# THE REACTIONS OF ACTIVE NITROGEN WITH METHANE AND ETHANE<sup>1</sup>

## By P. A. Gartaganis and C. A. Winkler

#### ABSTRACT

Reinvestigation of the active nitrogen - methane reaction in the temperature range 45° to 500°C. has confirmed hydrogen cyanide as the only product, other than hydrogen, formed in measurable amounts. An "induction" effect in the hydrogen cyanide production was observed with increase of methane flow rate. This induction decreased with increase of temperature and was shown to be due to concomitant hydrogen atom reactions, since it could be eliminated by addition of hydrogen atoms to the reaction mixture. Reinvestigation of the active nitrogen – ethane reaction over the temperature range –100° to 475°C. also confirmed hydrogen cyanide to be the only measurable product, other than hydrogen, of that reaction. There was some indication that an induction effect was present with ethane, as with methane, and it may be concluded tentatively that both reactions are carried substantially by hydrogen atom reactions.

#### INTRODUCTION

In a previous study in this laboratory (7), it was observed that the Arrhenius plot for the reaction of active nitrogen with neopentane showed a marked change of slope, indicative of two activation energies in the range of temperatures used. While there was some reason to believe that this behavior might be due to two reactive species in active nitrogen, one of which is almost certainly atomic nitrogen (4, 5), there remained the possibilities that it resulted from concomitant hydrogen atom reactions or from different rates of attack by a single species in active nitrogen at the primary and quaternary carbon atoms in the neopentane molecule. Since methane and ethane are incapable of suffering such different modes of attack, the reactions of active nitrogen with these two hydrocarbons have been reinvestigated over a wider range of conditions than those used previously (3), in an effort to examine further the possible significance of the two activation energies observed with neopentane.

#### EXPERIMENTAL

The investigations were made with conventional fast-flow techniques, In many experiments with methane, hydrogen atoms were introduced simultaneously with nitrogen atoms. The arrangement for doing this is illustrated in Fig. 1, which, with the accompanying legend, serves also to indicate all the essential details of the apparatus currently used in this laboratory for studies on active nitrogen reactions. When necessary, the reaction vessel was surrounded by an electrically heated furnace molded from asbestos or by a plastic vessel to contain an appropriate refrigerant.

The nitrogen discharge tube was operated by a 110 v.-5000 v. transformer which fed through a diode rectifier (Raytheon, 866-A-GAA) and a 2000 ohm resistance into two condensers in parallel (each  $4 \mu f.$ , 6000 v., Aerovox No. 3).

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## CANADIAN JOURNAL OF CHEMISTRY. VOL. 34, 1956



1458

Fig. 1. Diagram of apparatus. HA, NA: Manostats to control hydrogen and nitrogen inlet pressures. HF, NF: Furnaces filled with copper turnings at 450°C. to remove oxygen from the hydrogen and nitrogen streams. HT, NT: Liquid nitrogen traps to remove water and CO<sub>2</sub> from the hydrogen and streams. H1, N1: Liquid nitrogen traps to remove water and CO<sub>2</sub> from the hydrogen and nitrogen. HM, NM: Manometers to measure stream pressures. HB, NB: Calibrated capillary flow meters for hydrogen and nitrogen. HDT, NDT: Hydrogen and nitrogen discharge tubes with aluminum electrodes. J: Connecting tube, 20 cm. long, 1.8 cm. diam. RV: Reaction vessel (300 cc.), "poisoned" with phosphoric acid. P: Thermocouple. B1, B2, B3: Bulbs for condensed hydrocarbon. S1: Hydrocarbon storage vessel (5 liters). S2, S3: Calibrated hydrocarbon storage vessels (1100 cc. and 400 cc. respectively). CM1, CM2 CM2: Manometers to pressure pressures in hydrocarbon storage vessels. G: Scratched S2, S3: Cambrated hydrocarbon storage vessels (1100 cc. and 400 cc. respectively). CM1, CM2, CM3: Manometers to measure pressures in hydrocarbon storage vessels. G: Scratched stopcock to maintain constant pressure of hydrocarbon in ballast volume, L. CB: Calibrated flow meter for hydrocarbon. Q: Hydrocarbon jet. V1, V2, V3: Liquid nitrogen product traps. K: Absorber (to contain appropriate solution). X1, X2: Two Cenco "Megavac" pumps (or a single "Hypervac" pump).

These discharged across the discharge tube four to six times per second, depending on the operating pressure. The hydrogen discharge tube circuit was similar, but a variable transformer was inserted in the 110 v. line to permit controlled variation of the discharge frequency in the hydrogen discharge tube.

Hydrogen cyanide was estimated quantitatively by condensing it over frozen potassium hydroxide in the absorber, K, followed by titration of the cyanide with standard silver nitrate after the contents of the absorber had been allowed to come to room temperature.

# Methane

#### RESULTS

Only about 1% of the methane reacted at 45°C., (comparable with the possible amount of impurities present), but significant reaction occurred above 280°C. At 358°C. and 450°C., the reaction showed a striking feature hitherto unobserved in active nitrogen reactions. The yield of hydrogen cyanide was low at low flow rates of methane, but increased rather rapidly as the

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#### GARTAGANIS AND WINKLER: ACTIVE NITROGEN

methane flow was increased. At sufficiently high flow rates, the HCN yield became constant at a given temperature, presumably after all the available active nitrogen was consumed. Typical of the results that were obtained in numerous experiments are those shown in Fig. 2. For convenience, the acceleration in hydrogen cyanide production with increased methane flow rate will be designated as an "induction", but it should be realized that it is not an induction period in the usual sense since it is not a function of time but of concentration.

Hydrogen cyanide was the only product of the reaction obtained in measurable quantities over the range of temperatures used. No cyanogen, ammonia, or hydrazine could be detected by usual analytical methods, and the mass spectrometer failed to show more than possible traces of substances that might have been  $C_2$  and  $C_3$  hydrocarbons or cyanogen.

It was suspected that the induction in the reaction might be caused by fast reaction of active nitrogen with methyl radicals derived from attack of methane by atomic hydrogen produced in the initial reaction with active nitrogen. The reaction of methane with active nitrogen in the presence of added molecular and atomic hydrogen was therefore studied in some detail. A large number of experiments were made, the results of which may be summarized briefly to illustrate the behavior observed.

In preliminary experiments in which molecular hydrogen was added to the active nitrogen stream before it entered the reaction vessel, pronounced induction remained. This was also true at temperatures up to 330°C. when a relatively low concentration of atomic hydrogen was added, (low voltage across HDT, Fig. 1), although at higher temperatures (513°C.) this low H atom concentration did cause almost complete disappearance of the induction.

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Complete elimination of the induction was achieved with a higher concentration of H-atoms, the total pressure of hydrogen being greater than that of nitrogen. However, the maximal hydrogen cyanide yield was now quite low. Experiments were then made to determine whether the absence of the induction could be maintained without sacrificing the hydrogen cyanide yield. This was finally accomplished by suitable adjustment of the relative concentrations of atomic hydrogen and active nitrogen admitted to the reaction vessel. A final series of experiments was then made at 480°C., with all conditions rigorously controlled, to confirm that the behavior indicated by the many previous experiments could be associated with the operating conditions used, and especially that elimination of the induction was possible for different levels of hydrogen cyanide yield. The primary of the hydrogen discharge circuit was set first at 50 v., then at 100 v., and the hydrogen cyanide yields determined at different methane flow rates in the presence of molecular and atomic hydrogen with the nitrogen pressure greater than and less than that of hydrogen. The results are shown in Fig. 3.

When molecular hydrogen was present at a pressure *lower* than the pressure of nitrogen, some induction could be observed, but when atomic hydrogen was introduced under otherwise similar conditions the induction was eliminated for a relatively high yield of hydrogen cyanide. When the pressure of hydrogen was *greater* than that of nitrogen, no induction was observed under any of the

1459

1460





in the primary circuit of the hydrogen discharge tube, and (c) relative pressures of nitrogen and hydrogen in the reactions methane - active nitrogen, and methane - active nitrogen hydrogen (molecular or atomic). Тe

Temperature, 480°C.		
Pressure:	N <sub>2</sub> high, H <sub>2</sub> low	N2 low, H2 high
Voltage in primary of	No discharge	O No discharge
hydrogen discharge	🛦 50 v.	∆ 50 v.
circuit:	🗖 100 v.	🗆 100 v.

operating conditions, and the yield of hydrogen cyanide was quite low. Elimination of the induction in the presence of molecular hydrogen, i.e. without the hydrogen discharge in operation, was immediately traced to back diffusion of hydrogen into the nitrogen discharge tube under the pressure differential that prevailed. The characteristic reddish color of the hydrogen discharge was observed near the base of the nitrogen discharge tube, and undoubtedly enough hydrogen atoms were produced to eliminate the induction. It might be noted that the order of the curves in Fig. 3 was reversed when the relative pressures of nitrogen and hydrogen were reversed. Also, substitution of helium for hydrogen, under comparable conditions, had no effect on the induction, i.e. there was no effect of merely increasing the total pressure in the system.

#### GARTAGANIS AND WINKLER: ACTIVE NITROGEN

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Regardless of ethane flow rate or temperature, hydrogen cyanide was the only gaseous product obtained in measurable amounts from this reaction. No cyanogen, ammonia, or hydrazine was detected chemically or mass spectrometrically. At temperatures below room temperature, small amounts of a dark brown polymer were deposited in the reaction vessel and the main trap.

The relation between hydrogen cyanide production and ethane flow rate over the temperature range  $-100^{\circ}$ C. to  $475^{\circ}$ C. is shown in Fig. 4. For the data recorded in Fig. 4A, no attention was given to the temperature of the



FIG. 4. Relation between hydrogen cyanide production and ethane flow rate. Temperature, °C.:  $A: \equiv -100$ ,  $\times -50$ ,  $\oplus 55$ ,  $\oplus 175$ ,  $\bigcirc 298$ ,  $\oplus 400$ ,  $\Box 475$ , (+ Ethylene at 300°C  $B: \equiv -50$ ,  $\oplus 3$ ,  $\Box 50$ ,  $\oplus 122$ ,  $\bigcirc 253$ ,  $\oplus 404$ .

# 1462

## CANADIAN JOURNAL OF CHEMISTRY. VOL. 34, 1956

tube that connected the reaction vessel to the discharge tube. For the data of Fig. 4B, however, the lower half of this connecting tube was surrounded by appropriate refrigerant for the low temperature experiments; also, for these experiments, a new discharge tube and reaction vessel were used, and the active nitrogen concentration, estimated by reaction with ethylene (2, 6, 8), was about twice that in the experiments which yielded the data of Fig. 4A.

DISCUSSION

## Methane

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In the earlier investigation of the reaction of methane with active nitrogen (3), it was concluded that the production of hydrogen atoms in the initial attack on the methane molecule probably had little influence on the yield of hydrogen cyanide. However, the earlier experiments were made for the most part in the neighborhood of 400°C., and with a limited range of methane flow rates. The results of the present study leave little doubt that the reaction is, in fact, carried to a considerable extent by hydrogen atoms, probably by the following sequence of reactions:

$$N + CH_4 \rightarrow HCN + H_2 + H,$$
<sup>[1]</sup>

$$H + CH_4 \rightarrow CH_3 + H_2, \qquad [2]$$

$$H_3 + N \to HCN + 2H$$
[3]

There is little doubt that reaction [3] occurs with a low activation energy (1) and is very fast. Hence, as the methane flow rate is increased and reaction [2] increases in significance relative to recombination of hydrogen atoms, the hydrogen cyanide yield might be expected to show the induction effect observed. Addition of hydrogen atoms should, of course, eliminate the induction by accentuating the contribution of reaction [3] at all flow rates.

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The reversal in the order of the curves in Fig. 3, and the drastic change in hydrogen cyanide yield that may be caused by addition of hydrogen atoms, suggest that hydrogen atoms may deactivate active nitrogen, possibly by

$$N + H \rightarrow NH,$$
  
 $2NH \rightarrow N_2 + H_2.$ 

Owing to the induction effect, no reliable estimate of the activation energy of the methane – active nitrogen reaction was possible, but calculations (3) confined to low flow rates of methane, where secondary reactions are presumably minimal, gave an activation energy of about 13 kcal. and a steric factor of about  $10^{-2}$  (cf. E = 11 kcal.,  $P = 5 \times 10^{-3}$  from Ref. 3). In these calculations, the concentration of active nitrogen was assumed to be given by the maximum yield of hydrogen cyanide obtained in the reaction with ethylene (2, 6, 8). In view of its complicating features, the reaction of methane with active nitrogen would appear to give no information about the possible presence of two active species in active nitrogen.

#### Ethane

It is, perhaps, impossible to state categorically whether an induction effect is present or absent in the ethane – active nitrogen reaction. While a small

## GARTAGANIS AND WINKLER: ACTIVE NITROGEN

1463

induction has been drawn into some of the curves of Fig. 4, the magnitude of the effect is of the same order as the experimental error in determining the HCN yields from different experiments. (No attempt was made to establish the presence or absence of an induction by addition of hydrogen atoms, as in the experiments with methane, since such experiments are much more difficult and capable of less precision than those with a single discharge tube.) Since utmost care was taken with the experiments, it seems likely that an unequivocal result may not be possible with the present method of studying the reaction.

If second order rate constants are calculated for the different temperatures (2), and the Arrhenius lines plotted, the results of Fig. 4 lead, in both cases, to activation energies of approximately 2.7 and 6 kcal. in the temperature ranges -100°C. to about 150°C., and 150°C. to 475°C., respectively. The corresponding steric factors are of the order  $10^{-4}$  and  $10^{-2}$ .

The two activation energies may be attributed either to concomitant hydrogen atom reactions or to the presence of more than one chemically active species in active nitrogen. Of the two explanations, the first is probably to be preferred in view of the demonstrated effect of hydrogen atoms in the methane reaction.

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