# THE REACTION OF ACTIVE NITROGEN WITH ACETYLENE[1]

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## ABSTRACT

The main products of this reaction were hydrogen cyanide and polymer that contained approximately 32% nitrogen. Yields of these substances increased to constant values with increase of acetylene flow rate. Some cyanogen and methane were also formed. The yield of cyanogen passed through a maximum with increased flow rate of acetylene, but the methane yields were quite erratic.

Previous studies in this laboratory have served to outline the main features of several reactions involving the attack of active nitrogen on paraffin and olefine hydrocarbons (1, 3, 6, 8). The present paper summarizes the results of a similar study with acetylene, with an interpretation in terms of atomic nitrogen as the reactive species in active nitrogen (cf. 6).

## EXPERIMENTAL

The apparatus and general experimental and analytical techniques were identical with those described in the earlier papers. Hydrogen cyanide and cyanogen were estimated by an adaptation of the method of Wallis (9), acetylene by absorption in potassium iodomercurate (4), and methane and hydrogen by combustion (2).

## RESULTS AND DISCUSSION

The reaction was accompanied by a very bright flame, more reddish in color than similar flames with other hydrocarbons studied in this laboratory. The size of the flame was unaffected by hydrocarbon flow rate in the range used, and the flame was always located in the immediate vicinity of the hydrocarbon jet. The temperature indicated by a thermocouple in the center of the reaction vessel was approximately 165°C., but the true reaction (flame) temperature was probably much higher than this value.

The main products were hydrogen cyanide and a brown polymer that accumulated, for the most part, on the wall of the reaction vessel. A small amount of polymer of darker color was also deposited in two consecutive liquid nitrogen traps in the main pumping line. No ethylene or ethane was detected among the products.

Preliminary experiments showed that formation of polymer in one experiment reduced the amount of reaction in a subsequent experiment, presumably because the concentration of nitrogen atoms available for reaction with acetylene was reduced by their reaction with polymer. Prior to each experiment, the apparatus following the discharge tube was therefore cleaned thoroughly with chromic acid, followed by water, potassium hydroxide solution, and copious amounts of water. It was then poisoned with dilute phosphoric acid solution in the usual way.

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[1] *Manuscript received October 14, 1952.*
*Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que. Grateful acknowledgment is made to the Defence Research Board for financial assistance and permission to publish.*

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The yields of the various products as a function of the flow rate of acetylene are shown in Fig. 1.* At very low flow rates of acetylene, corresponding to at least a sevenfold excess of nitrogen atoms, negligible yields of hydrogen cyanide, cyanogen, or methane were obtained. The acetylene that reacted at these flow rates presumably appeared almost entirely as polymer. From appropriate carbon balances for the system at various flow rates, the curve for polymer formation (Fig. 1*B*) was plotted.

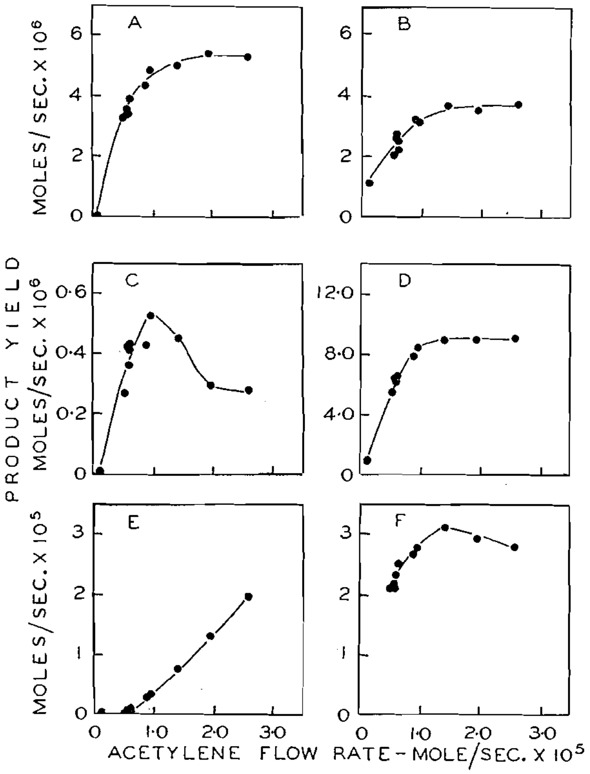

FIG. 1. Relation between yields of products and flow rate of acetylene.
Curve *A*—hydrogen cyanide.
Curve *B*—polymer (plotted as acetylene lost).
Curve *C*—cyanogen.
Curve *D*—total nitrogen reacted.
Curve *E*—acetylene (recovered).
Curve *F*—total hydrogen in noncondensable gases (i.e. as $H_2$ and $CH_4$).

The identity of the polymer has not been established with any certainty. From its rather mottled color it may be inferred that it was not entirely homogeneous. Two samples, one from the reaction vessel, the other from the traps, were obtained by washing some of the more loosely held polymer from the glass surface with distilled water. Dumas nitrogen analyses** showed that the material from the

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**The maximum yield of cyanogen corresponds approximately to a flow rate of acetylene just sufficient to react with the nitrogen atoms present, as estimated from the hydrogen cyanide produced in experiments with ethylene under similar conditions (8).*

***We are indebted to Mr. A. J. Matuszko for the analyses.*

reaction vessel contained 32% nitrogen, while that from the traps contained 16% nitrogen. A hydrogen balance at an acetylene flow rate of 1.2 × $10^{-5}$ mole per second indicated that the polymer contained only about 20% of the hydrogen originally present in the acetylene that was converted to polymer. Hence, the ratio of carbon to hydrogen in the polymer was probably about five to one.

The polymer was quite insoluble in the usual organic solvents and in dilute acids and alkalies. When heated to about 900°C. in a stream of nitrogen, no cyanogen was detectable but considerable hydrogen cyanide was formed. The residue, amounting to about 50% of the polymer taken, closely resembled graphite in appearance. It would seem, therefore, that the polymer contained little or no paracyanogen, which should decompose completely to cyanogen at 860°C. (7). On the other hand, it has been found (5) that the pyrolysis of methyl or ethyl cyanide at 865°C. and 675°C. respectively produces hydrogen cyanide and considerable amounts of carbon and tar, but no cyanogen. It is suggested, therefore, that the polymer contained nitrogen in a structure analogous to that of a nitrile, and that the monomer from which the polymer was derived may be regarded as a complex formed by collision of a nitrogen atom* with the acetylene molecule.

From the known amounts of hydrogen cyanide, cyanogen, and polymer produced, together with the approximate values for the nitrogen content (assumed to be 32%) and the carbon–hydrogen ratio of the polymer, the curve for total nitrogen reacted was obtained (Fig. 1*D*). The shape of this curve is reasonably explained if all the available acetylene is consumed at acetylene flow rates below about 0.6 × $10^{-5}$ mole per sec., while at flow rates above 1.2 × $10^{-5}$ mole per sec. all available nitrogen atoms are consumed. The curve for recovery of acetylene (Fig. 1*E*) is consistent with such an interpretation. In the range of acetylene flow rates between 0.6 × $10^{-5}$ and 1.2 × $10^{-5}$ mole per sec. recovery of acetylene increased slightly until at the upper limit of the range the recovery increased at approximately the same rate as the flow rate (quite apparent in larger scale plot). These observations would appear to imply incomplete reaction in the range of flow rates cited, whereas the small flame size observed in all the experiments would indicate complete consumption of one or other reactant over the entire range of flow rates used. The apparent contradiction can be resolved if it is assumed that nitrogen atoms may be removed from the gas stream by reaction with polymer on the wall. At sufficiently low acetylene flow rates there would still be enough nitrogen atoms present to react with all the hydrocarbon. At sufficiently high acetylene flow rates, nitrogen atoms would be almost completely consumed before significant reaction with the polymer on the wall could occur. At intermediate flow rates of acetylene, however, the extent to which nitrogen atoms were removed by the wall reaction would depend upon the acetylene flow rate. The variable nitrogen atom concentration then available for reaction with acetylene would make the relation between acetylene flow rate and product formation appear to change gradually from one of complete nitrogen atom consumption to one corresponding to complete hydrocarbon consumption. Such

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**If, for example, the $N_3$ molecule is a reactive species in active nitrogen, formation of such a complex might be represented by* $N_3 + C_2H_2 \rightarrow [C_2H_2N] + N_2$.

behavior is in marked contrast to the sharply defined conditions for complete hydrocarbon or complete nitrogen atom consumption in the ethylene reaction (3, 8), where virtually no polymer is formed.

Analyses for methane in the noncondensable products gave quite erratic results, from $0.3 \times 10^{-6}$ to $1.8 \times 10^{-6}$ mole per sec. The yields of hydrogen were also erratic, in the range zero to $2.3 \times 10^{-6}$ mole per sec. However, the total hydrogen in the noncondensable gases gave the regular relation with acetylene flow rate shown in Fig. 1*F*.

One experiment, at an acetylene flow rate of $1.08 \times 10^{-5}$ mole per sec., was made with the reaction vessel wrapped in glass wool, so that the temperature indicated by the thermocouple rose to 209°C. Increase in the yields of hydrogen cyanide (10%), cyanogen (35%), and hydrogen (8%), and in consumption of acetylene (25%), were then observed; the polymer yield decreased (25%). No change occurred in the total amount of nitrogen combined in nitrogenous products. The significance of the observed changes is difficult to assess, in view of the uncertainty in the true reaction temperature and in the effect that changes in amount and composition of the polymer on the surface might have on the gas phase reactions. No attempt was made, therefore, to make a more elaborate study of the effect of temperature on the reaction.

A mechanism for the acetylene – nitrogen atom reaction can be formulated in the same way that has been suggested for other reactions of similar type. Collision of a primary acetylene – nitrogen atom complex with a second nitrogen atom would readily account for the cyanogen observed in the products. On the other hand, as indicated previously, the conditions of formation and properties of the polymer obtained are perhaps most satisfactorily accounted for by polymerization of the complex. Decomposition of the complex could, of course, yield hydrogen cyanide. The reactions concerned would be represented

$$C_2H_2 + N \rightarrow [C_2H_2N] \qquad [1]$$

followed by

$$[C_2H_2N] + N \rightarrow (CN)_2 + H_2, \qquad [2]$$
$$n[C_2H_2N] \rightarrow (C_2H_2N)_n, \qquad [3]$$
$$[C_2H_2N] \rightarrow HCN + CH. \qquad [4]$$

The shape of the cyanogen curve (Fig. 1*C*) is similar to that observed with ethylene and may be explained in the same way.

The erratic, small amounts of methane found were probably due to reactions of the methyne radical derived from reaction [4]. The lack of reproducibility in the methane values suggests that the polymer might be involved in reactions of the type

$$CH + (RNH)_n \rightarrow CH_2 + (RN)_nH_{n-1}$$

or

$$CH + H_2 \rightarrow CH_3,$$
$$CH_3 + (RNH)_n \rightarrow CH_4 + (RN)_nH_{n-1}.$$

The relatively low hydrogen content of the polymer is in accord with the occurrence of such reactions. The regularity of the total hydrogen content of the noncondensable gases (Fig. 1*F*) compared with the erratic yields of free hydrogen might be accounted for by an erratic consumption of free hydrogen for the production of methane.

A point of interest is the possible difference between the complexes of ethylene and acetylene with nitrogen atoms, such that the acetylene but not the ethylene complex is capable of polymerization. The obvious implication is that the ethylene complex is not a free radical whereas the acetylene complex has free radical character. It is tentatively suggested that the difference may be due to expulsion of a hydrogen atom from the ethylene molecule, but not from the acetylene molecule when the complexes are formed,

$$C_2H_4 + N \rightarrow [C_2H_3N] + H,$$
$$C_2H_2 + N \rightarrow [C_2H_2N]^{\cdot}.$$

Such a concept makes no fundamental alteration necessary in the reaction mechanisms proposed previously for the reactions with olefines or paraffins.

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