# THE REACTION OF HYDROGEN ATOMS WITH **METHYL CYANIDE**<sup>1</sup>

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## ABSTRACT

Hydrogen atoms produced in a discharge tube were found to react with methyl cyanide to produce hydrogen cyanide as the main product, together with smaller amounts of methane and ethane. The proposed mechanism involves the formation of hydrogen cyanide and a methyl radical in the initial step; methane and ethane are attributed to secondary reactions of the methyl radicals.

## INTRODUCTION

The reaction of hydrogen atoms with methyl cyanide seems never to have been studied. A limited investigation of it has been made, partly for its intrinsic interest, and partly to provide information about the possible significance of hydrogen atom reactions during the reaction of active nitrogen with methyl cyanide, which will be reported in a later communication.

#### EXPERIMENTAL

The apparatus was essentially identical with that used for active nitrogen studies in this laboratory (1, 5) except for the methyl cyanide feed system. Methyl cyanide was stored as a liquid in a wide flat-bottomed bulb immersed in a thermostat regulated at  $20.25 \pm 0.05$  °C., and the vapor drawn directly from the liquid surface. The methyl cyanide flow rate was varied by placing jets of different sizes in a flowmeter.

The molecular hydrogen flow rate was  $7.95 \times 10^{-5}$  mole/sec., corresponding to an operating pressure of 0.95 mm. Hg in the system.

Methyl cyanide, "chemically pure", was purchased from Brickman and Company and thoroughly dehydrated by one distillation over calcium chloride, followed by six distillations over  $P_2O_5$  (13), and a final distillation over freshly fused potassium carbonate (9).

The condensable products of the reaction were distilled into a low temperature still of the type described by LeRoy (8). The  $C_2$  fraction was distilled off at  $-140^{\circ}$ C. and by mass-spectrometric analysis\* was found to contain only ethane. The remainder of the products were distilled into an absorber containing N/2 KOH immersed in liquid air. After the solution had melted, the cyanide was determined by titration with silver nitrate (6). Three experiments were made in which the products were analyzed for cyanogen by the method due to Rhodes (11); the result in each case was negative. Samples of noncondensable products were withdrawn from the hydrogen stream by a Toepler pump and analyzed on the mass spectrometer. They contained only methane,

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in addition to excess hydrogen. There were traces of a white solid on the walls of the tube leading from the reaction vessel into the first trap.





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The yields of hydrogen cyanide, ethane, and methane at 107° and 237°C. are plotted in Fig. 1 as functions of the methyl cyanide flow rate.

## DISCUSSION

The initial attack of a hydrogen atom on the methyl cyanide molecule can be represented in three ways:

$$H + CH_3CN \rightarrow CH_4 + CN - 2$$
 kcal. [1]

$$H+CH_3CN \rightarrow H_2+CH_2CN+3$$
 kcal. [2]

$$H + CH_3CN \rightarrow HCN + CH_3 + 10$$
 kcal. [3]

The heats of reaction in each case were calculated from heats of formation given in Reference (10). The heat of formation of the  $CH_2CN$  radical was estimated at about -70 kcal., and the heat of formation of the CN radical was taken as -93 kcal. (2, 10).

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If reaction [1] occurs to an appreciable extent, some of the cyanide radicals formed in [1] should, at least at low MeCN flow rates, recombine to cyanogen. Since HCN but no cyanogen was found, every cyanide radical formed in [1] would have to be removed quantitatively by reactions leading ultimately to hydrogen cyanide. Moreover, with reaction [1] as initial step, there should be one molecule of methane produced for every cyanide radical disappearing. Fig. 1 shows that no such relation exists between the formation of HCN and  $CH_4$ . It would also be difficult to account for the presence of ethane in the products on this basis. Hence reaction [1] must be ruled out as a possible primary step.

If reaction [2] is the initial step, it is difficult to visualize how methane, ethane, and hydrogen cyanide could arise by further reactions of the cyanomethyl radicals produced. While it is true that recombination of the  $CH_2CN$  radicals to succinonitrile would account for the white deposit observed on the walls of the reaction vessel, this cannot be taken as proof that reaction [2] occurs, since  $CH_2CN$  radicals may also be formed in the reaction

# $CH_3 + CH_3CN \rightarrow CH_4 + CH_2CN$

which is known to occur (12). While reaction [2] does not appear to be attractive for the primary step, the present experiments do not permit its importance to be assessed directly.

If reactions [1] and [2] are considered unimportant, and the primary step is assumed to be reaction [3], methane and ethane would have to arise by subsequent reactions of methyl radicals, and at any flow rate of methyl cyanide the following relation between the products of the reaction should exist:

2(moles of ethane) + (moles of methane) = (moles of HCN).

Inspection of Fig. 1 shows that this is approximately true, within the relatively large experimental error. This agreement may, perhaps, be taken as evidence that, compared with reaction [3], reaction [2] does not occur to an appreciable extent.

The two curves in Fig. 1 representing the production of hydrogen cyanide as a function of methyl cyanide flow rate show that above a flow rate of about  $8 \times 10^{-6}$  mole/sec. MeCN, further increase in MeCN flow rate does not increase the production of hydrogen cyanide. A reasonable explanation of this behavior seems to be that the available supply of hydrogen atoms becomes exhausted.

If the flat portion of each curve represents complete consumption of all the available hydrogen atoms, there is reason to expect that the plateau should be higher at the lower temperature, since presumably more hydrogen atoms should be available at the lower temperature owing to a decreased number of collisions (in the gas phase and at the wall) leading to their recombination. From the relative positions of the two plateaus in Fig. 1, the experimental results seem to imply that the opposite is true. On the basis of a detailed mathematical treatment, it will be shown in a later communication that the change of plateau values with temperature could be accounted for on the assumption that

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methyl cyanide acts as an efficient third body in the recombination of hydrogen atoms.

There are four obvious possibilities for secondary reactions of methyl radicals:

$$CH_3 + H \rightarrow CH_4$$
 [4]

$$CH_3 + CH_3 \rightarrow C_2H_6$$
<sup>[5]</sup>

$$CH_3 + H_2 \to CH_4 + H$$
[6]

$$CH_3CN + CH_3 \rightarrow CH_4 + CH_2CN.$$
 [7]

Reactions [4] and [5] have low activation energies, and both probably require a third body. Reactions [6] and [7] are both known to have activation energies of the order of 10 kcal. (14, 15). On the basis of this information, reactions [4] and [5] should be equally likely at 107°C. and 237°C., with reactions [6] and [7] becoming important only at the higher temperature. This conclusion appears to be borne out by the pattern of methane production shown in Fig. 1. At 107°C. the amount of methane formed rises with increasing methyl cyanide flow rate up to a maximum which corresponds roughly to the point where complete consumption of hydrogen atoms occurs, and then drops off sharply as the methyl cyanide flow rate is increased further. This suggests a strong dependence of methane production on hydrogen atom supply, and consequently reaction [4] must be responsible for a major part of the methane produced at this temperature. At 237°C. the decrease of methane production at MeCN flow rates corresponding to complete consumption of hydrogen atoms is less pronounced than at 107°C., and this may be taken as evidence that at this temperature reactions [6] and [7]—in addition to reaction [4] contribute significantly to the formation of methane, as expected.

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It is difficult to assess the relative importance of reactions [6] and [7]. It will be noted however that in reaction [6] a hydrogen atom is formed for each molecule of methane produced. If reaction [6] were the only important methaneproducing step at high MeCN flow rates, a chain reaction could conceivably be set up in conjunction with reaction [3], resulting in continued increase of hydrogen cyanide yield at high MeCN flow rates. Since the hydrogen cyanide production curve (Fig. 1) reaches a flat plateau (within experimental error), it is very improbable that at high flow rates appreciable amounts of methane are produced in reaction [6].

There can be little doubt that ethane is due to recombination of methyl radicals, and by reference to the discussion of methane production the only other important reaction competing at both temperatures for methyl radicals at low MeCN flow rates should be reaction [4]. The fact that production of ethane increases markedly with a rise in temperature would then seem to be a matter of methyl radical concentration. The increased amount of reaction at  $237^{\circ}$ C. increases [CH<sub>3</sub>] relative to its value at  $107^{\circ}$ C., and this should profoundly affect the rate of formation of ethane, which depends on the second power of [CH<sub>3</sub>]. The rate of formation of methane (reaction [4]) should also increase, though to a lesser extent.

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Actually, a decline in the yield of methane is observed at 237°C., and this appears to be attributable to a decrease in hydrogen atom concentration. At low MeCN flow rates, only relatively few hydrogen atoms are removed in reactions [3] and [4], and in third order recombination with methyl cyanide as the third body. As a result, under these conditions, an appreciable part of the hydrogen atoms will recombine by  $H-H_2$  collisions and at the wall, and, as mentioned, such recombination can be expected to exhibit a positive temperature coefficient. It appears that at 237°C. this hydrogen atom recombination is much more pronounced than at 107°C., to the extent that it may offset the effect of the temperature increase on  $[CH_3]$ , hence on the rate of formation of methane, and lead to a reduced yield of methane at the higher temperature.

The reaction of hydrogen atoms with methyl cyanide appears to be essentially similar to the reactions of methyl halides with hydrogen atoms (3, 4, 7). This is perhaps not surprising since in many inorganic reactions the cyanide group exhibits a strong resemblance to the halogens.

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