# THE REACTIONS OF ACTIVE NITROGEN WITH CYCLOPROPANE, CYCLOBUTANE, AND CYCLOPENTANE<sup>1</sup>

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## ABSTRACT

Cyclopropane, cyclobutane, and cyclopentane in order of increasing reactivity with active nitrogen yielded hydrogen cyanide and ethylene as the major products. The relative pro-portions of ethylene to hydrogen cyanide increased with number of carbon atoms in the reactant and with increase of temperature.

Alkenes have been found (1) to react with active nitrogen more rapidly than do the corresponding alkanes, to yield a larger proportion of unsaturated hydrocarbons (other than the initial reactant) relative to hydrogen cyanide in the products. It was of interest to determine whether cycloalkanes, in their reactions with active nitrogen, would resemble the corresponding *n*-alkanes or their olefin isomers, and whether the ease of reaction would depend upon the relative stabilities of the cycloalkane rings.

#### EXPERIMENTAL

The apparatus, experimental techniques, and analytical methods were essentially the same as those described in previous papers (2, 3, 4). A molecular nitrogen flow of 58 micromoles/second at a pressure of 1.5 mm Hg was used in the cyclopropane and cyclobutane reactions, while in the cyclopentane reaction the molecular nitrogen flow was 100 micromoles/second at a pressure of 1.8 mm Hg. In a brief examination of the atomic hydrogen reaction with cyclopentane and ethylene the flow of hydrogen was 120 micromoles/second at a pressure of 0.95 mm Hg.

Cyclopropane of 99.5% purity was used after a single bulb-to-bulb distillation. A limited supply of cyclobutane of approximately 99% purity was obtained through the courtesy of Dr. W. D. Walters, University of Rochester. The cyclopentane used had a refractive index  $n_{\rm D}^{20} = 1.4062$  ( $n_{\rm D}^{20} = 1.4064$  for highly purified cyclopentane (5)). Low temperature fractionation failed to reveal any lower molecular weight impurities.

Analyses for HCN,  $(CN)_2$ , and NH<sub>3</sub> were made by standard titration methods (6, 7), while mass-spectrometric and gas-chromatographic methods were used for other condensible and the non-condensible products.

#### RESULTS

Active nitrogen appeared to react only slowly with cyclopropane, since the purple-pink reaction flame completely filled the reaction vessel, even at high reactant flow rates. The flow rate of active nitrogen was taken to be equal to the maximum flow rate of hydrogen cyanide produced in the reaction of ethylene with active nitrogen at temperatures above 250° C (1) and found to be 3.9 micromoles/second.

The recovery of HCN increased as cyclopropane flow rate increased at all temperatures (Fig. 1), hence complete consumption of active nitrogen did not take place except, perhaps, at high flow rates at 350° C. The recoveries of  $C_2H_4$  and  $C_2H_2$  were much smaller than that of HCN (Fig. 1), and  $C_2H_6$  was detected only in trace amounts.

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FIG. 1. Relation of cyclopropane flow rate to product yields.

At high flow rates cyclobutane reacted with a relatively intense peach-colored flame in a small volume around the hydrocarbon inlet, from which it might be inferred that cyclobutane was considerably more reactive than cyclopropane. This is confirmed by the much higher conversion to HCN (Fig. 2). Complete reaction of the active nitrogen (the flow rate of which was 5.2 micromoles/second) appeared to be attained only above 250° C and 5 micromoles/second cyclobutane flow, when the production of HCN became independent of reactant flow rate.

The yields of other products in relation to cyclobutane flow rate are also shown in Fig. 2. Propane was detected among the products, but in even smaller amounts than propylene.



FIG. 2. Relation of cyclobutane flow rate to product yields.

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Cyclopentane reacted with active nitrogen with a reddish-violet flame that was concentrated near the hydrocarbon inlet at all but the lowest flow rates, i.e. the reaction appeared to be quite fast. The limiting production of HCN (Fig. 3) was essentially equal to the active nitrogen flow rate of 13 micromoles/second. The largest observed ratio of  $C_2H_4$  to HCN was 0.7, but this ratio would undoubtedly have increased at still higher cyclopentane flow rates (not readily attainable because of back diffusion from the reaction vessel).





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FIG. 4. Relation of cyclopentane flow rate to yields of methane and hydrogen.

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The recoveries of  $(CN)_2$ ,  $C_2H_6$ , and  $C_2H_2$  showed maxima with cyclopentane flow rate. Ammonia and  $C_3$  and  $C_4$  hydrocarbons were detected in amounts less than 1% of the HCN.

In another series of experiments, with an active nitrogen flow of 9.7 micromoles/sec the productions of  $CH_4$ ,  $H_2$ , and HCN were found to be related to cyclopentane flow, as shown in Fig. 4. Mass-spectrometric and gas-chromatographic analyses indicated that no product in excess of 1% of the HCN remained undetected.

To obtain information about the possible effect of atomic hydrogen on the cyclopentane-active nitrogen reaction, the relative rates of the H atom reactions with cyclopentane and ethylene were examined at 284° C. With the results shown in Table I.

| IADLE I |
|---------|
|---------|

Data for the reactions of hydrogen atoms with cyclopentane and ethylene at  $284^\circ\,C$ 

| cyclo-C₅H <sub>10</sub><br>input | C₂H₄<br>input             | Argon<br>input | C2H6<br>yield  | C2H4<br>yield  | C <sub>2</sub> H <sub>4</sub><br>destroyed |
|----------------------------------|---------------------------|----------------|--|--|--|
| 12.95ª<br>13.65<br>—             |                           | <br><br>11.95  | $\begin{array}{c} 0.170 \\ 0.170 \\ 0.920 \\ 1.250 \\ 0.920 \end{array}$ | $\begin{array}{c} 0.120 \\ 0.200 \\ 11.05 \\ 11.95 \\ 11.40 \end{array}$ |  |
| 13.30<br>13.20                   | $13.05 \\ 12.45 \\ 12.85$ | 12.00          | $\begin{array}{c} 0.900 \\ 0.520 \\ 0.420 \end{array}$                   | $11.55 \\ 12.10 \\ 12.45$  | 1.50<br>ca. $0.45^{b}$<br>ca. $0.45^{b}$   |

"All values refer to flow rates in micromoles/second.

<sup>b</sup>It was assumed that approximately 0.08 micromoles/second of ethylene was produced by reaction of hydrogen atoms with cyclopentane.

Since the hydrocarbon flow (13 micromoles/second) was in large excess over the H atom flow (estimated from the H atom – hydrogen iodide reaction to be about 6 micromoles/ second (8)), the reaction of H atoms should have been confined largely to their initial attack on the hydrocarbon. The results obtained with a mixture of ethylene and argon indicate that physical effects in the apparatus used do not invalidate direct comparison between the reactions of hydrocarbon mixtures and the reactions of pure hydrocarbons. Hence, it may be inferred from Table I that ethylene was destroyed three times more slowly when mixed with an equal amount of cyclopentane than when it reacted alone. Therefore, the rates of the reactions of atomic hydrogen with ethylene and cyclopentane are of the same order at 284° C, and any hydrogen atoms produced in the cyclopentane – active nitrogen reaction at 270° C would be expected to react to a large extent with cyclopentane.

| Cycloparaffin | Тетр.,<br>°С              | k, liter mole <sup>-1</sup> sec <sup>-1</sup> ×10 <sup>-5</sup> | <i>E</i> ,<br>kcal mole <sup>1</sup> | <br>×10⁴ |
|---------------|---------------------------|---|--------------------------------------|----------|
| Cyclopropane  | $50 \\ 150 \\ 250 \\ 350$ | $\begin{array}{c} 0.8 \\ 2.5 \\ 5.1 \\ 9.1 \end{array}$         | 3.2                                  | 0.6      |
| Cyclobutane   | $60 \\ 250$               | 1.2   | 4.6                                  | 4.7      |
| Cyclopentane  | 110 $270$                 | 2.4<br>19.  | 5.3                                  | 8.8      |

 TABLE II

 KINETIC CONSTANTS FOR THE REACTIONS OF ACTIVE NITROGEN WITH CYCLOALKANES

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Values of the second-order rate constants for the initial attack of active nitrogen on cyclopropane, cyclobutane, and cyclopentane are shown in Table II. The calculations were made for conditions of incomplete consumption of both cycloalkane and active nitrogen.

### DISCUSSION

As in previous papers, it will be assumed that atomic nitrogen is the main chemically reactive species in active nitrogen (9).

It would seem that the reactions of cyclopropane, cyclobutane, and cyclopentane with nitrogen atoms can be explained by similar mechanisms, the initial steps of which are analogous to the primary reaction suggested previously (1) for the reaction of active nitrogen with saturated hydrocarbons, i.e.,

$$cyclo-C_{5}H_{10} + N \rightarrow HCN + H_{2} + C_{4}H_{7}; \quad \Delta H = -10 \text{ to } -40 \text{ kcal.}$$
 [1]

$$\text{cyclo-C}_{4}\text{H}_{8} + \text{N} \rightarrow \text{HCN} + \text{H}_{2} + \text{C}_{3}\text{H}_{5}; \quad \Delta H = -58 \text{ kcal}$$

$$[2]$$

$$cyclo-C_3H_6 + N \rightarrow HCN + H_2 + C_2H_3; \quad \Delta H = -29 \text{ kcal}$$
[3]

An obvious alternative to reaction [1] which would permit a ratio for  $C_2H_4$  to HCN of 0.7, but which would seem to be forbidden by its endothermicity, is the reaction

$$cyclo-C_{b}H_{10} + N \rightarrow HCN + 2C_{2}H_{4} + H; \quad \Delta H = +14 \text{ kcal.}$$
<sup>[4]</sup>

The reaction

$$yclo-C_{\delta}H_{10} + N \rightarrow HCN + C_{2}H_{4} + C_{2}H_{5}; \quad \Delta H = -25 \text{ kcal}$$

$$[5]$$

is also a possible alternative to reaction [1]. However, it should be followed by very rapid reaction of  $C_2H_5$ , and subsequently  $CH_3$  radicals with active nitrogen to form HCN (1, 10, 11). The attack of nitrogen atoms on cyclopentane almost certainly has a higher activation energy than the radical-nitrogen atom reactions, and more nitrogen atoms should therefore be consumed in the primary step at higher temperatures and cyclopentane flow rates. Consequently, the radicals should suffer correspondingly less destruction and, contrary to the experimental results, the yields of ethane and methane should increase steadily with temperature and cyclopentane flow. Hence it may be concluded that reaction [5] is also of relatively little, if any, importance in the cyclopentane-active nitrogen reaction.

The unsaturated radicals formed in reactions [1], [2], and [3] should be attacked rapidly by nitrogen atoms in reactions such as

$$C_4H_7 + N \rightarrow HCN + C_2H_4 + CH_2$$
[6]

$$C_3H_5 + N \rightarrow HCN + C_2H_4$$
[7]

$$C_2H_3 + N \rightarrow HCN + CH_2$$
[8]

together with the reactions

$$CH_2 + N \rightarrow HCN + H$$
 [9]

 $CH_2 + N \rightarrow CN + H_2.$  [10]

If some of the  $CH_2$  produced in reactions such as [6] or [8] is in the triplet state, the reaction

$$CH_2^* + N \rightarrow CN + 2H$$
 [11]

might occur to an appreciable extent.

The large amounts of  $C_2H_4$  formed in the cyclopentane reaction at 270° C can be explained if the previous reactions are accompanied by

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and

 $cyclo-C_{5}H_{10} + H \rightarrow cyclo-C_{5}H_{9} + H_{2}$ [12]

 $cyclo-C_5H_{10} + CN \rightarrow cyclo-C_5H_9 + HCN$ [13]

followed by

$$cyclo-C_5H_9 + N \rightarrow HCN + 2C_2H_4.$$
[14]

The present study has shown that the attack of cyclopentane by H atoms at 270° C and high cyclopentane flow rates is quite probable even in the presence of considerable ethylene.

The maxima in the production of  $CH_4$  and  $C_2H_6$  from cyclopentane at the higher temperatures may be explained if it is assumed that these arise mainly from CH<sub>3</sub> radicals, and that the radicals are produced as suggested previously (1, 12),

$$C_2H_4 + N \rightarrow HCN + CH_3.$$
<sup>[15]</sup>

The extent of reaction [15] should pass through a maximum with flow rate of cyclopentane, since it is in competition with reaction [1], and this maximum should be more pronounced at higher temperatures, as observed, since the activation energy of reaction [1] (5.3 kcal/mole) appears to be higher than that of reaction [15] (3 kcal/mole (13)). The maximum should be less pronounced for methane than for ethane production, as observed, if methane production resulted mainly from reaction of CH<sub>3</sub> radicals with cyclopentane, while ethane was produced by their recombination.

Recovery of acetylene in small amounts from the three hydrocarbon – N atom reactions may be explained as in an earlier paper (1), i.e. reaction of N atoms with  $N \cdot C_2 H_4$  complexes to bring about recombination of N atoms and production of triplet ethylene which then decomposes to yield acetylene. Cyanogen probably resulted from the recombination of CN radicals formed in reactions such as [10] and [11].

The large value of the  $C_2H_4$ :  $C_3H_6$  ratio in the cyclobutane reaction and the increase of this ratio with temperature indicate that propylene was formed in secondary processes, perhaps by the hydrogenation of  $C_3H_5$  radicals. Similarly, the small quantities of ethylene recovered from the cyclopropane reaction could have resulted from hydrogenation of  $C_2H_3$  radicals, perhaps by abstraction from the parent hydrocarbon.

It is interesting to note that, of the three reactions studied, the cyclopropane reaction appears to have the lowest activation energy. This might be due to greater delocalization of carbon-carbon bond orbitals in cyclopropane (greater p-character), thus facilitating the approach of an electrophilic reagent such as a nitrogen atom. A similar situation exists in the ethylene – active nitrogen reaction which also has a low activation energy.

#### REFERENCES

- EVANS, H. G. V., FREEMAN, G. R., and WINKLER, C. A. Can. J. Chem. 34, 1271 (1956). BLADES, H. and WINKLER, C. A. Can. J. Chem. 29, 1022 (1951). FORST, W. and WINKLER, C. A. Can. J. Chem. 33, 1814 (1955). GARTAGANIS, P. A. and WINKLER, C. A. Can. J. Chem. 34, 1457 (1956).
  - $\mathbf{2}$
  - 3.
  - 4.
- 5
- KAARSEMAKER, SJ. and COOPS, J. R. KOLTOFF, I. M. and SANDELL, E. B. Rec. trav. chim. 71, 261 (1952). B. Textbook of quantitative inorganic analysis. Revised ed. The 6. Macmillan Co., New York. 1948. HODES, F. H. J. Ind. Eng. Chem. 4, 652 (1912).
- Rhodes, F. H.
- WILES, D. M. and WINKLER, C. A. EVANS, H. G. V. and WINKLER, C. Can. J. Chem. 35, 1298 (1957) 8
- Q Α. Can. J. Chem. 34, 1217 (1956)
- Can. J. Chem. 33, 1649 (1955). 10. ARMSTRONG, D. A. and WINKLER, C. A.
- ARMSTRONG, D. A. and WINKLER, C. A. GREENBLATT, J. H. and WINKLER, C. A. Can. J. Chem. 34, 885 (1956).
- Can. J. Research, B, 27, 721 (1949). Can. J. Research, B, 27, 732 (1949).
- 13. GREENBLATT, J. H. and WINKLER, C. A.

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