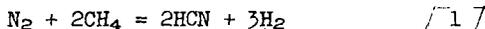


THE NATURE AND QUANTITATIVE DETERMINATION OF THE
REACTIVE SPECIES IN A NITROGEN PLASMA JET

Mark P. Freeman
Central Research Division
American Cyanamid Company
Stamford, Connecticut

INTRODUCTION

One of the "natural" reactions found to proceed in a plasma-jet reactor is the formation of hydrocyanic acid by the introduction of methane into a nitrogen jet:



The reaction can be made to proceed in good yield (based on methane consumption) and, furthermore, the main by-products, acetylene and hydrogen, are of considerable chemical significance. This reaction therefore, has received more than passing interest from various investigators purely as a production possibility.

In an ever widening circle of plasma-jet applications this reaction is almost unique in that it is almost certain that the chemistry must proceed via thermally produced intermediate species of a sort unknown at ordinary temperatures. This is the interesting sort of process one would like to contemplate when considering possibilities for plasma jet chemistry. One feels that if insight can be gained into the detailed mechanism for this key reaction, then it is quite possible that avenues will open to exploit other high temperature species in chemical synthesis or, indeed, to use the active species of a nitrogen jet in other reactions.

In the "active nitrogen" research (1,2,3) that has persisted in vigorous

-
- (1) K. R. Jennings and J. W. Linnett, *Quart. Rev.* 12, 116 (1958).
 (2) G. G. Mannella, *Chem. Rev.* 63, 1 (1963).
 (3) N. E. V. Evans, G. R. Freeman and C. A. Winkler, *Can. J. Chem.* 34, 1271 (1956).

activity for more than half a century, HCN plays an equally important role. In fact when cold methane is added to nitrogen at low pressure that has been recently passed through a high-voltage electric discharge, one gets exactly the stoichiometry of [1]. That the experimental systems themselves are different is apparent for the high-voltage discharge is a high-excitation device whereas the plasma jet is thought to be nearly in thermal equilibrium and hence a low-excitation device (spectroscopically speaking (

-
- (4) F. A. Kovolev and Yu. K. Kvaratskheli, *Optics & Spectroscopy*, 10, 200 (1961).

intermediate between arc and spark). Furthermore the plasma jet experiments reported here were performed at one-half atmosphere (as opposed to ~1 torr) and at a temperature twenty times as high on the absolute scale as room temperature, where the bulk of active nitrogen experiments have been performed. Finally, the reactive carbon-containing species evidently does not contact the active nitrogenous species as methane. That is, the products other than HCN are mainly acetylene and higher acetylenes with various degrees of saturation. These are the same products that would form if the jet were, say, argon. It has been shown elsewhere (5) that the precursors

(5) M. P. Freeman and J. F. Skrivan, *AIChE Journal*, 8, 450 (1962).

For these products form rapidly compared to the time for mixing of the methane with the jet.

In spite of these differences it nevertheless does not seem reasonable to say the two systems are only superficially related for the chemistry seems too specific and unique to permit one to accept this interpretation lightly. If one is willing to accept the fact of the chemistry given in equation [1] ... perhaps modified by an asterisk to indicate the nitrogen has been subjected to an excitation of some kind ... as an operational definition for active nitrogen then this study is in a true sense a study of active nitrogen. It is true that the plasma jet provides a difficult environment in which to do precise work. On the other hand this difficulty would seem to be offset by the fact that the relative concentration of active species is observed to be as high as 12% which is two orders of magnitude higher than the (at most) tenths of a percent quoted in conventional research (6).

(6) J. M. Benson, *J. App. Phys.* 23, 759 (1952).

Furthermore, whereas in conventional research on active nitrogen the partial pressure of the active species itself is on the order of hundredths of a torr, it is here observed to be in the tens of torrs. Naturally, this high concentration promotes a considerable simplification in the recovery and analysis of products. Perhaps most significant is the fact that owing to the high temperatures available in a plasma jet atomic nitrogen can be produced in large amount as an equilibrium constituent of the stream and hence serves as an important new variable.

The procedure followed was to add methane through an annular slot to a confined nitrogen jet of precisely defined average enthalpy. It has been shown that under these conditions mixing is very rapid as is the drop in temperature (5). After about 1 millisecond the resulting flow of high temperature species was further chilled by the entrainment of cold product gas .. (the fastest quench known) ... and the flow of HCN in the product gas relative to the effluent nitrogen flow chemically determined. Data were taken at about 350 torr reactor pressure in two reactors that differed in a significant way. In one reactor the methane mixes with the jet as it emerges from the head into a water cooled channel the same size as the front electrode orifice. In the other reactor, the jet enters a plenum chamber, with an exit orifice, and then expands to more than twice the original diameter. Only after the jet has persisted outside the head for more than a millisecond, during which it has lost about half of its enthalpy, is the methane added.

As the methane is added at various flow rates the corresponding rate of production of HCN relative to the effluent nitrogen flow is noted. Just as in Winkler's (7) work with active nitrogen, a plateau is observed which indicates that some active species is indeed determined. Because of equipment availability work was done with the second of the two reactors described above several months in advance of the first, a reactor that is both hotter and more amenable to an enthalpy-dependence study. Because the data from the earlier study indicated an HCN flow rate within a factor two of the nitrogen atom flow rate for a nitrogen stream of enthalpy equal to the average enthalpy (7) it was tentatively concluded (8) that the reagent

(7) F. Martinek, *Thermodynamic and Transport Properties of Gases, Liquid and Solids* (McGraw-Hill, New York, 1959), p. 130.

(8) H. M. Hulburt and M. P. Freeman, *Trans. N. Y. Acad. Sci.*, II, 25, 770 (1963).

species is the nitrogen atom. It is clear from the more complete study reported here

that this conclusion is, in fact, erroneous and that the apparent agreement was fortuitous, a consequence of the choice of power level used in that part of the study.

In order not to confuse what is observed with the immediately apparent interpretation, these factors are separated in the following presentation: After a reasonably complete presentation of the experimental procedure and details (EXPERIMENTAL) sample data are presented together with such generalizations about the data as seem warranted from simple inspection (RESULTS). Following this section, an attempt is made to discuss each of the observations in terms of the various interpretations they would seem to warrant (DISCUSSION). Included in this section is a brief discussion of the principal questions remaining unresolved. Finally, (SUMMARY) those interpretations that would seem most probable are collected together to present a plausible sequence for the observed reaction.

EXPERIMENTAL

Apparatus. Plasma-jet reactors consist of three parts, head or arc unit, intermediate section, and quenching section. The plasma-jet head used for this study is a Thermal-Dynamics L-40 Plasma-jet with "turbulent nitrogen" electrodes and it is powered by two 12 kw welding power supplies open circuit voltage 160 volts connected with their outputs in parallel, but with opposite phase rotations on the input so as to minimize power supply ripple in the output. The intermediate sections (Figures 1 and 2) are made of copper and fully water-cooled as is the head. The SOR (local designation) shown in Figure 2 has ducts and thermometers located so that heat lost to the cooling water upstream of the slot is determined independently from that lost downstream. The quenching section where the hot stream of plasma and reaction products is quenched by entrainment of cold product gas is simply a heat exchanger, i.e., it is a stainless steel pot 11 inches in diameter and 11 inches long sparsely wound with soldered copper tubing. Between the windings it gets hot enough to cause flesh burns but all parts subject to heat damage, such as seals, are well cooled. At the outlet of the quenching section is six feet of 1 inch I.D. thick-walled rubberized fabric acid tubing. This in turn is attached to the bottom of a 3 foot vertical mixing section of 2 inch stainless steel tubing loosely packed with glass wool. At the bottom of this mixing section carbon dioxide is mixed with the now cold discharge from the plasma-jet reactor. The top of the mixing section is connected to a high capacity steam jet vacuum pump with an automatic controller for maintaining desired pressures.

A Toeppler pump is arranged to withdraw 522 ml. of gas from the top of the mixing section at room temperature and at the reactor pressure. This aliquot may then be collected for analysis in a suitable gas collection system.

Gas flows, except for methane, are metered by orifice gages calibrated to within 1% for CO_2 and N_2 respectively by water displacement. Methane flow, much less critical, is determined by a rotameter calibrated by calculation. All cooling water flows are determined by experimentally calibrated rotameters. Cooling water temperature rise is determined by suitably graduated interconsistent mercury thermometers.

Procedure. Heat flow in the nitrogen plasma at the point of methane introduction is determined by subtracting from the voltage-current product in the arc the heat lost to all cooling-water supplies up to that point. (In the case of the TR reactor, a local designation for the reactor configuration of Figure 1, this is just the head cooling water.) For data taken at a particular heat flow (and hence average enthalpy) an attempt was made to keep this heat flow constant. In this endeavor the relatively great intrinsic stability of plasma jets made by this manufacturer

helped, but because data for a typical run extended over several hours there was an appreciable drift with occasional overcorrection (about 15%). This is undoubtedly the principal source of scatter in the data; note that the methane flow rates were set in random order so that trends in the data due to net power drift would not be observed except as scatter.

Except where noted, in all systems the pressure at the sampling tap (called reactor pressure was 350 ± 20 torr. The actual pressure of each sample was known to ± 1 torr but this is not a significant datum in the data analysis. Reactor pressure does not directly measure pressure in the head because of the pressure drop through the arc, which is quite large when the head is operating. Although this unit is not instrumented for an in-head static pressure measurement, some exploratory pressure measurements were run with a tap at the inlet to the head. It was found that pressure changes at this point at the standard flow rate were fairly insensitive to power level, as well as to reactor pressure in the range covered in these experiments. At 350 torr with a gas flow of $0.0171 \text{ gm. mole sec.}^{-1}$ the inlet pressure was observed to be 710 torr. No condition realized in this experiment at this flow rate altered this pressure by more than 10%. Lowering the gas flow rate by 27% reduced the pressure to about 600 torr, a change still less than 20%.

Whenever methane, power and/or pressure conditions were changed the system was operated for eight minutes before taking a sample. This was found to be sufficient time to establish a constant composition.

The collected gas aliquot was slowly sparged through 100 ml. of ice-cold caustic containing 12.50 millimoles of base. The half-liter space over the caustic was initially evacuated so that the entire sample, together with the air used to flush out residual product gas from the lines, might be collected in the caustic and the space over it. This was followed by one minute of vigorous shaking. This procedure has been found satisfactory for the quantitative recovery of CO_2 and HCN. Total acid in the aqueous solution was then determined by titration with 0.500 N HCl until all of the carbonate had been converted to bicarbonate (pH 8.3). Ammoniacal KI was then added as an indicator and cyanide determined alone by precipitometric titration with 0.0100 N silver ion. This permits the initial ratio of partial pressures and hence relative flow rates of HCN and CO_2 to be determined. But the ratio of the flow rates of N_2 (effluent) and CO_2 is known both from the calibrated gages and to similar precision from titration of a blank run done without power or methane. Consequently the ratio of HCN to effluent N_2 follows immediately.

Accounting for the various sources of uncertainty the actual ratio of HCN to N_2 is estimated to be within about 10% of the reported value and the heat flow to within about 5%. Air leakage into the system, a potential source of error, was between 0.1 and 0.01% of the total gas flow.

The quenching section is mounted with a window through which, for a time after each cleaning, the exhaust of the intermediate section can be observed. Under some conditions (notably high enthalpy and low gas flows) rapid solids formation occurred leading, indeed, to plugging at the highest heat flow. It is, therefore, of some interest that when totaled over all runs an inconsequential amount of solid product formed. More than 3 Kg of methane was used in the course of these experiments, resulting in less than 6 g. of recovered solid. This very bulky solid was found on Kjeldahl analysis to contain about 5% nitrogen by weight; it is apparently a mixture of HCN polymer and carbon.

Although temperatures are not quoted (and as will be shown below, cannot be meaningfully quoted because of a substantial departure from equilibrium) it is instructive to note that the eight-fold range of average enthalpy covered in this experiment,

would, on the assumption of equilibrium, correspond to temperatures from 3250°K. to 7000°K.

RESULTS

Yield. In Figure 3 typical results for the yield of hydrocyanic acid as a function of methane feed rate is shown for the TR reactor at a nitrogen flow of 0.0171 g. mole sec.⁻¹, at three widely different enthalpy levels. Several important observations may be made immediately:

- a. At every enthalpy level a limiting value of HCN production is achieved, as observed by Winkler, et al. (3)
- b. After the limiting or saturation value is reached a further excess of methane does not decrease the yield, suggesting a condition of frozen equilibrium.
- c. Before saturation is reached all of the yield curves coincide with each other and with a line slope of 1/3. That is when insufficient methane is added to reach the limiting production, only one carbon atom in three is converted to HCN.

The thing that strikes the investigator is the stability and reproducibility of these effects despite the difficulties inherent in keeping a plasma-jet system operating at precisely defined conditions for several hours. Figure 4 shows a yield curve as in Figure 3 for the highest enthalpy run done in the TR reactor at substantially reduced gas flow. Although this run was plagued by plugging and unstable operation it is clear that no qualitative difference in behavior is to be observed. Also shown in this figure is the initial run done in the SOR reactor at a single enthalpy. Again, essentially the same behavior occurs.

Variation with enthalpy. Because the yield varies rapidly with enthalpy, the enthalpy variations encountered during runs of several hours duration make average values determined from full yield curves such as those of Figures 3 and 4 no more precise than single points using methane flows corresponding to the plateau regions of the curve. At all available enthalpy levels a methane flow rate equal to one-half the nitrogen flow is seen to give the limiting yield of HCN and much of the data describing enthalpy dependence was taken at this feed ratio.

In Figure 5 the logarithm of the flow rate of active species (as measured by the saturation HCN production) is plotted vs reciprocal enthalpy. The open points represent "one point" data; the filled points were determined by a full yield curve of the sort shown in Figure 3. Circular points represent data from the TR reactor, at a nitrogen flow of 0.0171 g. moles sec.⁻¹ while triangular points represent data from the same reactor at 0.0125 g. moles sec.⁻¹. The square point represents data taken on the SOR reactor using average enthalpy determined at the slot. Also shown in this figure is a line segment representing the population of atomic nitrogen at 0.46 atmospheres as a function of enthalpy as calculated from equilibrium considerations (7). Two important conclusions can be drawn from this figure:

- d. The production of active species appears to be a smooth and reproducible function of enthalpy for a particular reactor regardless of flow rate.

- e. The population of active species correlates very poorly with nitrogen atom population based on average enthalpy, being many orders of magnitude too high at low enthalpy and a factor of 10 low at high enthalpy.

Pressure dependence. Although the experiment was principally run at a nominal reactor pressure of 350 torr some indication of sensitivity to pressure is necessary to assess the importance of the small pressure variations encountered. At a net power of 7000 ± 100 watts and a nitrogen flow of 0.0171 g. moles sec.^{-1} , the data of Table I were taken.

TABLE I

Relative Yield of HCN as a Function of Reactor
Pressure at Moderate Power

Total Reactor Pressure (torr)	195	350	484
n HCN/G	0.052	0.074	0.078
Heat Flow (watts)	6991	6992 (avg.)	7216
Conductance (mhos.)	1.27	0.58	0.68

Note that at 195 torr an appreciable fraction of the total enthalpy is tied up in directed kinetic energy so the free stream enthalpy is substantially lower than the heat flow would indicate. This leads to the further rather surprising observation:

- f. The fraction of nitrogen capable of ultimate reaction with the carbon containing species to HCN is nearly independent of reactor pressure.

Methane Utilization. Four gas samples were taken for mass spectrometric analysis at the 7000 watt level, corresponding to four points on the center curve of Figure 3, two below saturation and two above. Unreacted methane accounts for 10% of the methane flow at the highest flow rate ($\text{CH}_4/\text{H}_2 \approx 0.6$) but at all lower flows the conversion was found to be complete. In every case acetylene was found to be by far the major product, although for the points above the saturation value some carbon (a few percent) is found as other C_2 , C_4 and C_6 unsaturated hydrocarbons. If HCN production is estimated from Figure 3, the observed carbon balance is satisfactory to within the limited precision of the mass spectrometric analysis. This leads to the final observation:

- g. When the nitrogen is in excess all of the methane reacts to make for each molecule of HCN one of acetylene. When the methane is in excess, the excess methane that reacts forms chiefly acetylene, with minor amounts of C_4 and C_6 species.

DISCUSSION

General

In light of the observations a. and b. above, there would appear to be little question that the earlier interpretation (7) of the data taken on the SOR reactor was correct to the extent that a nitrogen plasma jet evidently contains some active species,

perhaps more than one, capable of reacting with the immediate decomposition products of methane to make HCN or its precursor. It seems equally clear that the procedure employed here quantitatively determines the flow rate of this (these) species.

Reactive Nitrogen Species

Atomic Nitrogen. From the welter of confusing evidence, and conflicting views that have accumulated over the decades of "active nitrogen" research, a sort of general agreement has recently been reached that at least the most important constituent must be atomic nitrogen in its ground state (1). With the high temperature thermal plasma investigated here it would seem that this possibility can be immediately excluded by observation. Taking into account all the known characteristics of a plasma-jet reactor, one can not account for the very low production rate of active species at high enthalpy. That is, on account of the intrinsic steep temperature gradient near the walls of a contained plasma-jet, one must always consider the possibility that the non-uniform radial temperature profile might cause observed effects. Furthermore, the enthalpy fluctuations to which a plasma jet is subject (9)

(9) M. P. Freeman, S. U. Li and W. vonJaskowsky, J. App. Phys. 33, 2845 (1962).

are not to be ignored. However, by actual computation one may very quickly satisfy himself that while a non-uniform temperature distribution might account for a total nitrogen atom population somewhat in excess of the average concentration calculated, no reasonable distribution of enthalpies could account for the observed dearth at high enthalpy.

Ionic Nitrogen. One of the theories of active nitrogen that has in the past enjoyed some popularity is that of Mitra (1). This theory invokes the molecular ion N_2^+ as the active species. This suggests attempting to correlate the production of active species with the rate of production of positive ions in the arc process. (The equilibrium population of ions at reactor conditions is much too small to be interesting.) This is, of course, just the rate of production of electrons, since the plasma remains electrically neutral. Note that at the higher power levels, even allowing for the considerable amount of heat involved in non-equilibrium ionization this implies, the temperature should still be high enough that the principal positively charged species is the atomic ion rather than the molecular ion. Since there is no reason to suppose that their ultimate products should be any different, this presents no difficulty.

A number proportional to the rate of production of electrons, and hence of positive ions, may be estimated in the following way: The conductivity, σ , in the actual arc discharge path is proportional to the density of electrons, n_e , and their mean free path (10). On allowing for the pressure dependence of the mean free path:

(10) H. O. G. Alfven, Cosmical Electrodynamics (Oxford, Clarendon Press, 1950) p. 47.

$$\sigma \propto n_e/P \quad [2]$$

There is also a weak temperature dependence, but this may be ignored as the temperature in the actual discharge path probably does not change much. If the discharge path occupies a fractional area, γ , of the total plasma-jet channel then the conductance M is proportional to:

$$M \propto \sigma \gamma \quad [3]$$

Now we make the assumption that the ion production rate, R , is just equal to the ion (and hence electron) population density in the discharge path times the velocity (proportional to $1/P$) of that part, γG , of the total flow, G , that flows through the discharge column:

$$R \propto n_e \gamma G/P \quad [4]$$

Combining [2], [3] and [4] we obtain the simple result that the conductance is proportional to the flow rate of ions out of the discharge path divided by the effluent flow rate:

$$M \propto R/G \quad [5]$$

Assuming that the heat flow, W , leaving the head is proportional to the energy actually dissipated in the arc (as opposed to energy dissipated to the cooling water in electrode processes) then from Watt's law:

$$R/G \propto I^2/W = M \text{ (mhos)} \quad [6]$$

Where I is the measured current through the head.

Figure 6 is a plot of conductance vs. relative rate of HCN production for all the data taken at 350 torr. Considering the crudeness of the derivation of [6] the agreement would seem to be extraordinarily good. It is fortunate that the analysis turns out to show little dependence on the reactor pressure as this variable was not held precisely constant for all the runs. Furthermore, this would seem to be consistent with observation elsewhere, despite the widely disparate reactor pressures employed, the active species production in the derivation of [6] now become apparent when one considers the conductance for it changes appreciably for the low pressure run. The points from the data of Table I are represented by asterisks on Figure 6. One might suppose the obvious disparity to be due to the arc length or mode of operation changing at low reactor pressure. As explained above, much larger changes in pressure are produced in the arc chamber by changing the flow rate than by changing the reactor pressure. Yet, if there is any real discrepancy between data taken at 0.0125 (Δ) and 0.0171 g. moles sec.⁻¹ (o) it is small.

Equilibrium Considerations. Apparently a charged specie (s) that persists in the jet is responsible for the observed HCN production rate. But now the question arises as to whether that species is present because of a slow recombination reaction and, hence large departures from local thermodynamic equilibrium (LTE) or whether it is due to the radial temperature profile discussed above. The square point in Figure 6, the datum for the SOR reactor, contributes a very direct answer to this question. For this reactor the methane is added only after the jet has been fired into a plenum, choked and then expanded. In the process it has lost nearly half the enthalpy it had on leaving the head: and yet it still agrees well with the correlation between HCN production and head conductivity exhibited by the TR reactor. Since even the maximum radial temperature in this case is well below that at which ions could exist at equilibrium, one must conclude that the back reaction destroying charged species in the jet is very slow compared to jet residence times (on the order of milliseconds for this reactor).

Another question that should be considered is whether so much enthalpy is tied up in non-equilibrium ionization that, assuming all other degrees of freedom to be equilibrated, the resulting temperatures are too low to allow an appreciable amount of atomic nitrogen. This could account for the unexpected lack of HCN generated by this species. However, in the worst possible case, subtracting from the

total enthalpy the heat of formation of a nitrogen ion for each HCN molecule formed, one finds that in the runs at highest heat flow there is still sufficient enthalpy to provide as much as 35% atomic nitrogen. Clearly one must look elsewhere to explain the inactivity of this species.

Unresolved Questions. It remains to identify, if possible the actual ionic species involved in the reaction from among the four likely candidates:



These may be quickly reduced to three by the following reasoning. If one positive ion is the reactive species then they both must be reactive since no difference is observed in Figure 6 between data taken at high power and at low. They must, in fact, be indistinguishable as reagents in this reaction. As a matter of convenience we may denote them both by the low temperature species, the molecular ion. Because the atomic ion is always surrounded by atoms and chilling is very rapid in the mixing zone of the reactor, it may be that the molecular ion is in fact the actual reagent.

The negative species presents more of a difficulty. It is certain that if charged particles of one sign are involved in the chemistry, so must particles of the opposite for the product emerges electrically neutral. The likely species to be involved, the electron gas, has certain drawbacks. Foremost among the drawbacks, it is hard to accept the slow recombination rate between electrons and positive ions implied. This would furthermore represent a disappointing departure from conventional active nitrogen research for by the use of microwave techniques Benson (6) has shown the concentration of electrons to be orders of magnitude too small to be paired in one-to-one correspondence with the active species (although the long persistence of conductivity could indicate the electrons were in equilibrium with some other species).

It has, to be sure, been almost axiomatic for three decades that the negative nitrogen ion can not form because in its ground state it is unstable, or nearly unstable, with respect to dissociation to the atom. However, Boldt (11) has recently

(11) G. Boldt, Z. f. Physik 154 330 (1959).

shown through spectroscopic evidence that a metastable nitride ion forms and persists in appreciable concentration in an arc discharge that is not appreciably different from the plasma generating arc employed here so that this possibility may not be lightly disregarded. The transition of this metastable ion to the ground state is spin forbidden. Its ionization potential is 1.1 ev to an excited metastable atomic state that lies 2.38 ev above the ground atomic state.

There would seem to be no good way to determine within the context of the present experiment whether the positive or negative species is involved in the reaction in a path determining way. More important perhaps within the context of active nitrogen research is the manifest inactivity of atomic nitrogen ... even under conditions of heavy methane flow.

Reactive Carbon Species

As a completely unexpected by-product of this work. observations c and g would seem to give interesting confirmation to the work of Skell and Wescott (12).

(12) P. S. Skell and L. D. Wescott, J. Am. Chem. Soc. 85, 1023 (1963).

These investigators have identified the principle species in carbon vapor at low pressures as a dicarbene:



[8]

by the chemical identification of its addition products with olefins when they are sublimed together onto a cold surface.

Observation c., that only one carbon atom in three may react to make HCN when the nitrogenous reactive species is in excess, the other two going to acetylene, is quite reasonably explained if in the principle step a nitrogen kernel is attached to a dicarbene which then subsequently forms one HCN and C_2H_2 . Observation g. follows equally well by postulating that when the dicarbene is in excess it dimerizes and then forms mono-, di-, and tri-acetylene units on subsequent attack by atomic hydrogen; partial hydrogenation of the higher acetylenes by atomic or molecular hydrogen to make vinyl- and divinyl-acetylene then completes the reaction sequence.

SUMMARY

This experiment, simple in concept and interpretation, would appear to shed considerable light on the details of the reaction of methane with a nitrogen plasma-jet. Although there are still many details requiring further work, at the present time we can propose the following simple concept for the reaction sequence:

1. A part of the nitrogen as it passes through the arc head unit, passes through the arc column or discharge path. There it is completely dissociated and ionized to the extent required by the arc process.
2. As the fresh gas enters the discharge column, atoms, atomic ions, and electrons are swept out where they mix with the relatively cold gas that is bypassing the discharge column.
3. The mixture equilibrates in most degrees of freedom to some reproducible steady state consisting of a mixture of at least atoms, molecules, atomic and molecular ions and electrons.
4. Some process leading to equilibration of that degree of freedom of the mixture involving the existence of the active species is effectively "frozen" or nearly so; the flow of active species in the stream is equal, or almost equal to the rate at which it or its precursor is displaced from the arc zone.
5. The rate at which the active species or its precursor is blown out of the arc zone is proportional to the rate at which charged particles of either sign are blown out, which is presumed to indicate that the active species or its precursor is charged.
6. As the end products are necessarily electrically neutral, ions of both polarities are required in the chemistry. Those with positive charge are probably an equilibrium mixture of the molecular and atomic ions, presumed to be chemically indistinguishable, while the negative charge carrier could be electrons, free nitride ion gas, or possibly some equilibrium mixture. From the present experiment there is no indication of the sign of the ions which initiate and determine the path of the reaction.
7. As the methane enters the reactor it rapidly mixes into the hot plasma and is converted to C_3 dicarbene molecules. The nitrogen containing active species

reacts with it to form one molecule of HCN and one of C_2H_2 on subsequent cooling and attack by atomic hydrogen. When the C_3 is in excess, the excess dimerizes; on subsequent cooling and attack by atomic hydrogen it goes mainly to acetylene with small amounts of C_4 and C_6 molecules with varying degrees of unsaturation.

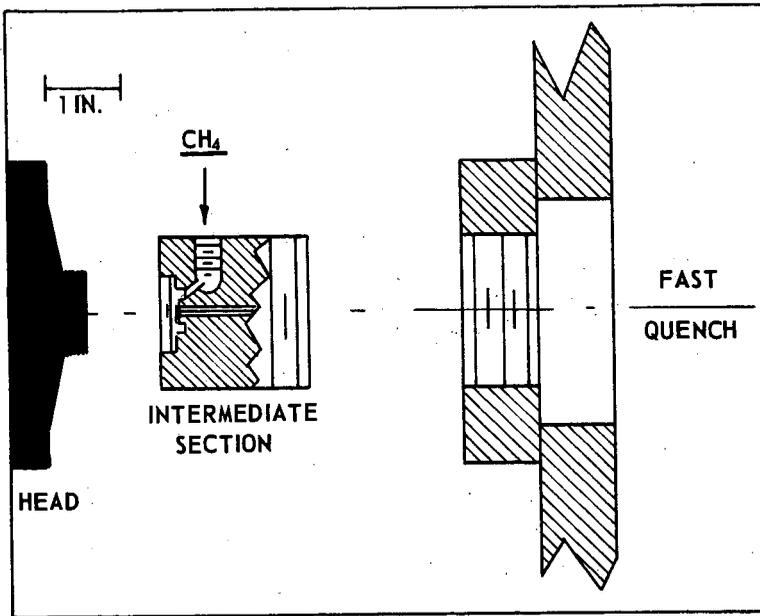
This reaction sequence is of course only appropriate to the plasma jet situation; however, the outstanding factor emerging from this study that one should keep in mind when considering the greater relevance of this work is that an active species has been found that has chemical properties generally attributed to ground state atomic nitrogen in conventional active nitrogen research. This species has been shown to be:

- a) Not atomic nitrogen in the ground state.
- b) In direct proportion to the number of charged particles produced in the arc process.

ACKNOWLEDGEMENT

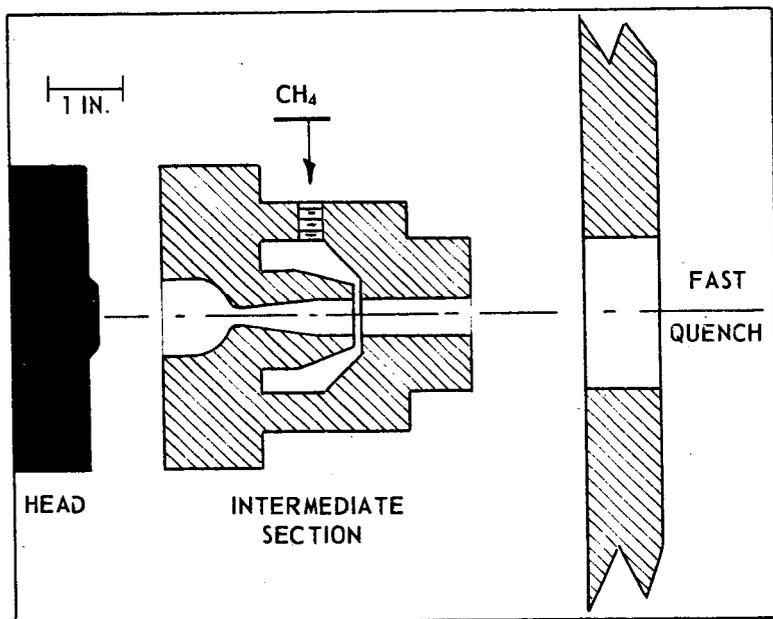
Among the numerous people who have contributed in some way to the conception and performance of the research the author must especially acknowledge the encouragement and helpful discussions of Drs. A. K. Hoffmann, H. M. Hulburt, J. E. Longfield and J. F. Skrivan, all of this organization. He wishes furthermore to acknowledge the considerable technical assistance of Mr. C. W. Beville.

Figure 1



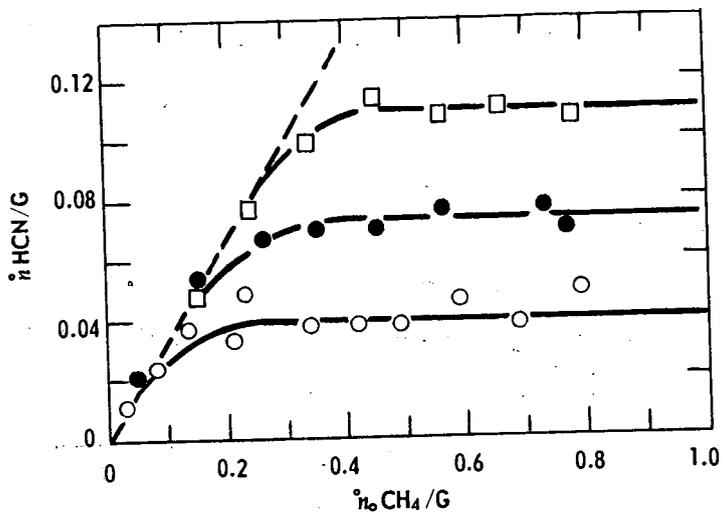
Exploded view of TR reactor. Intermediate section shown in simplified cross section. Material: Copper

Figure 2



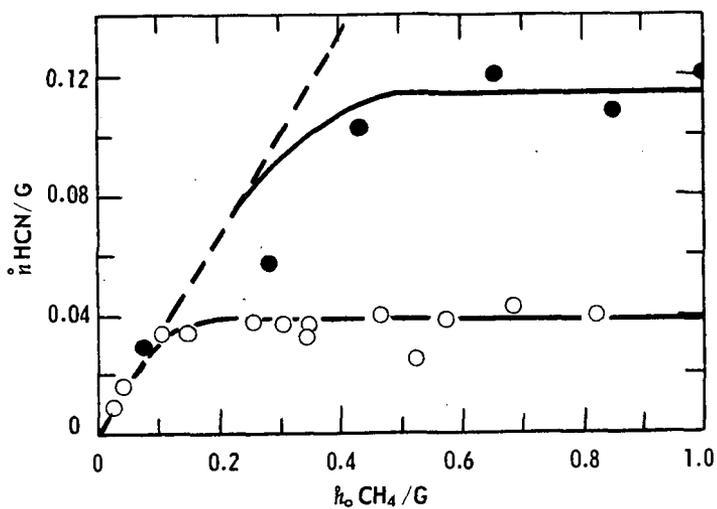
Exploded view of SOR reactor.
Intermediate section shown in simplified cross section.
Material: Copper

Figure 3



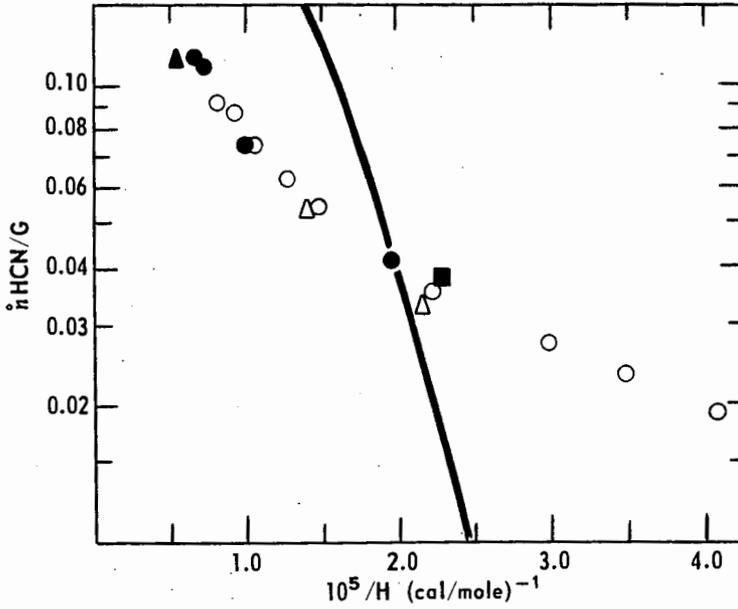
Rate of production of HCN vs. feed rate of methane (both relative to effluent nitrogen flow, G, of 0.0171 gram moles sec. $^{-1}$) at three net power levels: 3522 watts - \circ ; 6992 watts - \bullet ; and 9782 watts - \square TR reactor. Dashed line has slope of one-third.

Figure 4



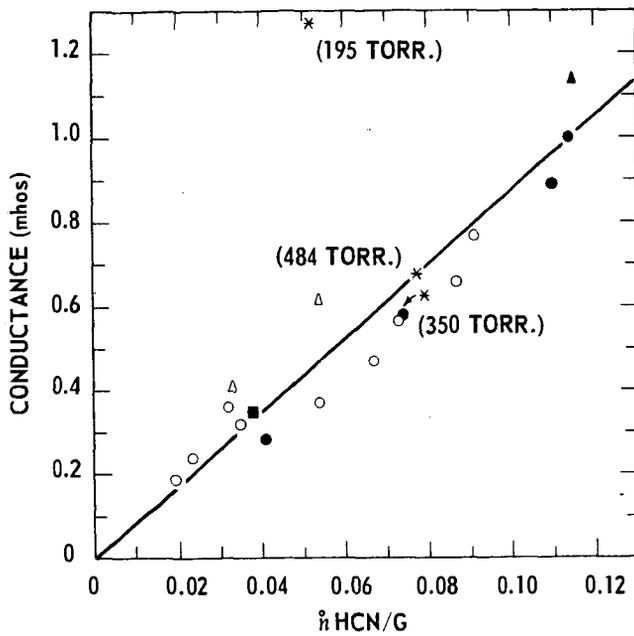
Same plot as Figure 3. \bullet -TR reactor at 9506 watts net power with reduced nitrogen flow ($G = 0.0125$ gram moles sec.^{-1}); highest enthalpy run. \circ -SOR reactor at 2989 watts net power at feed slot ... power leaving head in gas was 5517 watts ... nitrogen feed rate 0.171 gram moles sec.^{-1} . Dashed line of slope one-third again shown.

Figure 5



Logarithmic plot of the flow rate of HCN (assumed equal to the flow rate of active species) relative to the flow rate of effluent nitrogen as a function of reciprocal average enthalpy at the point of introduction of methane. Point legend given in text. Line shown represents expected nitrogen atom population based on average enthalpy as calculated from equilibrium considerations.

Figure 6



Conductance (proportional to the fraction of nitrogen molecules ionized) vs. active species flow rate relative to effluent nitrogen. Legend of points corresponds to that of Figure 5. Points marked with asterisks correspond to the data of Table I.