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The Reaction of Active Nitrogen with Simple Hydrocarbons at −196°[1]

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Active nitrogen reacted with methane, ethane, ethylene, acetylene and hydrogen cyanide at −196°. The possible mechanisms which may account for the reactions and products are discussed.

The reactions of methane, ethane, ethylene, acetylene, and hydrogen cyanide with active nitrogen, which was produced in a condensed discharge, were studied at −196°. Methane showed little or no reactivity but considerable amounts of ammonia and hydrogen cyanide were produced from ethane and ethylene. Some hydrogen cyanide was produced from acetylene. In the reaction of active nitrogen with hydrogen cyanide, about 15% of the decomposed hydrogen cyanide was recovered as cyanogen.

Experimental

The apparatus and experimental technique were identical with those used in the study, conducted in this Laboratory, of the reaction of active nitrogen with ammonia at −196°.[2] The molecular nitrogen flow rate was 6.4×10^{-3} mole/min., and the flow rate of nitrogen atoms, as determined by the hydrogen cyanide produced from the gas phase reaction with ethylene, was 2.5×10^{-4} mole/min.

Results

The results of a time study of the reaction of active nitrogen with ethane are given in Table I.

TABLE I

DECOMPOSITION OF ETHANE BY ACTIVE NITROGEN AT −196°

All quantities in micromoles

Reaction time, min.	C_2H_6 reactant	C_2H_6 decomposed	HCN produced	NH_3 produced
5.0	81.5	23.2	11.2	0.5
10.0	81.0	42.5	16.8	3.8
20.0	73.5	41.9	20.8	2.8
30.0	78.0	73.6	28.6	2.4
40.0	74.5	56.6	28.8	2.4

The erratic destruction of ethane probably was due to surface effects. Since both hydrogen cyanide and ammonia are destroyed by active nitrogen at −196°, the quantities produced in the ethane reaction must have been minimum, and not actual amounts produced. The maximum extent of decomposition of the ethane under these conditions was found to be about 20 μmoles/min.

The results of a time study of the reaction of active nitrogen with ethylene are shown in Table II. The maximum extent of decomposition of ethylene was found to be about 30 μmoles/min.

TABLE II

DECOMPOSITION OF ETHYLENE BY ACTIVE NITROGEN AT −196°

All quantities in micromoles

Reaction time, min.	C_2H_4 reactant	C_2H_4 decomposed	HCN produced	NH_3 produced
5.0	122.7	24.8	7.9	0.8
10.0	125.7	56.2	16.9	1.1
10.0	124.3	51.8	18.4	1.1
15.0	126.2	41.0	16.1	1.6
15.0	123.0	39.0	15.9	2.2
20.0	124.1	48.1	23.1	2.3
30.0	124.2	61.0	24.6	2.7
40.0	122.8	86.7	36.6	3.3

The reaction of active nitrogen with acetylene at −196° gave extremely erratic and irreproducible results, apparently because the acetylene is incorporated in the polymer produced in almost all active nitrogen-hydrocarbon reactions. When active nitrogen reacted with the polymer produced in the acetylene reaction, as much as 30% of the supposedly decomposed acetylene, from the preceding acetylene reaction, was recovered. Only trace amounts of hydrogen cyanide were produced. The maximum extents of decomposition of hydrogen cyanide and acetylene at −196° were found to be 4.5 and 2 μmoles/min., respectively.

Discussion

Several fundamental reactions conceivably could be responsible for the production of ammonia and hydrogen cyanide from ethane and ethylene. Ground state nitrogen atoms could react according to the reactions

$$N + C_2H_6(W) \longrightarrow [C_2H_6N] \longrightarrow HCN + CH_3 + H_2 \quad (1)$$

$$N + C_2H_4(W) \longrightarrow [C_2H_4N] \longrightarrow HCN + CH_3 \quad (1a)$$

On the assumption that the radical intermediates in reaction 1 are sufficiently stable, and that these complexes react with a second nitrogen atom, the initial reaction would correspond to a decomposition induced by nitrogen atom recombination. Thus

$$N + N + C_2H_6(W) \longrightarrow N_2 + C_2H_5 + H + 120 \text{ kcal.} \quad (2)$$

The radicals produced then could undergo reactions of the type[3]

$$C_2H_5(W) + N \longrightarrow [C_2H_5N] \longrightarrow HCN + CH_3 \quad (3)$$

$$C_2H_5N(W) + N \longrightarrow CH_3N + HCN = 2HCN + H_2 \quad (4)$$

$$N + H \xrightarrow{(W)} NH + 87 \text{ kcal.} \quad (5)$$

$$NH(W) + H_2 \xrightarrow{(W)} NH_3 + 90 \text{ kcal.} \quad (6)$$

$$NH(W) + H \longrightarrow NH_2 + 90 \text{ kcal.} \quad (7)$$

$$NH_2(W) + H \longrightarrow NH_3 + 104 \text{ kcal.} \quad (8)$$

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[2] E. R. Zabolotny and H. Gesser, *J. Phys. Chem.*, **66**, 408 (1962).

[3] Heats of Reaction are based on:
$D(N_2)$ = 225 kcal. J. M. Hendrie, *J. Chem. Phys.*, **22**, 1503 (1954).
$D(CH_3\text{–}H)$ = 101 kcal. T. L. Cottrell, "The Strength of Chemical Bonds," Sec. Ed., Butterworths, Washington, D. C., 1958.
$D(N\text{–}O)$ = 162 kcal. T. L. Cottrell, *ibid.*
$N(^2D)$ = 55 kcal. "Atomic Energy Levels," National Bureau of

If equations 1 and 2 represent predominant reactions, then the decomposition of nitric oxide[4] also would be expected to occur, since only 162 kcal. are required to break the N—O bond, and 225 kcal. are evolved when nitrogen atoms recombine. Reaction 2, however, probably accounts for only a small percentage of the total decomposition since nitric oxide was not decomposed in a similar system.

The reaction

$$\mathrm{N} + \mathrm{C_2H_6(W)} \longrightarrow \mathrm{NH} + \mathrm{C_2H_5} + 38\ \mathrm{kcal.} \quad (9)$$

could proceed quite readily with ^{2}D and other excited nitrogen atoms, but the low concentration of these species in active nitrogen precludes their importance in the reactions studied.[5,6]

Metastable $A^3\Sigma$ nitrogen molecules have been postulated[7,8] as the species in active nitrogen which is responsible for the destruction of ammonia in the gas phase and probably accounts for the major process by which ammonia and the hydrocarbons are decomposed at −196°. Ammonia and hydrogen cyanide then could be produced by reactions 4 to 9.

$$\mathrm{N_2(A^3\Sigma)} + \mathrm{C_2H_6(W)} \longrightarrow \mathrm{N_2(^1\Sigma)} + \mathrm{C_2H_5} + \mathrm{H} + 46\ \mathrm{kcal.} \quad (10)$$

Since cyanogen was found as a product in the reaction of active nitrogen with hydrogen cyanide, CN radicals must have been formed. Thus either reaction 11

$$\mathrm{HCN(W)} + \mathrm{N} + \mathrm{N} \longrightarrow \mathrm{CN} + \mathrm{H} + \mathrm{N_2} + 95\ \mathrm{kcal.} \quad (11)$$

or reaction 12

$$\mathrm{HCN} + \mathrm{N_2(A^3\Sigma)} \longrightarrow \mathrm{CN} + \mathrm{H} + \mathrm{N_2(^1\Sigma)} + 12\ \mathrm{kcal.} \quad (12)$$

probably occurs. The cyanogen then would be produced by coupling of CN radicals.

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D(N–H) = 87 kcal. G. Pannetier and A. G. Gaydon, *J. Chem. Phys.*, **48**, 221 (1951).

D(NH–H) = 90 kcal. A. P. Altschuller, *ibid.*, **22**, 1947 (1954).

D($\mathrm{NH_2}$–H) = 104 kcal. M. Swarcz, *Chem. Rev.*, **47,** 75 (1950).

$\mathrm{N_2(A^3\Sigma)}$ = 142 kcal. K. D. Bayes, *Can. J. Chem.*, **39**, 1074 (1961).

D(H–CN) = 130 kcal. L. Brewer and A. W. Searcy, *Ann. Rev. Phys. Chem.*, **7**, 259 (1956).

(4) E. R. Zabolotny and H. Gesser, *J. Chem. Phys.*, in press.

(5) H. P. Broida and O. S. Lutes, *ibid.*, **24**, 484 (1956).

(6) H. I. Schiff, *Ann. N. Y. Acad. Sci.*, **67**, 518 (1957).

(7) K. D. Bayes, *Can. J. Chem.*, **39**, 1074 (1961).

(8) R. L. Nelson, A. N. Wright and C. A. Winkler, Symposium on Some Fundamental Aspects of Atomic Reactions, Sept., 1960, McGill University, Montreal.

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The Photolysis of Carbon Suboxide. I. Reaction with Ethylene

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Carbon suboxide has been photolyzed in the presence of ethylene using the unfiltered radiation from a medium pressure mercury arc. The major products are allene, methylacetylene and carbon monoxide. In the limit of large ethylene to suboxide ratios, one mole of C_3H_4 is formed for every two moles of CO. The reactive intermediate is probably a CCO molecule. The intermediate can also react with carbon suboxide, resulting in polymer formation. The rate constant for the attack on suboxide is 1.4 times that for the attack on ethylene. It is suggested that if CCO is the reactive intermediate, it is formed initially in a low lying singlet state. The possible mechanisms which could yield two C_3H_4 isomers are discussed.

Introduction

The photolysis of carbon suboxide in the presence of an olefin results in a simple insertion of a carbon atom: *e.g.*, allene is formed from ethylene.[1] The nature of the reactive intermediate has not been established, but probably it is either a CCO molecule or a free carbon atom. Energy considerations, based on estimated heats of formation for carbon suboxide, favor the CCO molecule as the reactive intermediate.[2,3] Carbon atoms produced by nuclear transformations react with ethylene to give products different from those observed in the photolysis of carbon suboxide,[2] which further suggests that carbon atoms are not involved in the photolysis of carbon suboxide. The reaction with ethylene has been further studied in order to determine the nature of the reactive intermediate and the mechanism of attack on the hydrocarbon.

Experimental

The carbon suboxide was prepared by the low temperature dehydration of malonic acid.[4] After several bulb-to-bulb distillations, the suboxide was fractionated at reduced pressure on a Dry Ice–acetone cooled column, the middle third being collected and stored at liquid nitrogen temperature. The ultraviolet absorption spectrum was recorded on a Cary spectrometer, model 14, and is shown in Fig. 1. The spectrum shows the typical carbonyl band, with maximum absorption at 2650 Å., and part of the ethylenic absorption at shorter wave lengths. The intensity of the carbonyl absorption ($\epsilon_{\max}$ 94 liter/mole cm.) is stronger than in other ketenes,[5] probably due to conjugation effects. Further purification did not alter the absorption coefficients. The peak intensities of the mass spectrum of the purified suboxide, taken with a CEC model 21-081A mass spectrometer using 70-volt ionizing electrons, are given in Table I. In addition to a small amount of CO_2 (mass 44 equals 0.21), the following peaks, probably due to impurities, were observed: 23(0.04), 27(0.04), 32(0.04), 56(0.05).

Research grade ethylene from Phillips Petroleum Co. was used. After removing non-condensable gases, the only impurities observed were approximately 0.1% CO_2 and a trace of acetylene. Commercial samples of allene, methylacetylene and carbon monoxide were used to calibrate the gas chromatograph.

The irradiations took place in a cylindrical quartz cell 3 cm. i.d. and 20 cm. long. At room temperature (23°) some decomposition of the suboxide was observed even in the ab-

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(1) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(2) C. MacKay, P. Pollak, H. E. Rosenberg and R. Wolfgang, *ibid.*, **84**, 308 (1962).

(3) H. B. Palmer and T. J. Hirt, *ibid.*, **84**, 113 (1962).

(4) A. Klemenc, *Mh. Chem.*, **66**, 337 (1935); D. A. Long, F. S. Murfin and R. L. Williams, *Proc. Roy. Soc.* (*London*), **A223**, 251 (1954).

(5) G. B. Kistiakowsky and B. H. Mahan, *J. Am. Chem. Soc.*, **79**, 2112 (1957).