

# MASS SPECTROMETRIC STUDY OF THE REACTIONS OF SOME HYDROCARBONS WITH ACTIVE NITROGEN<sup>1</sup>

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#### ABSTRACT

The reactions of active nitrogen with acetylene, ethylene, and propylene have been studied in a flow system using a mass spectrometer to analyze the products continuously. Certain features of the mass spectra of the products can be explained on the basis of cyano radical replacement reactions.

Winkler and his co-workers have studied the reactions of active nitrogen with acetylene (1), ethylene (2), and propylene (3), in addition to a large number of other compounds (4). The major product containing nitrogen, aside from small amounts of cyanogen, was HCN. In the case of the acetylene reaction an additional product was found in the form of a polymer, containing about 32% nitrogen.

We have made a mass spectrometric study of these reactions, using a flow system. The nitrogen atoms were produced by passing a stream of nitrogen gas at from 1 to 5 mm pressure through a 2450 Mc electrodeless discharge. The atom concentration as measured by gas titration with NO (5) was of the order of 2 mole %. The reactor was made of 10-mm i.d. glass tubing. Hydrocarbons were added to the system through an inlet located about 20 cm ahead of a small glass leak through which the gas stream was continuously sampled and analyzed by a mass spectrometer. With linear flow rates of the order of 1 meter/second, the time for the gas to pass from the hydrocarbon gas inlet to the sampling leak was about 0.02 second.

This type of experimental arrangement does not permit observation of any but very long-lived free radicals. Since the reaction flames themselves extended only a few centimeters from the reactant inlet, it seems reasonably certain that our analytical results refer only to stable products.

In general our results are very similar to those of Winkler and co-workers. However, several new features were observed. For acetylene we found the major product to be HCN, along with smaller amounts of  $(CN)_2$ , as indicated by their peaks at m/e 27 and

TABLE I

| $\begin{array}{c cccc} Reactant, & & & \\ \hline m/e & C_2H_2 & C_3H_4 \\ \hline 50 & 22 & 100 \\ 51 & 100 & 380 \\ 53 & - & - \\ 62 & - & - \\ 63 & - & 34 \\ \end{array}$ | C <sub>2</sub> H4               |  |
|---|---------------------------------|--|
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  |                                 | C₃H6   |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 30<br>100<br>100<br>—<br>—<br>— | $   \begin{array}{r}     100 \\     270 \\     370 \\     \hline     40 \\     70 \\     70 \\     40 \\     100   \end{array} $ |

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52 respectively. In addition, however, there were peaks at m/e 50 and 51, but no peaks at higher masses. Similarly, for methyl acetylene, there were peaks at m/e 50, 51, and m/e 63, 64, 65, but again none at higher masses. The relative magnitudes of the ion currents are shown in Table I. The m/e 52 peak has been omitted.

In the case of the acetylene reaction, the absence of peaks at masses greater than m/e 52 ( $C_2N_2$ ) makes it difficult to conceive of the m/e 51 peak being due to anything other than  $C_3HN$  which we feel certain is cyanoacetylene. The mass 50 peak is probably  $C_2CN^+$  from  $C_2HCN$ . It is not diacetylene, since other peaks from the mass spectrum of diacetylene were absent.

Similarly the mass 65 peak probably corresponds to the methyl cyanoacetylene ion,  $CH_3C_2CN^+$ , the ions of mass 64 and 63 would represent the loss of one and two hydrogens from the parent molecule. Of course, the peaks at 63, 64, 65 could also be attributed to propargyl cyanide, though we think this less likely.

It is difficult to account for these products other than through direct replacement of a hydrogen by a cyano radical. Since diacetylene is not found in either reaction, it seems certain that the  $C_2H$  radical does not play an important part. Hence we cannot account for the cyanoacetylene as resulting from the reaction

## $CN + C_2H \rightarrow C_2HCN.$

Furthermore, the methylacetylene reaction leads to the formation of considerably more cyanoacetylene than methyl cyanoacetylene as is shown in Table II. The absence of a peak at m/e 78 in the products of reaction with methylacetylene shows that the  $C_3H_3$  radical probably plays very little part in the reaction and thus suggests that recombination of this radical with CN is not responsible for the  $C_3H_3CN$  observed.

| Per cent of N in products for typical experiments               |                    |                       |                      |                     |                                 |       |       |
|---|--------------------|-----------------------|----------------------|---------------------|---------------------------------|-------|-------|
| Product<br>reactant   | NH3                | HCN                   | C₃HN                 | $C_2N_2$            | C <sub>3</sub> H <sub>3</sub> N | C₄H₃N | C₄H₅N |
| $\begin{array}{c} C_2H_2\\ C_3H_4\\ C_2H_4\\ C_3H_6\end{array}$ | 13<br>6<br><1<br>? | 62<br>75<br>97<br>>78 | $7 \\ 6 \\ <1 \\ <4$ | 18<br>12<br>2<br>12 | ?<br><1<br>5                    | 1     | 1     |

TABLE II

We consider the most plausible set of reactions to be:

 $\begin{array}{rll} \mathrm{CN} + \mathrm{C}_2\mathrm{H}_2 & \rightarrow \mathrm{C}_2\mathrm{H}\mathrm{CN} + \mathrm{H} & \Delta H^* = -12 \\ \mathrm{CN} + \mathrm{CH}_3\mathrm{C}_2\mathrm{H} & \rightarrow \mathrm{C}_2\mathrm{H}\mathrm{CN} + \mathrm{CH}_3 & \Delta H = -22 \\ & \rightarrow \mathrm{CH}_3\mathrm{C}_2\mathrm{CN} + \mathrm{H} & \Delta H = -12 \\ & \rightarrow \mathrm{CH}_2\mathrm{CN}\mathrm{C}_2\mathrm{H} + \mathrm{H} & \Delta H = -7 \end{array}$ 

Table II gives the per cent of the total nitrogen in each product. The actual numerical values are necessarily somewhat crude, inasmuch as we had no way of determining the relative sensitivities of the various products. In addition the formation of brown deposits on the walls of the reactor largely negates any attempt at exact analyses.

Nevertheless, it can be seen that the proportion of products containing the cyano radical is quite high, i.e. of the order of 25%. This would seem to argue that the cyano radical plays a rather important part in these reactions. It is interesting to note that

\*Kcal/mole, estimated from group equivalent values (ref. 6).

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in the case of the acetylene reaction, as the flow rate of acetylene is increased, the amount of cyanogen increases quite steeply, and then falls off again as conditions approach complete consumption of the active nitrogen (1). The cyanogen is presumably produced by the recombination of CN radicals.

With the olefins studied, the major product containing nitrogen was again HCN, which accounted for 97% of the nitrogen in the ethylene reaction, and more than 78% in the propylene reaction. The later reaction also yielded appreciable amounts of cyanogen.

Although the mass spectra over the range of masses 50-70 show several interesting features, it would be unwise to draw overly firm conclusions from them, since the peaks are quite small. The spectra are shown in Table I.

With ethylene the largest peaks were at masses 51, 52, and 53 with a series of smaller peaks extending to mass 56. The peak at mass 52 can be attributed at least in part to cyanogen, while that at mass 53 can be attributed to  $C_3H_3N$ , which could be cyanoethylene. The peaks at 50, 51 may be due in part to cyanoacetylene, since acetylene is a product of this reaction (2). As can be seen from Table II the proportion of nitrogen in products other than HCN is very small.

In the case of propylene, however, this may not be the case. Propylene gave a series of peaks from masses 50 to 58, and from 63 to 67, the two largest being at 52 and 53. The series at 63 to 67 is probably due to  $C_4H_5N$ , which may be either propenyl cyanide, isopropenyl cyanide, allyl cyanide, or a mixture of them. The peak at mass 53 may be cyanoethylene.

By analogy with the corresponding acetylene reactions, the following reactions can be written to describe the olefin reactions:

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| CN + C₂H₄         | $\rightarrow$ C <sub>2</sub> H <sub>3</sub> CN + H                 | $\Delta H \text{ (ref. 6)} = -10$ |
|-------------------|--|-----------------------------------|
| $CN + CH_3C_2H_3$ | $H \rightarrow C_2 H_3 CN + CH_3$                                  | $\Delta H = -22$                  |
|                   | $\rightarrow CH_{3}C(CN)CH_{2} + H$                                | $\Delta H = -11$                  |
|                   | $\rightarrow$ CH <sub>3</sub> C <sub>2</sub> H <sub>2</sub> CN + H | $\Delta H = -8$                   |
|                   | $\rightarrow$ CH <sub>2</sub> (CN)CHCH <sub>2</sub> + H            | $\Delta H = -7$                   |

Unfortunately, we were unable to obtain samples of pure cyanoacetylene or methyl cyanoacetylene in order to compare mass spectra. We have obtained the mass spectra of the three possible  $C_4H_5N$  products. They are very similar, and have approximately the spectra m/e 67: 66: 65: 64: 63; 100: 35: 6: 20: 7. In view of the presence of a large m/e 53 peak, the discrepancy in the spectra from m/e 65 to 63 may be due to the presence of a  $C_3H_4$  component.

It is of interest that ammonia was produced in the reactions with both acetylenes and with ethylene,\* although it was not detected in the propylene reaction (Table II). Very approximately, the amount of ammonia produced increased with the proportion of cyano containing products. We are unable to propose a mechanism for this formation of ammonia. It might come about by successive recombination of N atoms, which are relatively abundant, with H atoms, but this is purely speculative.

The complete mechanism for the reaction of N atoms with the lower acetylenes and olefins is certainly very complex and we have made no effort to determine it. We do think that the evidence points to the importance of the CN radical in the reaction and strongly suggests that it forms several important products by displacement reactions at one of the carbons of the double or triple bond.

\*In agreement with an earlier observation on the ethylene reaction by J. T. Herron and H. I. Schiff (1955, unpublished).

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