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# THE REACTION OF ACTIVE NITROGEN WITH AZOMETHANE<sup>1</sup>

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### ABSTRACT

The main products of the reaction between active nitrogen and azomethane were hydrogen cyanide and ethane. Traces of methane, ethylene, and acetylene were also formed, together with small amounts of an unstable product. Activation energies of about  $0.5\pm0.4$  and  $1.9\pm0.3$  kcal. per mole, with corresponding steric factors of  $10^{-1}$  to  $10^{-3}$  and  $10^{-2}$  to  $10^{-4}$ , were estimated for the reactions of active nitrogen with methyl radicals and azomethane respectively, on the assumption that atomic nitrogen is the reactive component of active nitrogen. Azomethane appeared to catalyze the deactivation of active nitrogen.

### INTRODUCTION

Free alkyl radicals have been postulated as intermediates in many of the hydrocarbon – active nitrogen reactions studied in this laboratory, and it has been invariably assumed that they were very rapidly destroyed by reaction with active nitrogen. The present study represents an attempt to evaluate experimentally the kinetic characteristics of the methyl radical active nitrogen reaction.

## EXPERIMENTAL

The apparatus and analytical methods have been described in earlier papers (4). Two concentrations of active nitrogen, which differed by a factor of approximately ten, were used. For the higher concentration, molecular nitrogen at a flow rate of  $9.75 \times 10^{-5}$  mole/sec. was admitted to the condensed discharge. The lower concentration was obtained by reducing the flow of nitrogen to  $3.53 \times 10^{-6}$  mole/sec., while the pressure in the system was maintained at the previous value (ca. 1.0 mm.) by introducing argon into the discharge tube at a flow rate of  $7.28 \times 10^{-5}$  mole/sec. In two experiments on the hydrogen atom - azomethane reaction, a comparable hydrogen-argon mixture was passed through the discharge tube.

Three samples of azomethane were prepared from dimethylhydrazine by the method of Leitch\* (11); these showed identical vapor pressure-temperature relations.

Reaction temperatures were measured with two copper-constantan thermocouples. One of these was situated directly below the hydrocarbon inlet tube in the center of the reaction vessel, while the other was located near the top of the vessel at the active nitrogen inlet.

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<sup>2</sup>Holder of a National Research Council Studentship, 1953-1954, and a Cominco Fellowship, 1954–1955. \*The authors are grateful to Dr. L. C. Leitch of the National Research Council, Ottawa, for one

sample of azomethane and for some of the dimethylhydrazine. Further supply of the latter was obtained from Brickman and Company of Montreal.

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# RESULTS

A preliminary experiment with azomethane mixed with molecular nitrogen in approximately the proportions used in the subsequent studies of the active nitrogen reaction showed no significant thermal decomposition of azomethane under these flow conditions at 400°C. Also no decomposition was observed when argon alone was passed through the discharge tube and allowed to mix with azomethane in the reaction vessel.



 $FIG.\,1.\,$  Relations between flow rate of azomethane and yields of products in the reaction between azomethane and active nitrogen.

A: HCN production	on at high active nitrogen c	oncentration:	
	HCN	Temp. (°C.)	
		390	
	ō	160	
	$\bigtriangleup$	85	
B: Production of (	$C_2$ hydrocarbons at high act	ive nitrogen conce	ntration:
$C_2H_6$	$C_2H_4$	Te	mp. (°C.)
			390
0	•		160
$\bigtriangleup$			85
C: Production of I	ICN and C <sub>2</sub> hydrocarbons	at low active nitro	gen concentration:
HCN	C <sub>2</sub> H <sub>6</sub>	Te	mp. (°C.)
			400
$\bullet$	0		180
<b>A</b>	$\bigtriangleup$		50
D: Production of concentration:	the unstable product and	azomethane recove	ery at low active nitrogen
Recovered AM	Unstable product	Te	mp. (°C.)

overed AM	Unstable product	Temp. (°C.)
		400
•	0	180
<b>A</b>		50

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The condensable products of the active nitrogen – azomethane reaction consisted mainly of hydrogen cyanide and ethane. Unreacted azomethane was also recovered. A Le Roy still (10) was used to separate the ethane fraction, which was subsequently analyzed with a mass spectrometer.\*

The HCN content of the remaining fraction was estimated by absorption in KOH solution and titration with standard  $AgNO_3$  solution (9). Unreacted azomethane was obtained by difference. The yields of HCN and C<sub>2</sub> hydrocarbons for three different temperatures, at each of the active nitrogen flow rates used, are shown in Fig. 1A, B, and C.

Analysis of the uncondensed gases from two experiments at the higher active nitrogen flow rate indicated that methane was produced only in small amounts in the azomethane – active nitrogen reaction and that the hydrogen production approximated to the HCN yield.

In all of the active nitrogen - azomethane experiments small amounts of methane and nitrogen (in roughly equal proportions as determined by mass spectrometer analysis of several samples) were evolved when the condensable products were evaporated from one vessel to another, and also during distillation in the Le Roy still. The evolution of these gases in the same proportion was also observed from the products of the two experiments with the hydrogen atom - azomethane reaction. These observations indicate that the formation of an unstable product in the active nitrogen – azomethane reaction is a result of secondary hydrogen atom - azomethane reactions. From the total amounts of methane and nitrogen formed by complete decomposition of the unstable product, it was possible to estimate its yield on the assumption that one molecule of the unstable material decomposed to one molecule of methane and one molecule of nitrogen. The data obtained from such estimates, together with the recovery of azomethane, have been plotted in Fig. 1D as a function of the azomethane flow rate for a number of experiments at the lower active nitrogen flow rate.

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No products other than residual azomethane and hydrogen cyanide were detected in significant amounts by mass spectrometric analysis of the final fraction from two experiments at 45° and 177°C. with the lower active nitrogen concentration. The hydrogen cyanide yields calculated from these analyses agreed with those obtained by the chemical method mentioned previously.

At the lower temperatures material balances were within a few per cent of the theoretical. However, at higher temperatures the material balances were between 88 and 100% and some polymer formation was observed.

Experiments with ethylene and propylene at high temperatures and high flow rates, such that consumption of the active nitrogen should be complete (4), indicated a value of about  $1.60\pm0.10\times10^{-5}$  mole/sec. for the higher active nitrogen flow rate (dotted line, Fig. 1A). Similar experiments with ethane and ethylene gave a value of  $1.31\pm0.06\times10^{-6}$  mole/sec. for the lower flow rate.

Apart from the unstable product, the hydrogen atom – azomethane experiments yielded large quantities of ethane and a higher boiling fraction. Material

\*The authors are indebted to Dr. H. I. Schiff of this department for the mass spectrometer analyses.

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balances, calculated on the assumption that the latter fraction was residual azomethane or dimethylhydrazine, were well over 100%, a feature in which the hydrogen atom – azomethane experiments differed from those with active nitrogen.

# DISCUSSION

Although evidence has recently been obtained (3) to indicate the presence of more than one reactive species in active nitrogen, the identities of the species have not been established. As in most of the previous studies, therefore, the present results will be discussed on the assumption that atomic nitrogen is the only reactive species involved.

At the lower active nitrogen concentration the hydrogen cyanide production increased rapidly with azomethane flow rate, and attained a constant maximum value which was virtually independent of temperature. The close agreement between this maximum hydrogen cyanide yield and the corresponding yields from ethane and ethylene suggests that the hydrogen cyanide production from azomethane represents the complete consumption of the relatively small amount of active nitrogen available in these experiments.

On the other hand, the hydrogen cyanide production from azomethane at the higher active nitrogen flow rate never approached the value obtained with ethylene and propylene, although the constant yield observed for higher azomethane flow rates would again imply complete consumption of the available active nitrogen at 160° and 400°C.

The apparent loss of active nitrogen in the presence of azomethane might be due to catalyzed recombination of nitrogen atoms with azomethane as a third body; thus:

$$N+N+CH_{3}-N=N-CH_{3} \rightarrow N_{2}+CH_{3}-N=N-CH_{3}^{*}.$$
 [1a]

This would be in competition with the reaction:

$$N + CH_3 - N = N - CH_3 \rightarrow HCN + N_2 + H_2 + CH_3 \qquad [1b]$$

which appears to be the most reasonable process for the initial nitrogen atom attack on azomethane.

Both of these reactions are first order in respect of azomethane. A competition between them would thus explain the constant hydrogen cyanide production observed at azomethane flow rates in excess of the critical flow rate. A difference in activation energy would explain the increase in hydrogen cyanide production with temperature. Also, since the recombination reaction is second order in respect of the nitrogen atom concentration, a significant reduction in the concentration of this reactant should favor conversion of the active nitrogen to hydrogen cyanide, and the apparent difference in behavior at high and low active nitrogen concentrations can be explained.

It might be noted parenthetically that if excited or metastable nitrogen molecules, rather than atoms, were the major component of active nitrogen it would be difficult to account for this behavior, which has also been observed with other compounds (1, 2).\*

\*It is hoped that a general discussion of the behavior may be published shortly.

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Methyl radicals formed in the initial process may react with nitrogen atoms as follows:

$$+CH_3 \rightarrow HCN + 2H$$
 [2a]

$$\rightarrow$$
 HCN+H<sub>2</sub> [2b]

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$$\rightarrow CN + H_2 + H. \qquad [2c]$$

Reaction [2c] is probably slightly endothermic; moreover if it were extensive, cyanogen might have been expected as a significant product. Although reaction [2a] is thermodynamically less favorable than [2b], it permits conservation of spin (1), while [2b] does not.

Ethane formation presumably occurred by the reaction:

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$$CH_3 + CH_3 + M \to C_2H_6$$
<sup>[3]</sup>

which seems to have a negligible activation energy and a steric factor close to unity (12).

Methane, ethylene, and acetylene are all minor products and were probably produced in relatively unimportant processes (for example methane might have been formed in reactions involving hydrogen abstraction by methyl radicals).

From the results of the present investigation and from previous studies of the hydrogen atom – azomethane reaction (5) it would seem that secondary hydrogen atom – azomethane reactions must have been relatively insignificant in the reaction of active nitrogen with azomethane. However, formation of the unstable product implies that a small concentration of atomic hydrogen was present in the system. This may be taken as evidence for the occurrence of reaction [2a]. Indeed it is possible to infer from the relative proportions of HCN,  $C_2H_6$ , and the unstable product that this reaction largely predominated over reaction [2b].

The chain characteristics observed in previous studies of the hydrogen atom – azomethane (5) indicated that hydrogen atom – azomethane complexes might be relatively stable. Since such complexes might decompose to yield methane and nitrogen in roughly equal proportions (and possibly other products which are condensable in liquid nitrogen) they might well be identical with the unstable product recovered in the present investigation.

By making certain simplifying assumptions it is possible to obtain estimates for the activation energies of reactions [1b] and [2] from the results of the experiments at the lower active nitrogen concentration where the occurrence of reaction [1a] could be neglected.

On the basis of the mechanism already outlined the equations required for these calculations may be formulated as follows:

$$N + AM \xrightarrow{k_1} HCN + H_2 + N_2 + CH_3$$
 [1b]

$$N + CH_3 \xrightarrow{k_2} HCN + 2H \text{ (or } H_2)$$
[2]

$$CH_3 + CH_3 \xrightarrow{k_3} C_2 H_6$$
[3]

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$$d(\text{HCN})/dt = k_1(\text{AM})(\text{N}) + k_2(\text{Me})(\text{N}) = R_1$$
  
$$d(\text{Me})/dt = k_1(\text{AM})(\text{N}) - k_2(\text{Me})(\text{N}) - k_3(\text{Me})^2$$
  
$$d(\text{C}_2\text{H}_6)/dt = \frac{1}{2}k_3(\text{Me})^2 = R_2.$$

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The usual steady state approximation for the methyl radical concentration gives:

$$\frac{k_2}{k_3^{\frac{1}{2}}} = \frac{(Q_1 - 2Q_2)}{2^{3/2} \cdot F_n \cdot Q_2^{\frac{1}{2}}} \times \frac{RT}{pV^{\frac{1}{2}}} \times \text{(total molar flow rate)}$$
[i]

$$\frac{k_1 \cdot k_3^{\frac{1}{2}}}{k_2} = \frac{2^{\frac{1}{2}} \cdot (Q_1 + 2Q_2)}{(Q_1 - 2Q_2)} \times \frac{Q_2^{\frac{1}{2}}}{F_a} \times \frac{RT}{pV^{\frac{1}{2}}} \times \text{ (total molar flow rate)} \qquad [ii]$$

$$k_1 = \frac{(Q_1 + 2Q_2)}{2 \cdot F_n \cdot F_a} \times \left(\frac{RT}{pV^{\frac{1}{2}}}\right)^2 \times (\text{total molar flow rate})^2 \qquad [\text{iii}]$$

 $F_a$  and  $F_n$  are the flow rates of azomethane and nitrogen atoms in the reaction zone, and  $Q_1$  and  $Q_2$  are the observed rates of production of hydrogen cyanide and ethane respectively.

Calculations were made for the higher azomethane flow rates, where the reaction flame was confined to the upper part of the reaction vessel and the reading of the upper thermocouple could be assumed to indicate the reaction temperature. With the assumption of completely turbulent flow in the reaction zone,  $F_a$  and  $F_n$  may be assigned steady-state values. As a rough approximation the values of  $F_a$  and  $F_n$  in the reaction zone were assumed to be equal and independent of temperature. A value of  $1.30 \times 10^{-6}$  mole/sec. (equal to the average hydrogen cyanide production) was therefore taken to represent both  $F_n$  and  $F_a$ .

The reaction volume V was assumed to remain constant over the temperature range studied and was estimated from the dimensions of the reaction flame to be about 50 cm<sup>3</sup>. It was also necessary to assume negligible ethane consumption by the reaction:

$$N+C_2H_6 \rightarrow HCN+CH_3+H_2$$
.

Collision diameters of 3.0, 3.5, and 5.5 Å for nitrogen atoms (4), methyl radicals (6), and azomethane (8) respectively were used in the calculation of the collision numbers and estimation of the steric factors.

The ratios  $k_2/k_3^{\frac{1}{2}}$  calculated for the three different temperatures gave a value of  $0.5 \pm 0.4$  kcal. per mole for  $E_2 - \frac{1}{2}E_3$  and the ratio  $P_2/P_3^{\frac{1}{2}}$  was found to be between  $10^{-1}$  and  $10^{-2}$ . Allowing for the possible decreases in  $P_3$  at low pressures (7) a lower limit of  $10^{-3}$  may be set for  $P_2$ . If secondary hydrogen atom – azomethane reactions, which led to the formation of methyl radicals or ethane, were responsible for some of the decomposition of the azomethane, the fraction of hydrogen cyanide formed in the methyl radical – active nitrogen reaction would be greater than indicated and the ratios  $k_2/k_3^{\frac{1}{2}}$  and  $P_2/P_3^{\frac{1}{2}}$  would be correspondingly greater. The values of the ratios  $k_2/k_3^{\frac{1}{2}}$  and  $P_2/P_3^{\frac{1}{2}}$  calculated above can thus be regarded as lower limits.

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A value of  $2.0\pm0.3$  kcal. with a corresponding steric factor between  $10^{-2}$ and  $10^{-4}$  was estimated for  $E_1$  from the values of  $k_1$  calculated by equation [iii] for the three temperatures. Relation [ii], which is independent of  $F_n$ , gave a value of  $1.4\pm0.3$  kcal. for  $E_1-E_2+\frac{1}{2}E_3$ . This is consistent with the values of  $2.0\pm0.3$  and  $0.5\pm0.4$  kcal. per mole calculated for  $E_1$  and  $E_2-\frac{1}{2}E_3$ with the other two relations. These calculations indicate that the reaction of nitrogen atoms with azomethane was far more rapid than their reaction with saturated hydrocarbons and comparable in rate with their attack on unsaturated hydrocarbons.

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