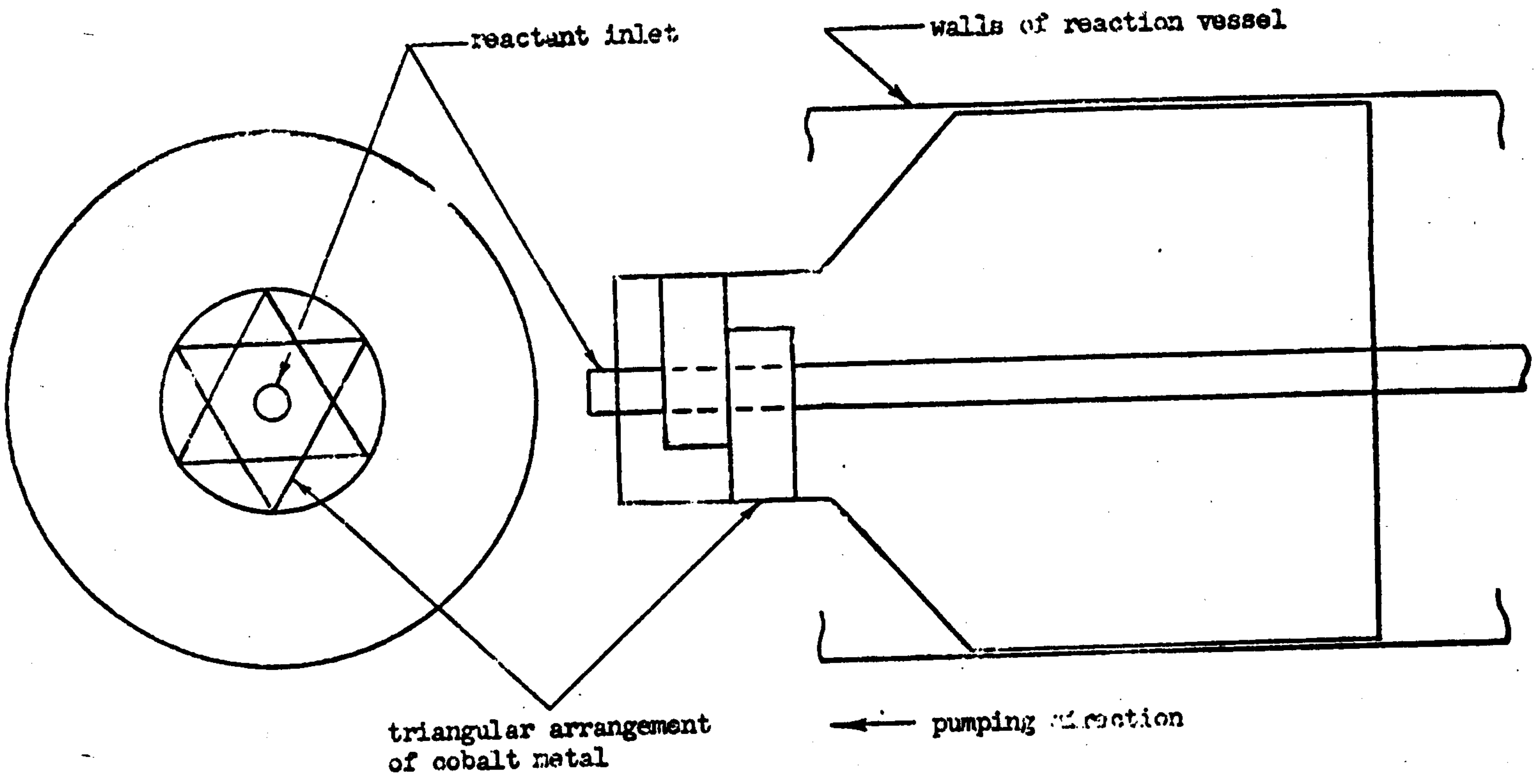


Fig. 7. Diagram of typical glass nozzle showing triangular arrangement of cobalt metal.

Scale: Full size.

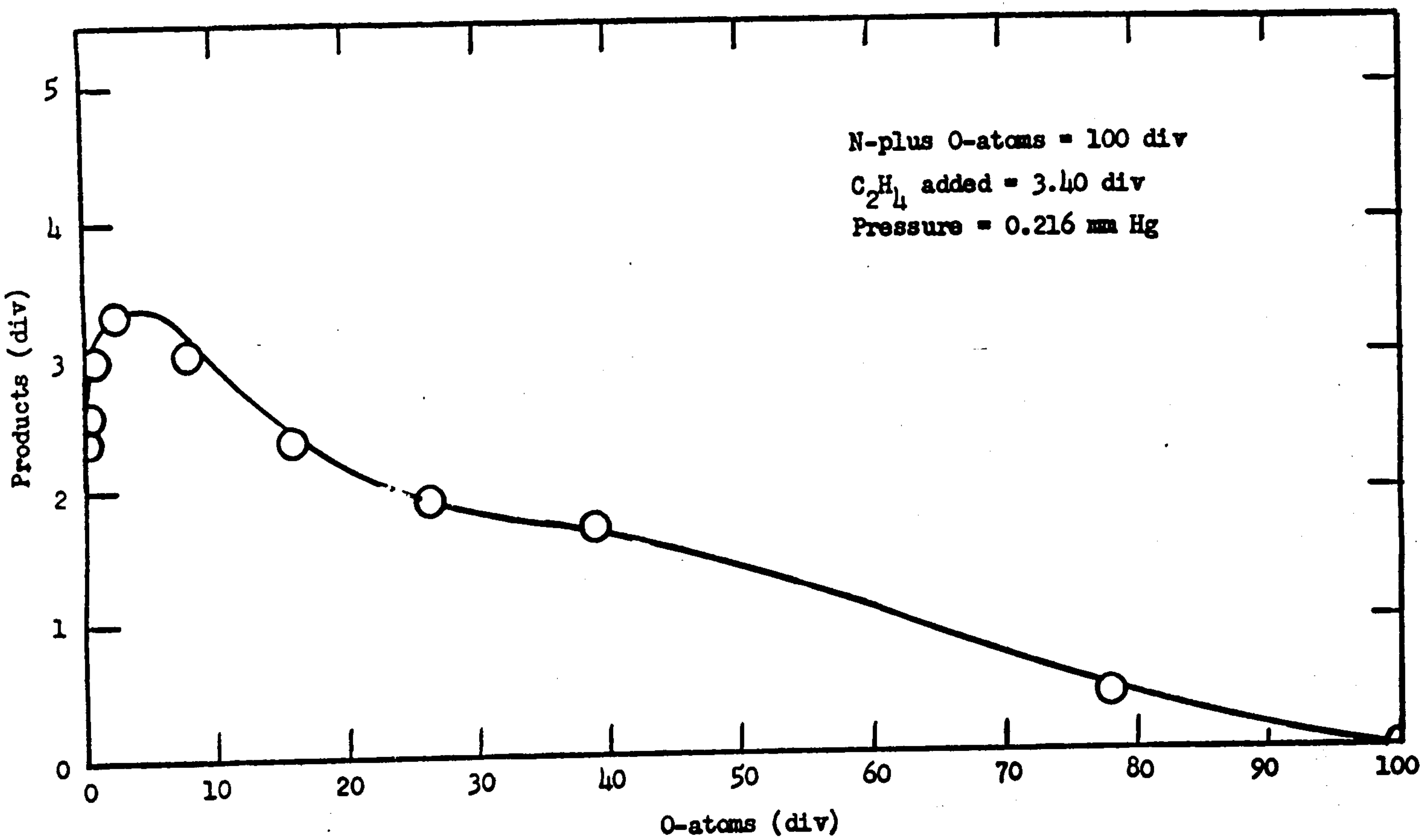


Fig. 8 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

HCN produced vs divisions O-atoms.

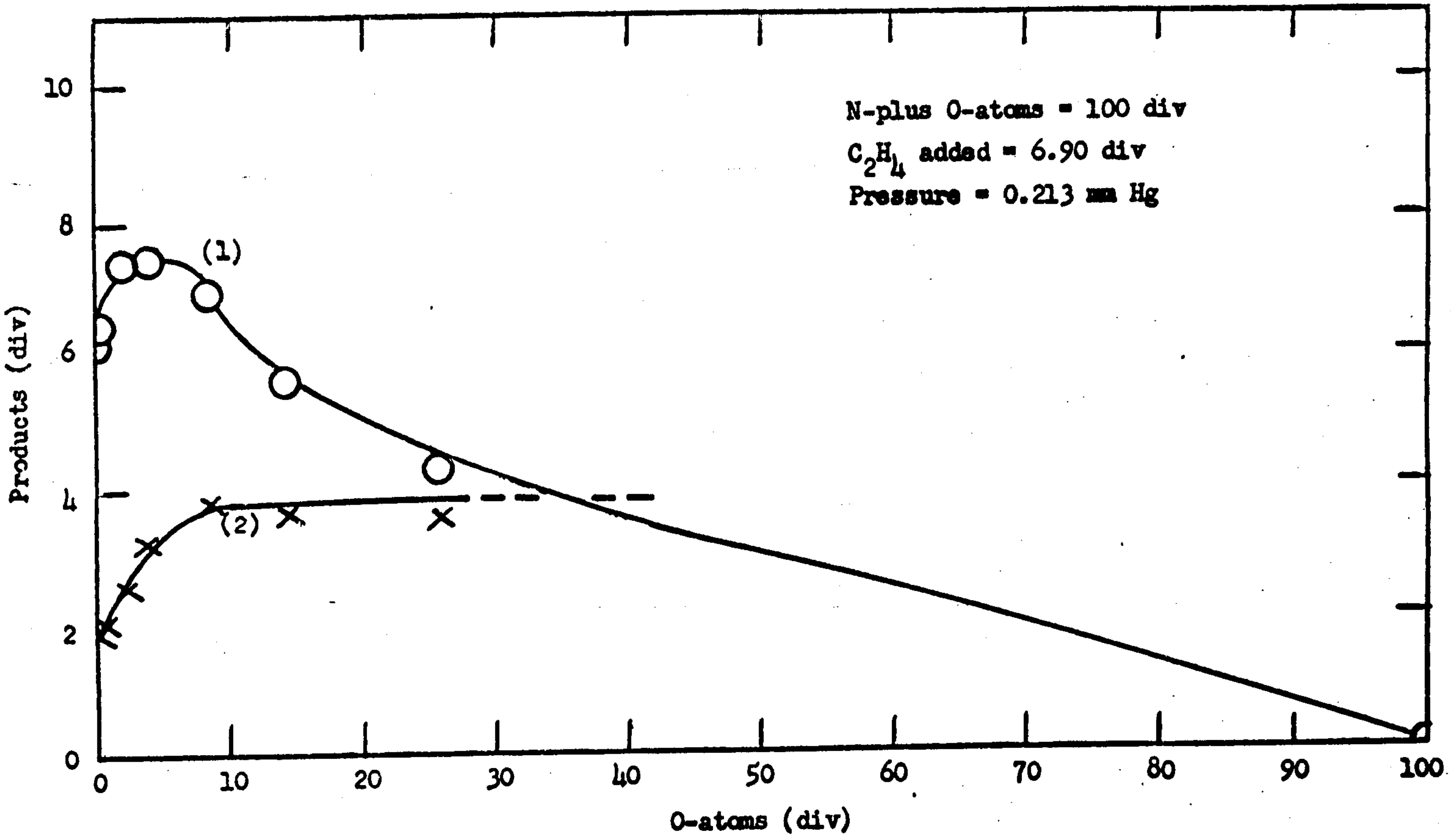


Fig. 9 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

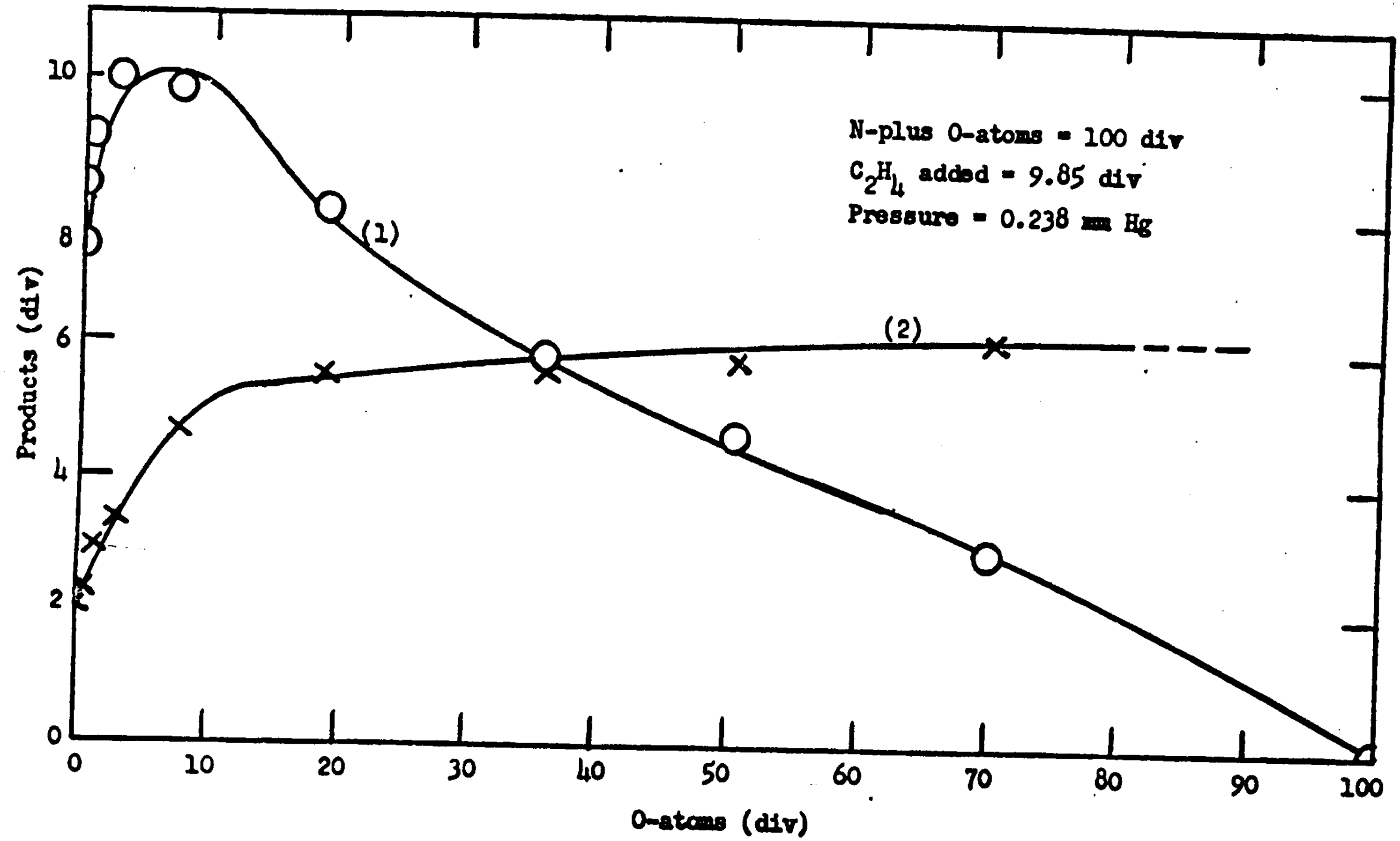


Fig. 10 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

(1) HCN produced *vs* divisions O-atoms.

(2) H_2 produced *vs* divisions O-atoms.

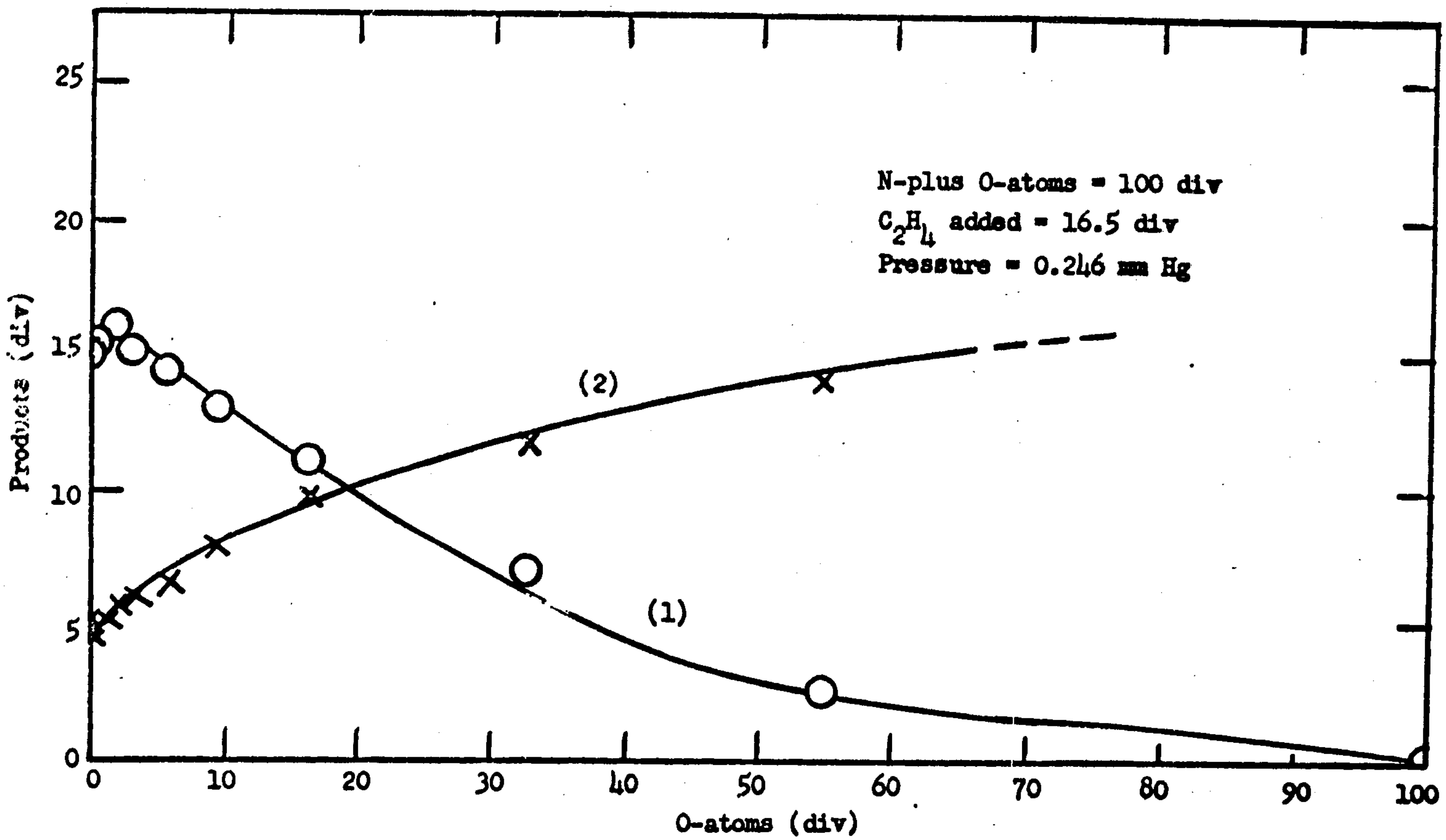


Fig. 11 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

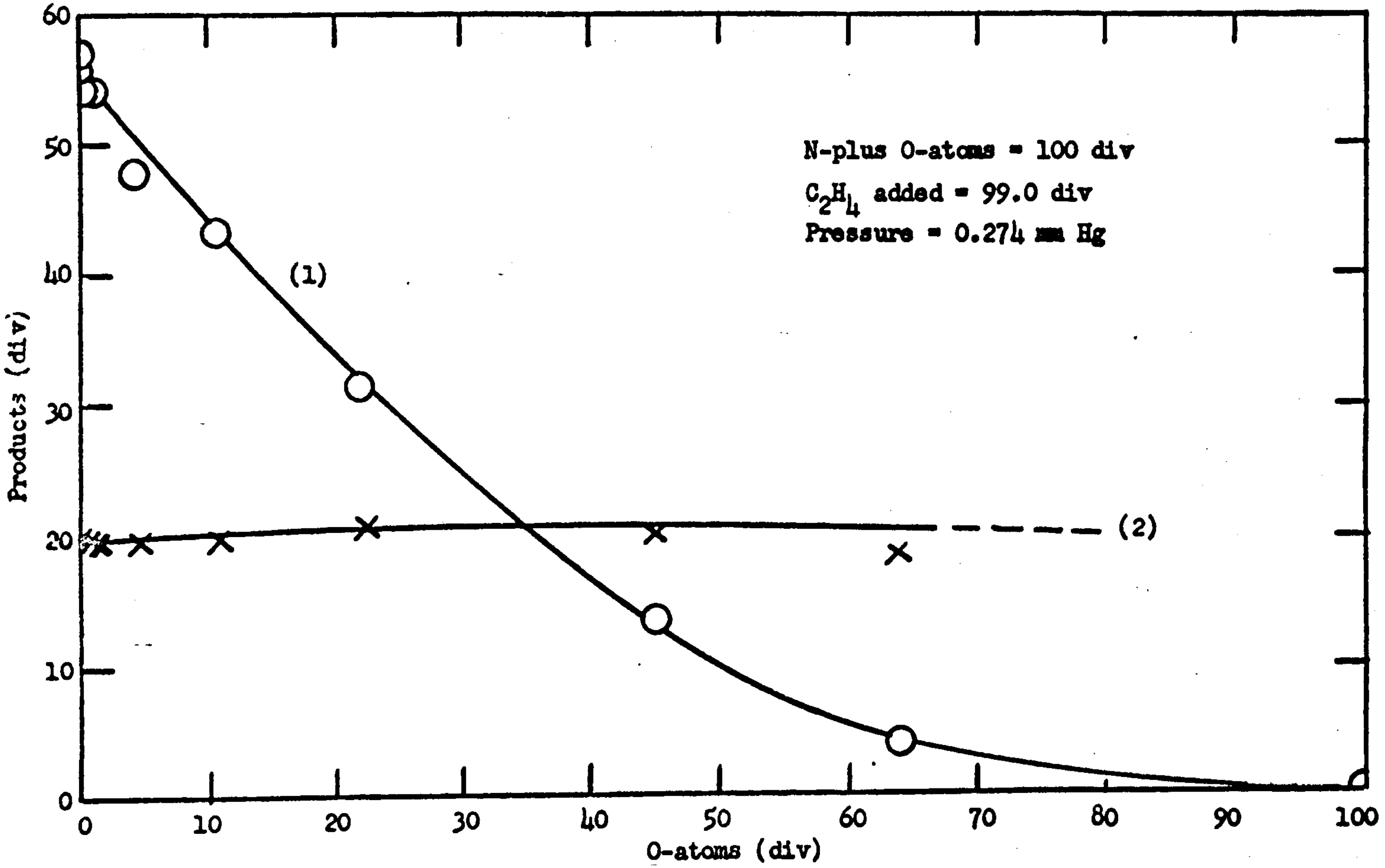


Fig. 12 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

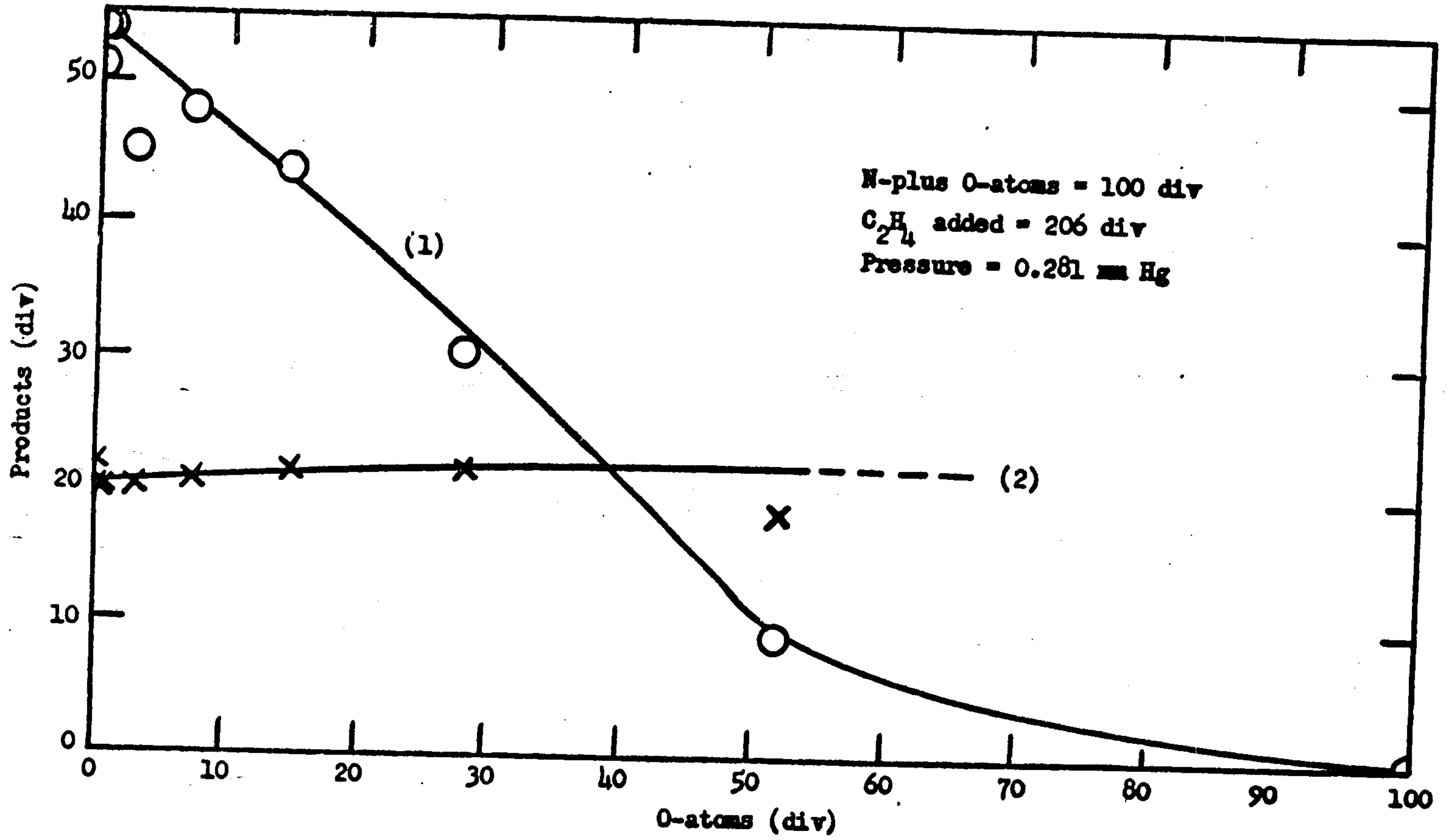


Fig. 13 - Reaction of C_2H_4 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

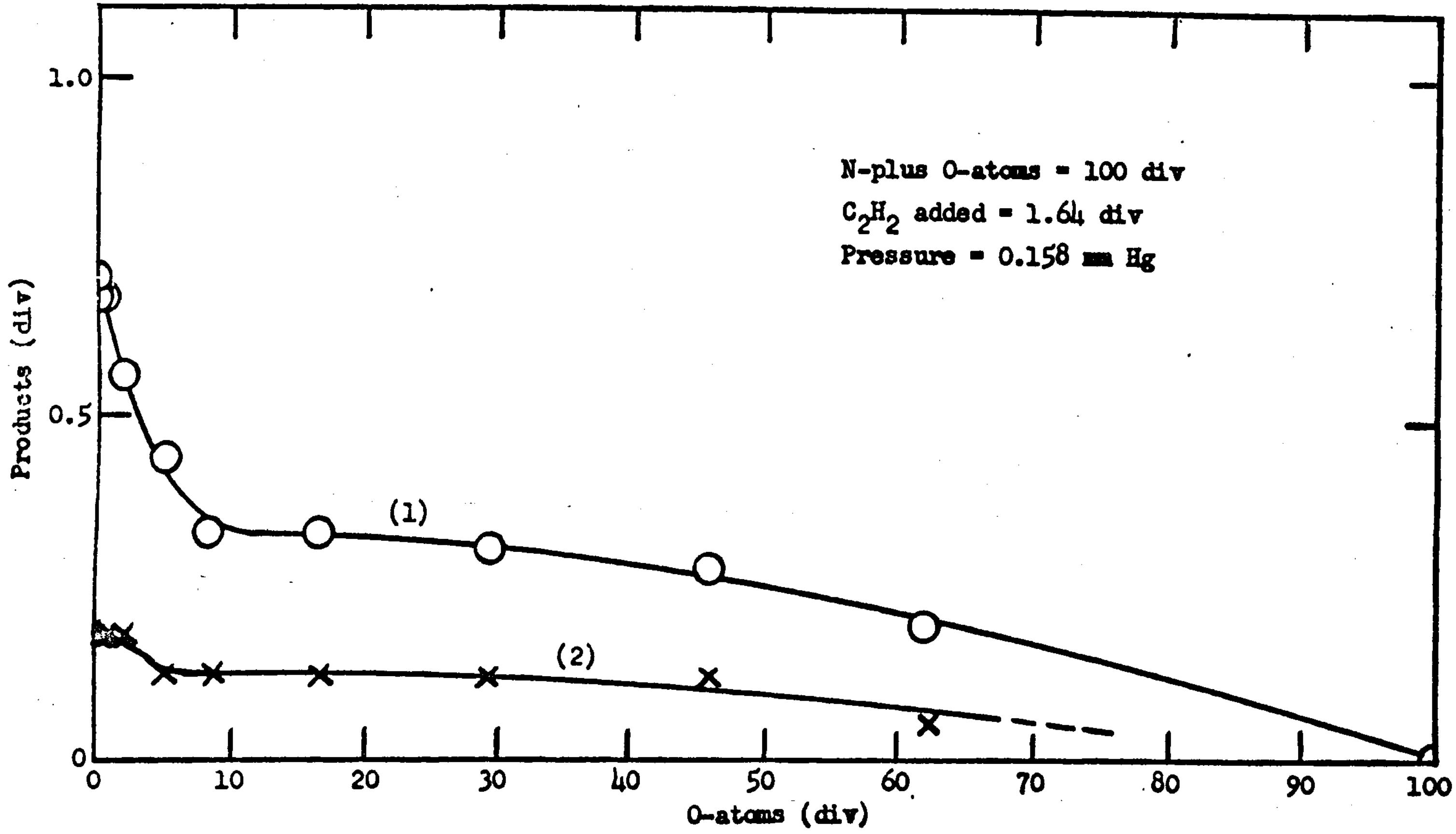


Figure 14 - Reaction of C_2H_2 with a mixture of N- and O-atoms.

(1) HCN produced <u>vs</u> divisions O-atoms.

(2) H_2 produced <u>vs</u> divisions O-atoms.

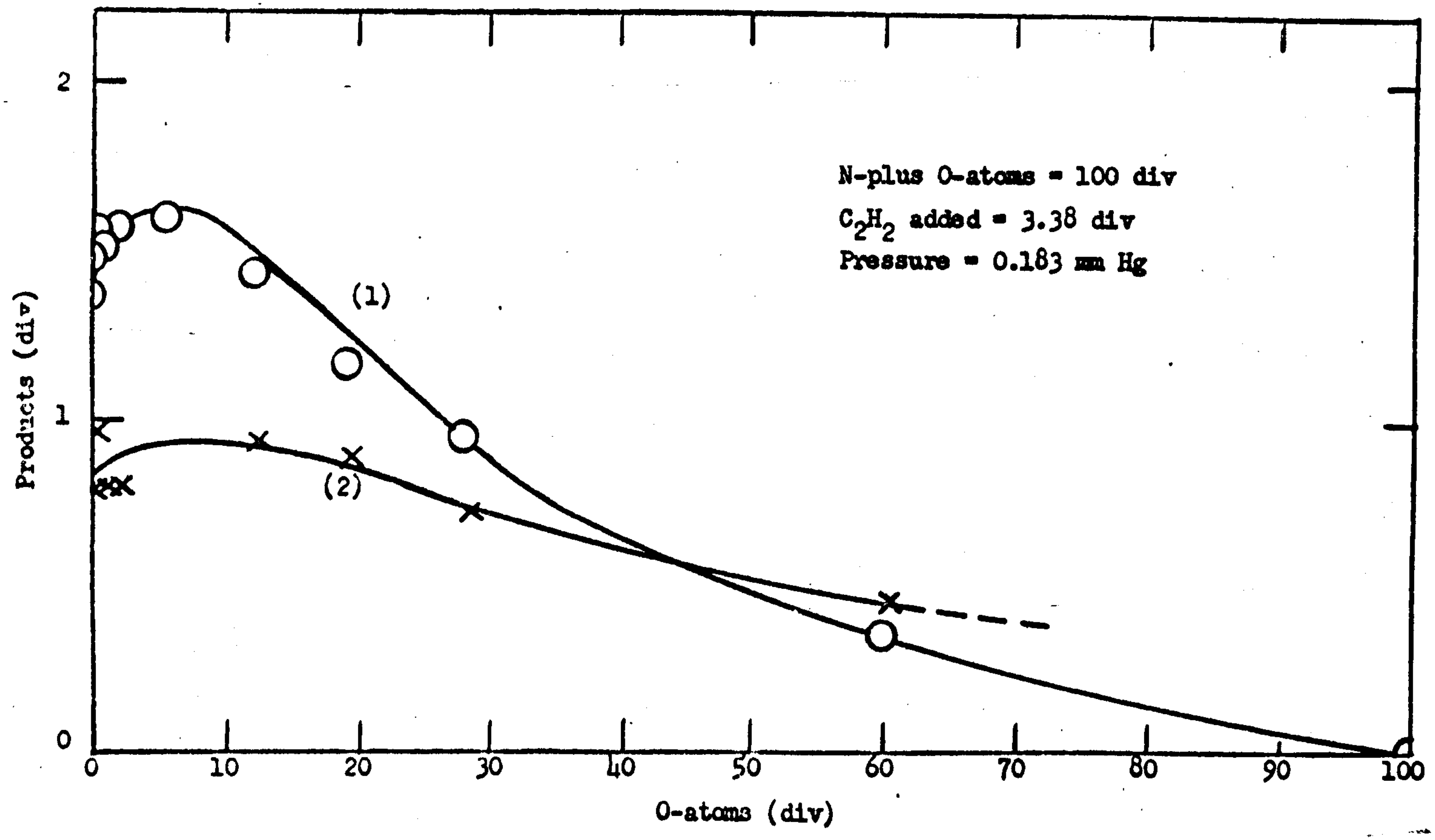


Fig. 15 - Reaction of C_2H_2 with a mixture of N- and O-atoms

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

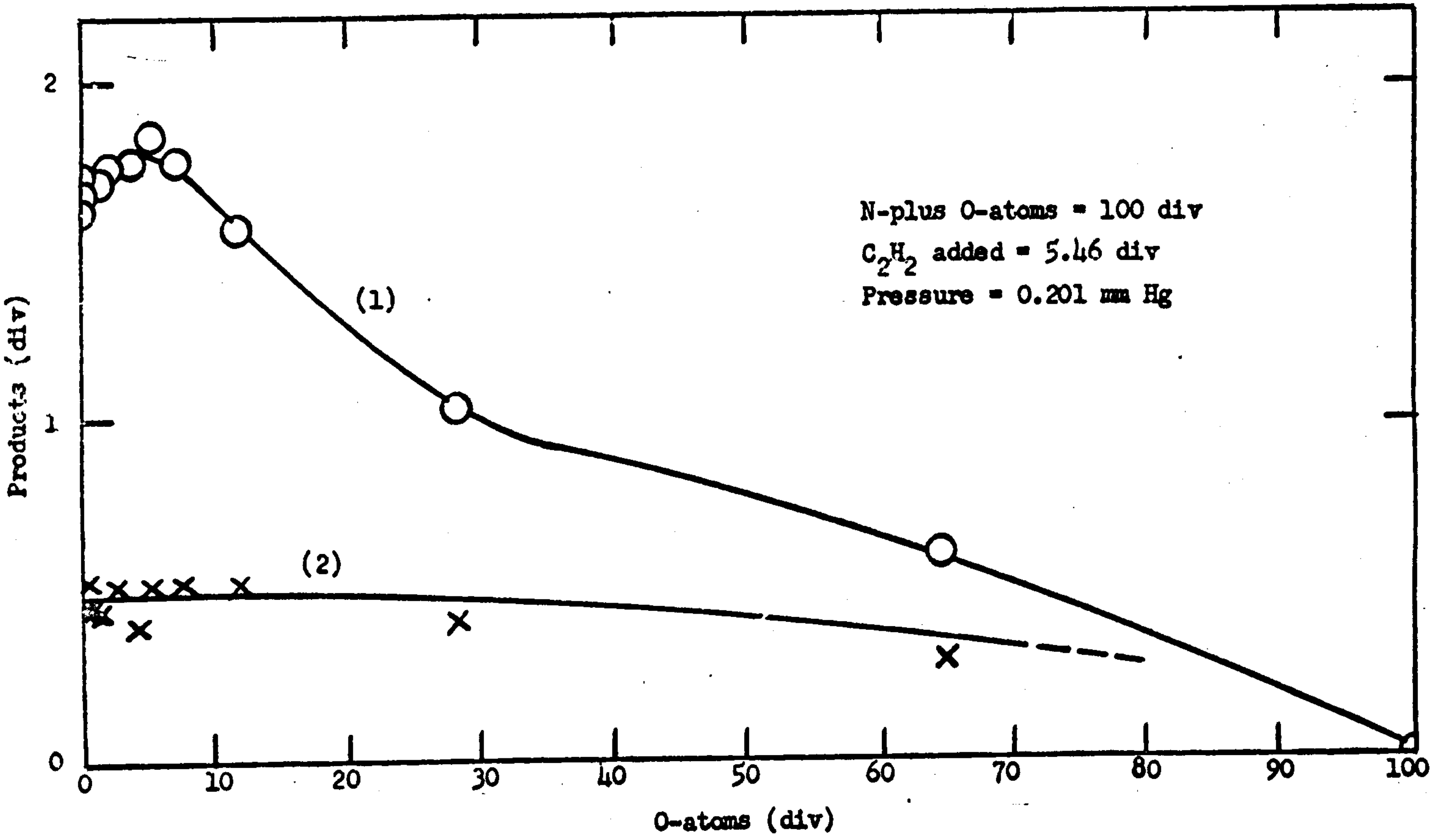


Fig. 16 - Reaction of C_2H_2 with a mixture of N- and O-atoms.

(1) HCN produced <u>vs</u> divisions O-atoms.

(2) H_2 produced <u>vs</u> divisions O-atoms.

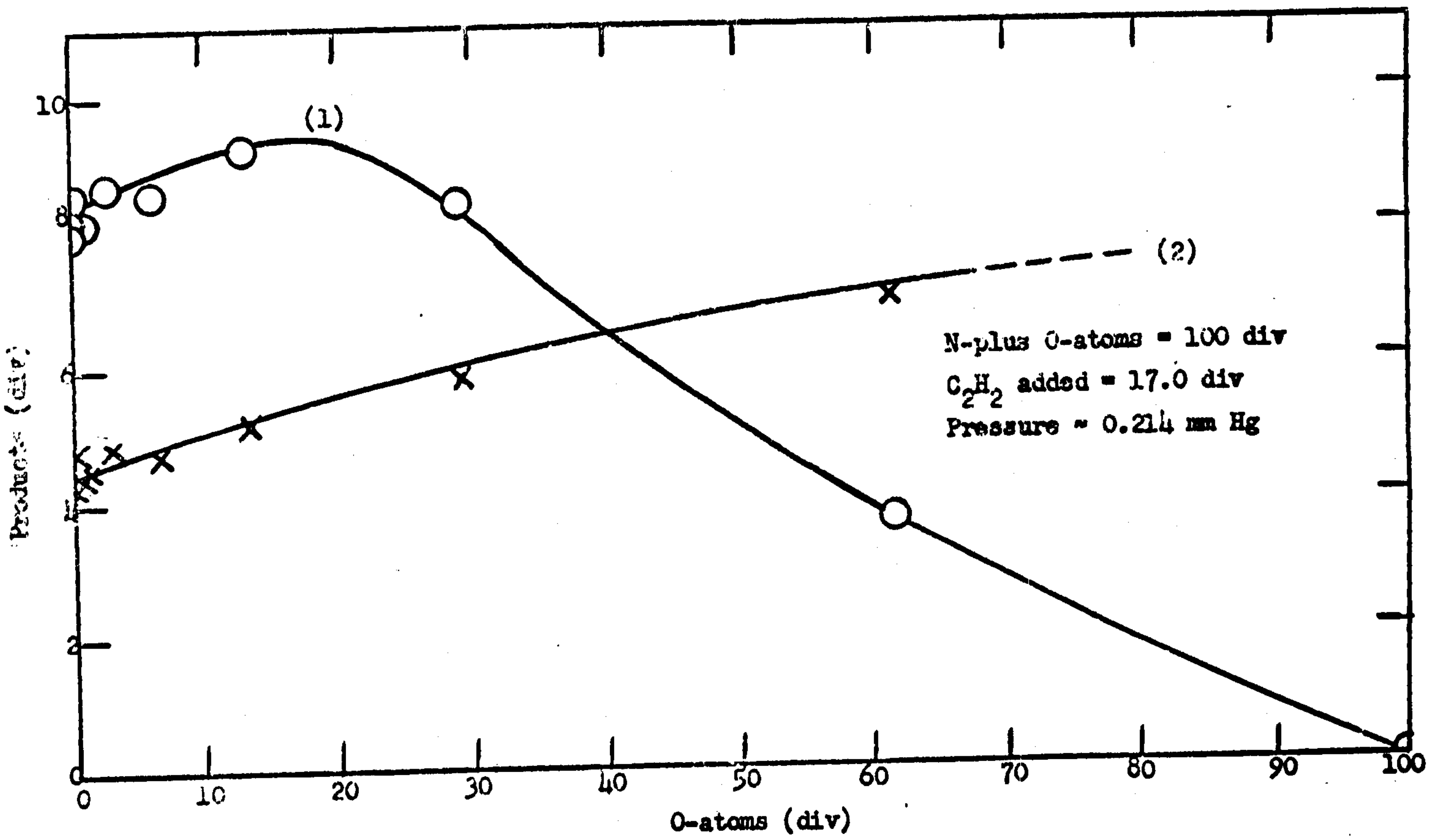


Fig. 17 - Reaction of C_2H_2 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

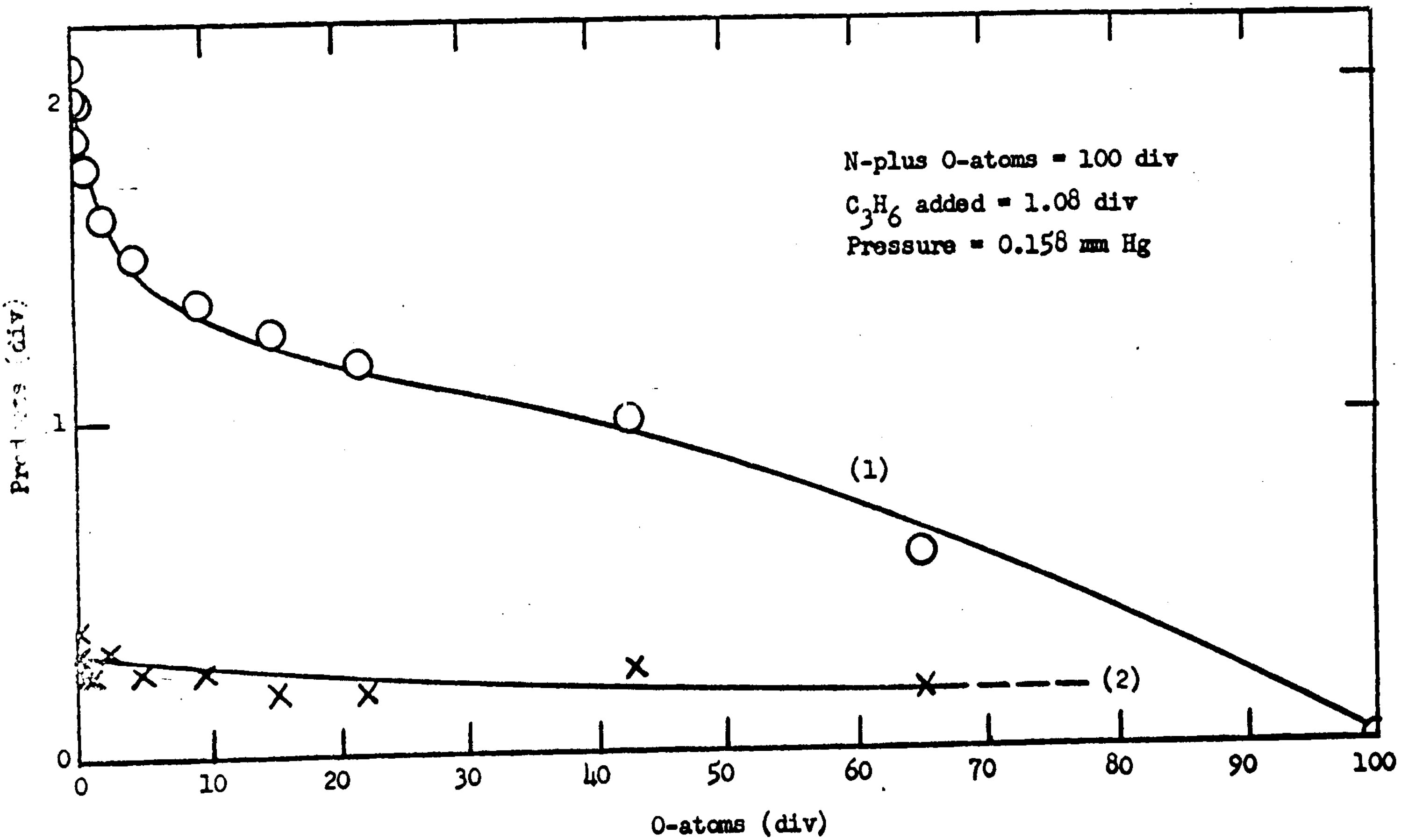


Fig. 18 - Reaction of C_3H_6 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

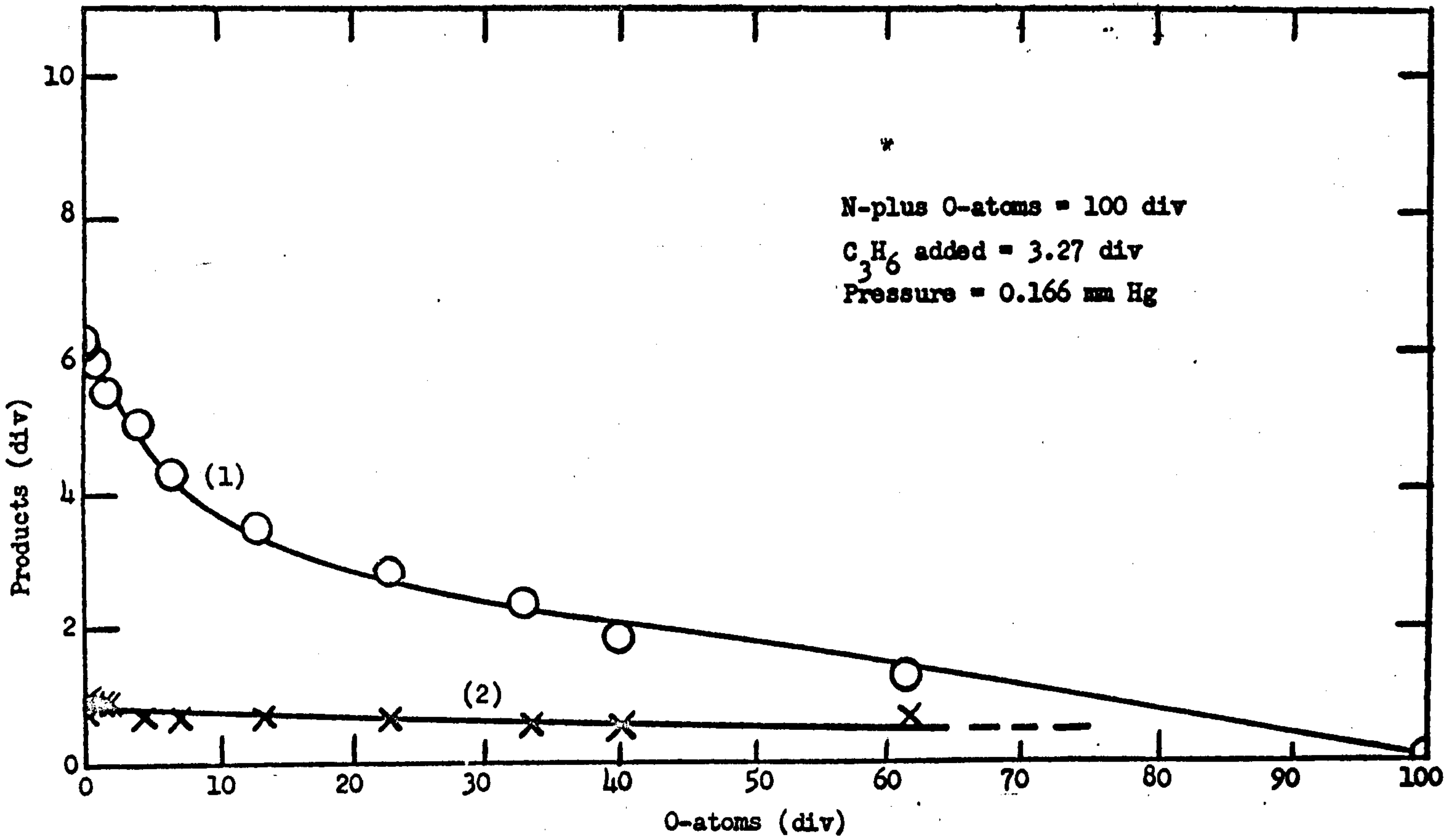


Fig. 19 - Reaction of C_3H_6 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

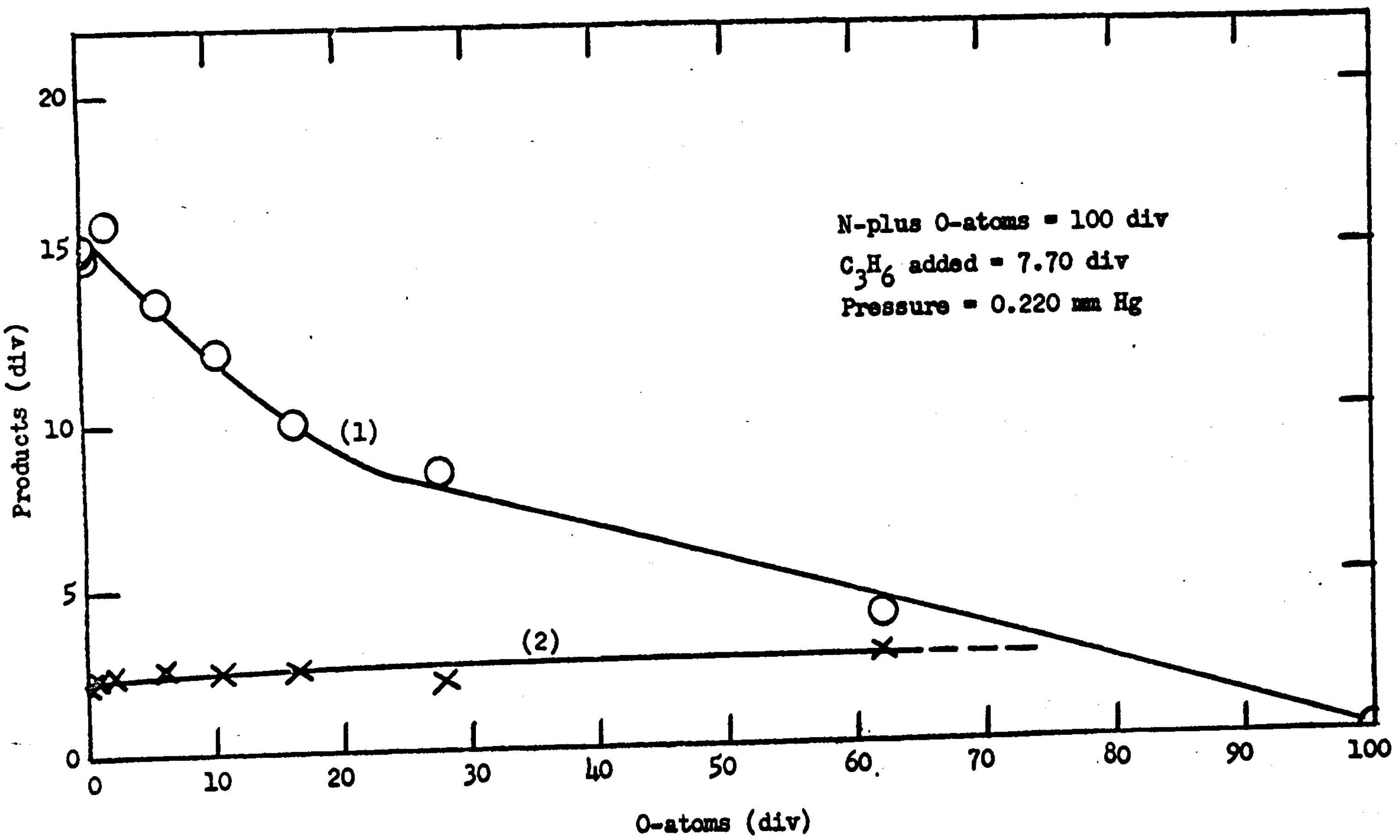


Fig. 20 - Reaction of C_3H_6 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

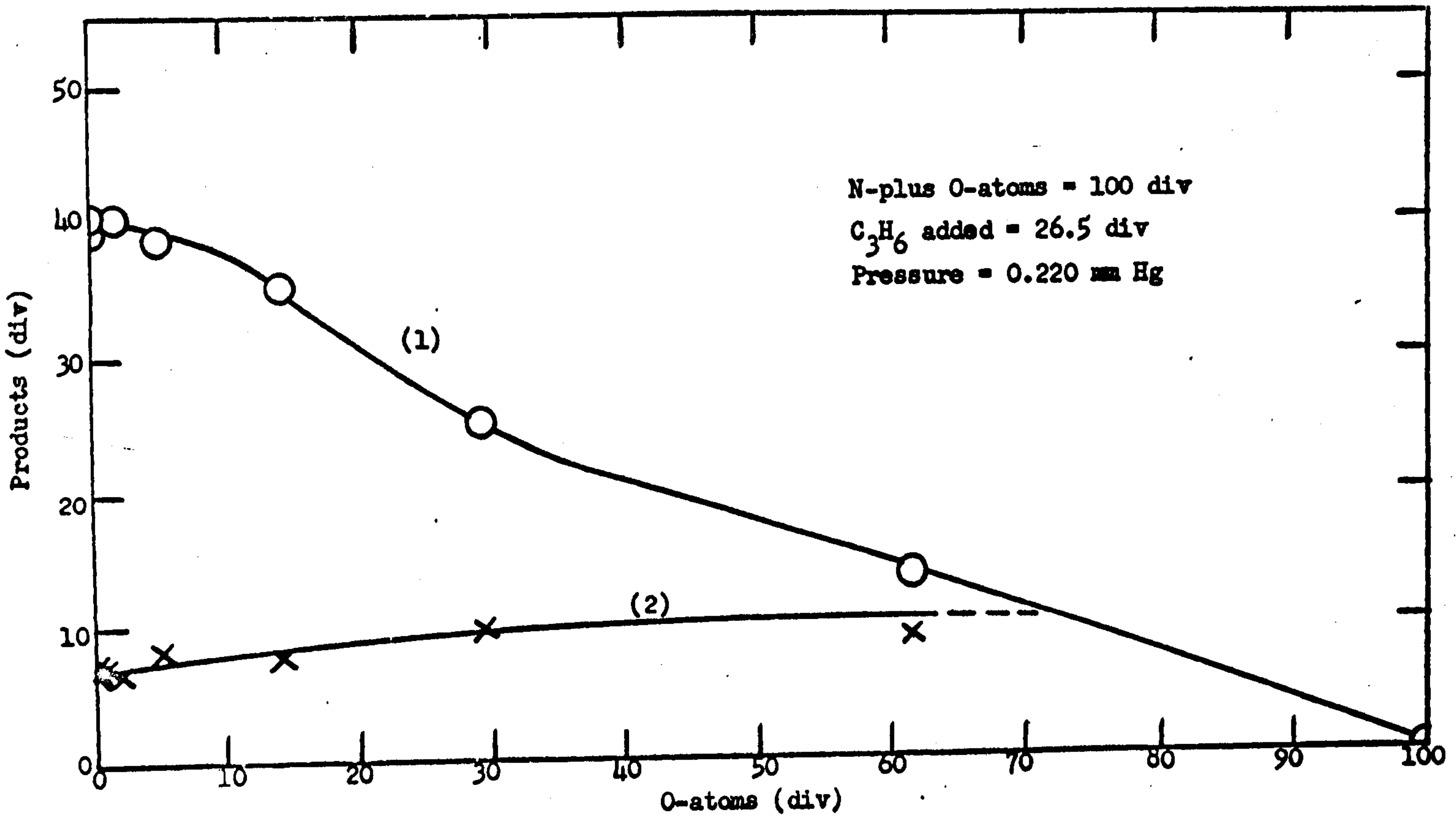


Fig. 21 - Reaction of C_3H_6 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

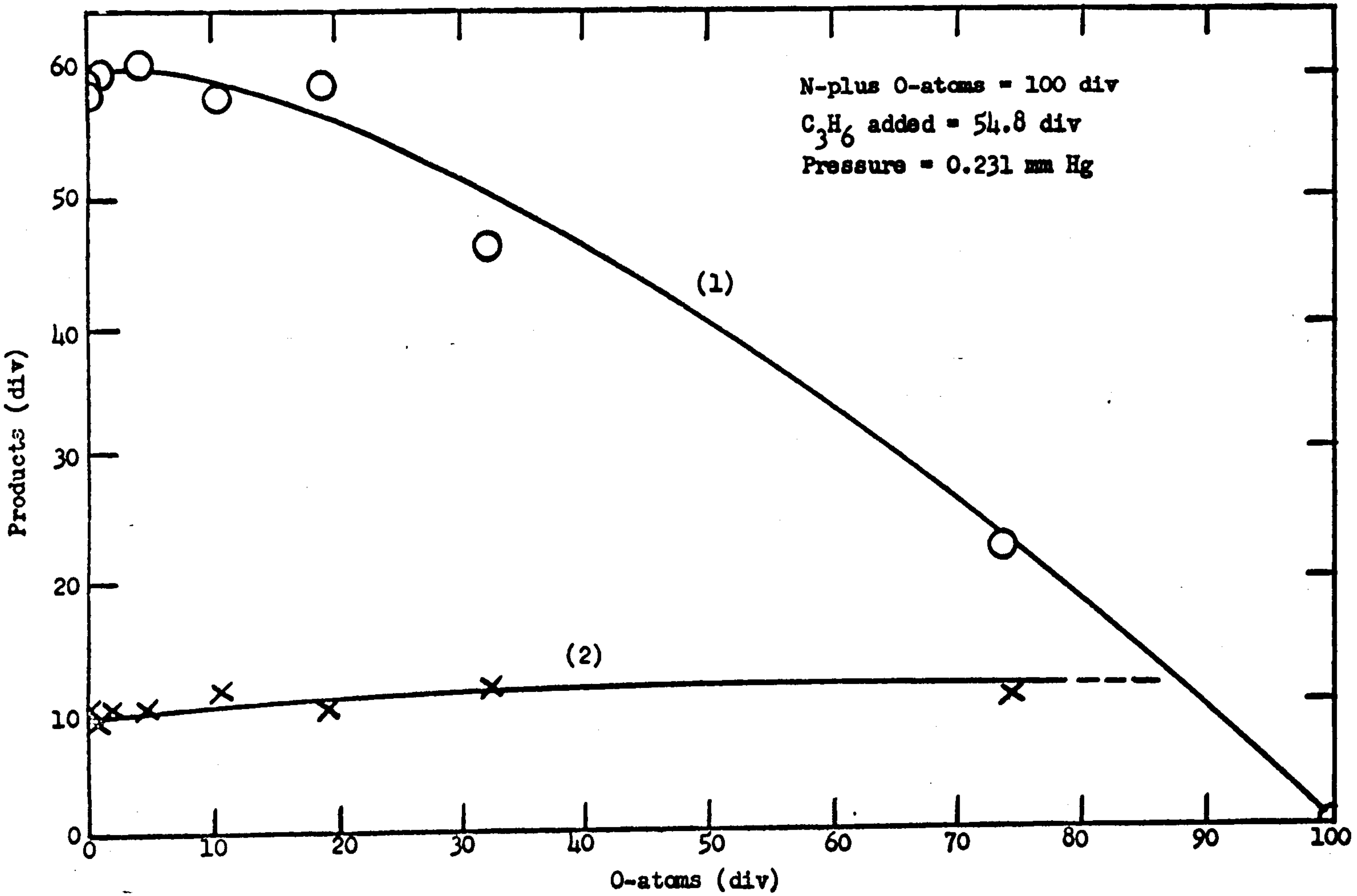


Fig. 22 - Reaction of C_3H_6 with a mixture of N- and O-atoms.

(1) HCN produced vs divisions O-atoms.

(2) H_2 produced vs divisions O-atoms.

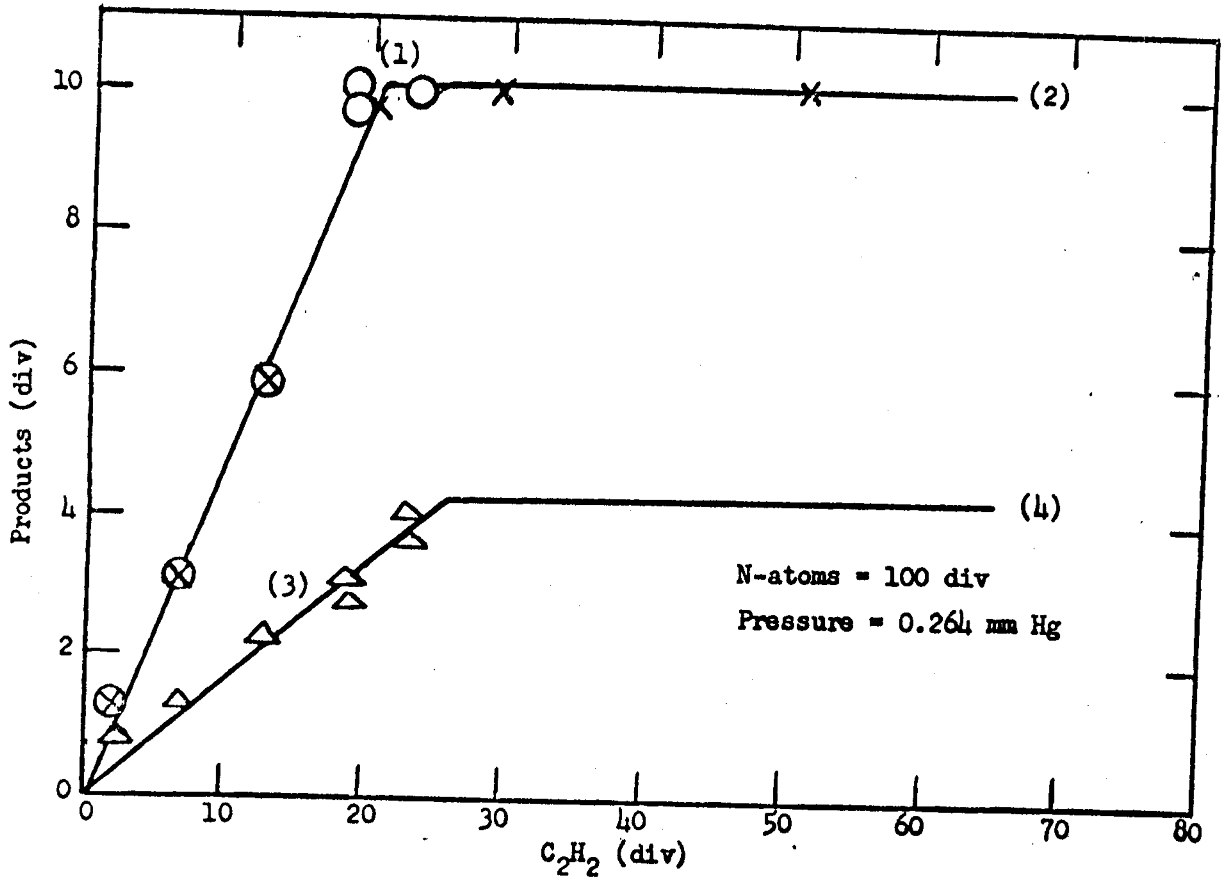


Fig. 23 - Reaction of N-atoms with C_2H_2; no O-atoms.

(1) HCN produced <u>vs</u> C_2H_2 reacted.
(2) HCN produced <u>vs</u> C_2H_2 added.
(3) H_2 produced <u>vs</u> C_2H_2 reacted.
(4) H_2 produced <u>vs</u> C_2H_2 added.

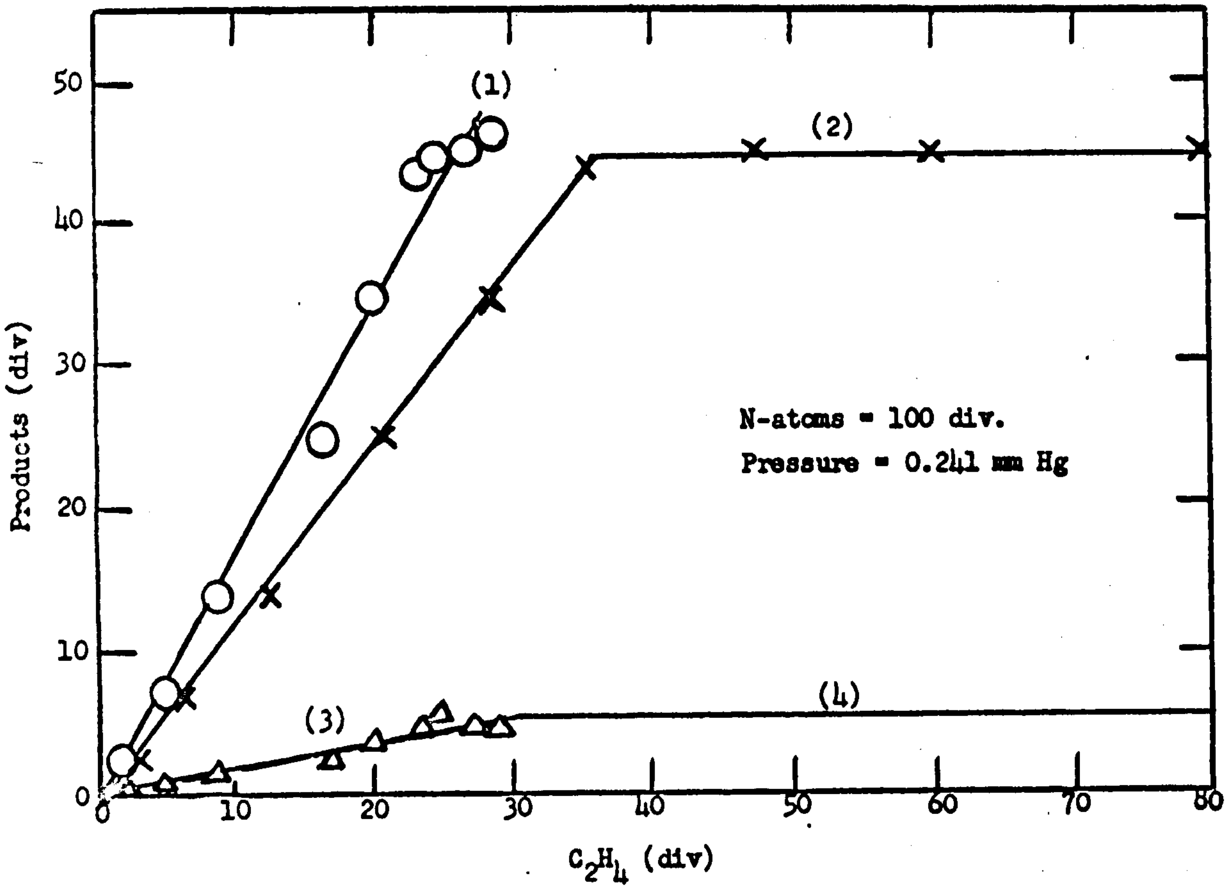


Fig. 24 - Reaction of N-atoms with C_2H_4; No O-atoms.

(1) HCN produced vs C_2H_4 reacted.

(2) HCN produced vs C_2H_4 added.

(3) H_2 produced vs C_2H_4 reacted.

(4) H_2 produced vs C_2H_4 added.

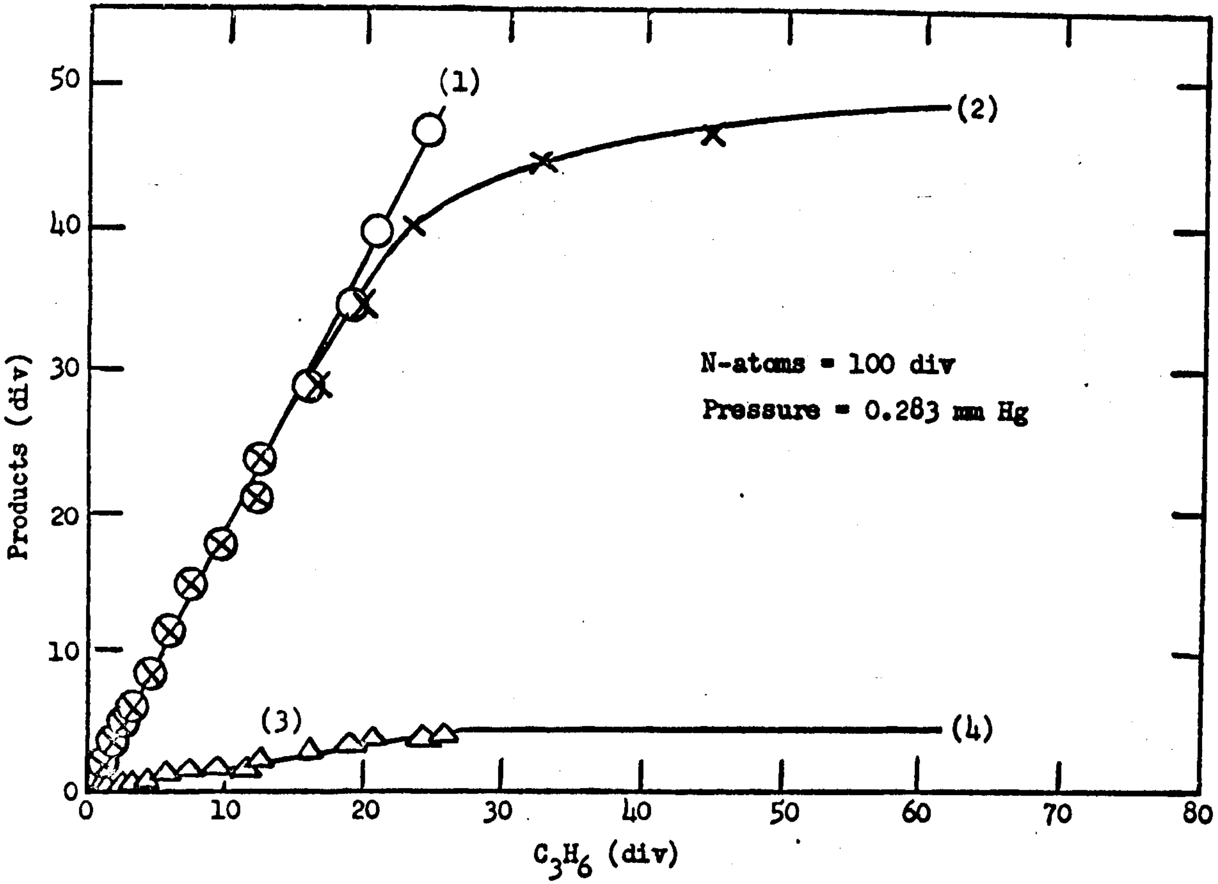


Fig. 25 - Reaction of N-atoms with C_3H_6; no O-atoms.

(1) HCN produced vs C_3H_6 reacted.
(2) HCN produced vs C_3H_6 added.
(3) H_2 produced vs C_3H_6 reacted.
(4) H_2 produced vs C_3H_6 added.

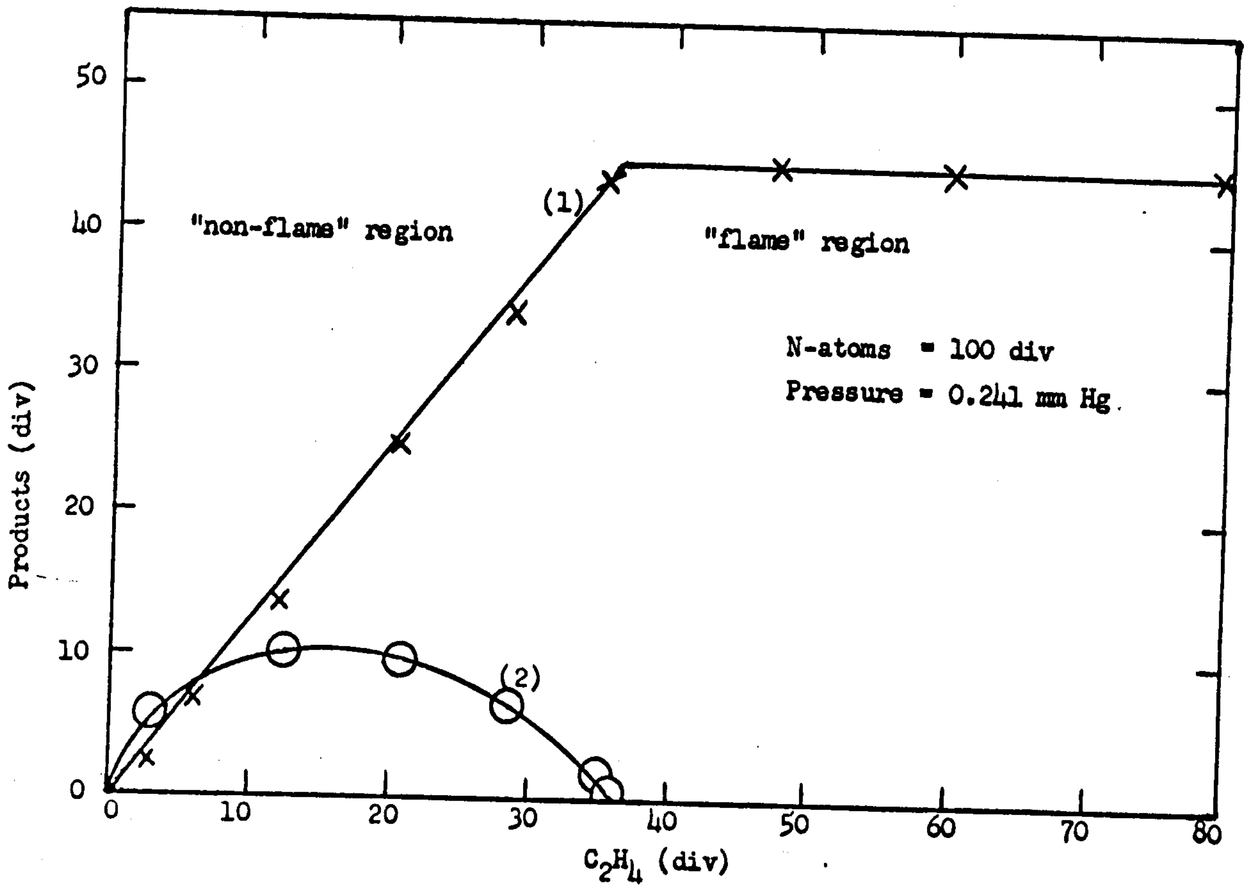


Fig. 26 - Formation of NH_3 compared with HCN in the reaction of N-atoms with C_2H_4; no O-atoms.

(1) HCN produced <u>vs</u> C_2H_4 added.

(2) NH_3 produced <u>vs</u> C_2H_4 added.

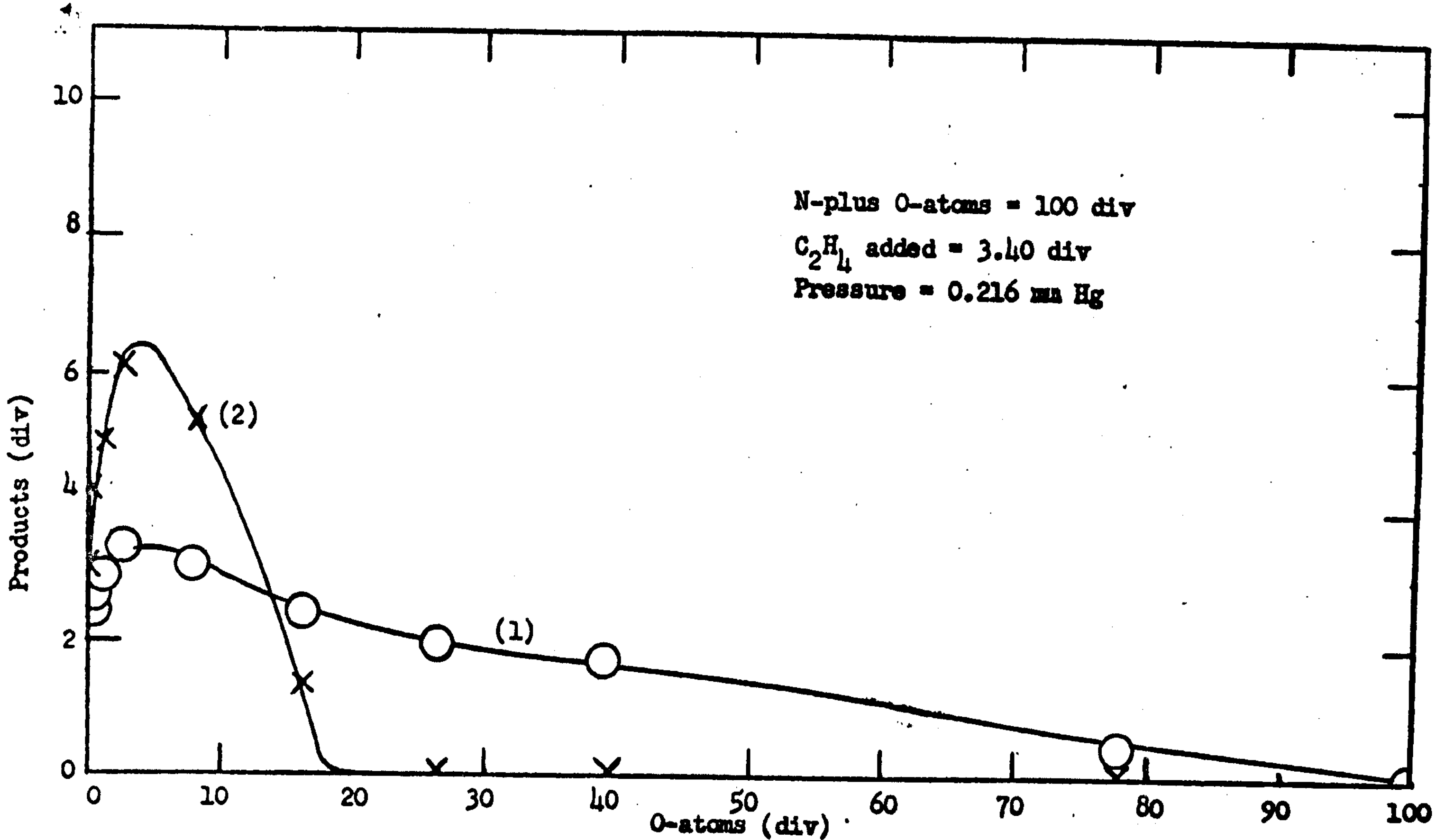


Fig. 27 - Reaction of C_2H_4 with a mixture of N- and O-atoms; the formation of NH_3 under non-flame conditions.

(1) HCN produced vs divisions O-atoms.

(2) NH_3 produced vs divisions O-atoms.

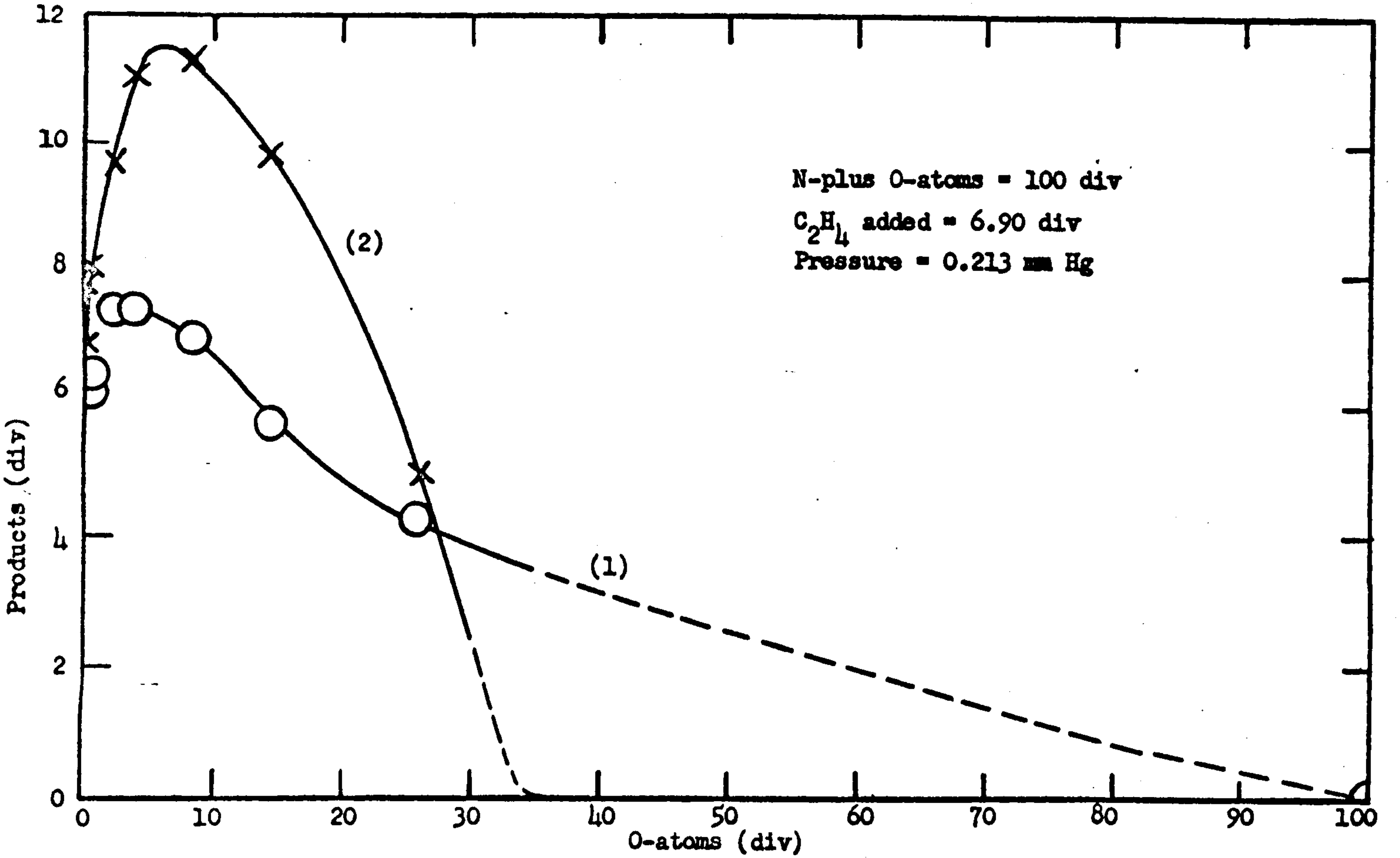


Fig. 28 - Reaction of C_2H_4 with a mixture of N- and O-atoms; the formation of NH_3 under non-flame conditions.

(1) HCN produced vs divisions O-atoms.

(2) NH_3 produced vs divisions O-atoms.

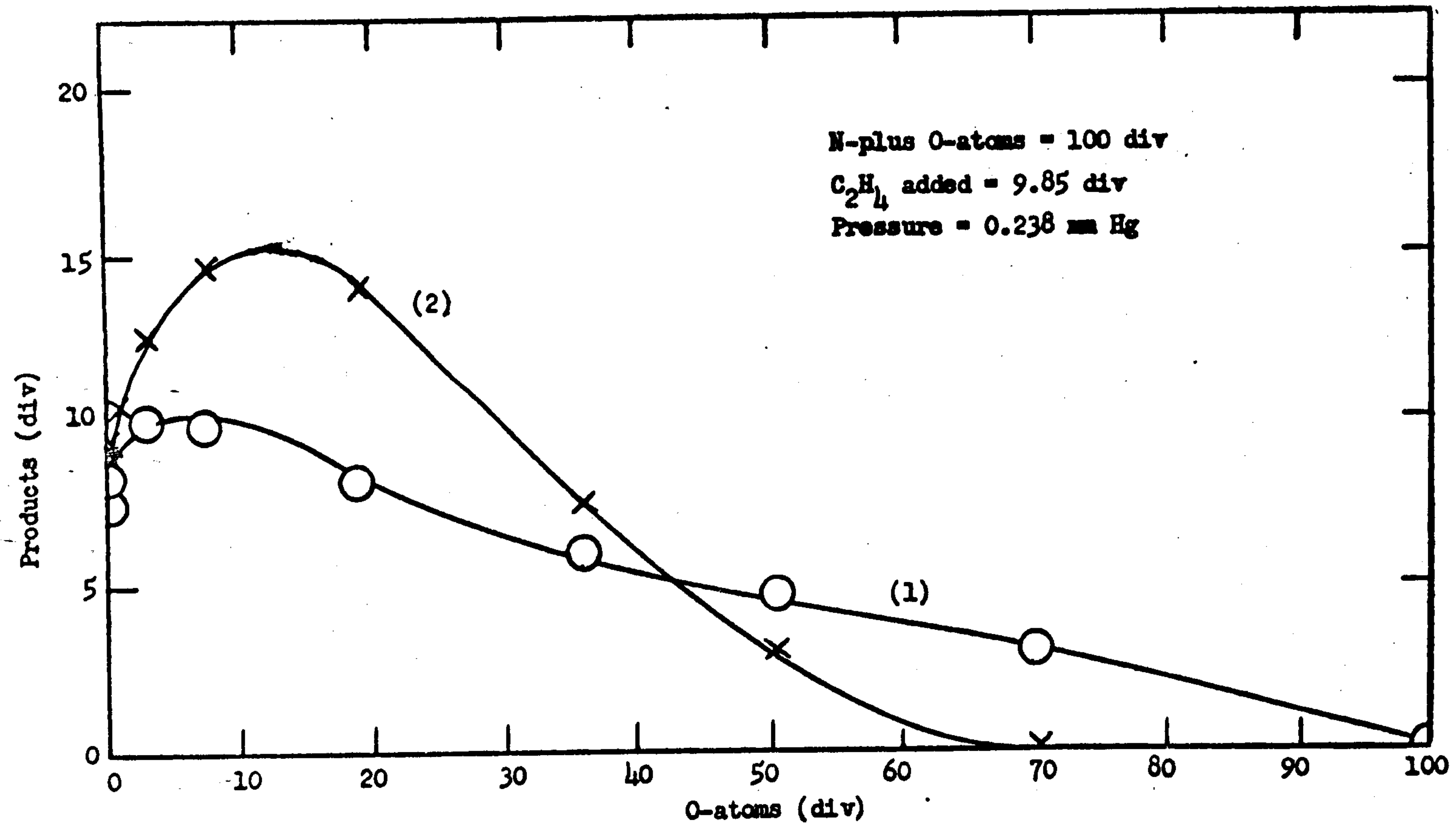


Fig. 29 - Reaction of C_2H_4 with a mixture of N- and O-atoms; the formation of NH_3 under non-flame conditions.

(1) HCN produced vs divisions O-atoms.

(2) NH_3 produced vs divisions O-atoms.