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The Reactions of the Nitrogen Atom with Ethylene and Ethylene-d_4

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Synopsis. In the N–C_2H_4 system, the main final product was HCN, and the stoichiometry (ΔN/HCN) of the reaction was about 1.3. In the N–C_2D_4 system, CD_2 and CD_2N were found as the reactive intermediates. We suggested a mechanism different from that proposed by Herron.

On the reaction of N with C_2H_4, the following reaction mechanism was postulated by Herron:[1)]

$$N + C_2H_4 \longrightarrow HCN + CH_3 \quad (1)$$

$$N + CH_3 \longrightarrow HCN + 2H \quad (2)$$

$$H + C_2H_4 \longrightarrow C_2H_5 \quad (3)$$

$$H + C_2H_5 \longrightarrow 2CH_3 \quad (4)$$

$$N + C_2H_5 \longrightarrow NH + C_2H_4 \quad (5)$$

$$N + NH \longrightarrow N_2 + H \quad (6)$$

The features of this mechanism are that the amount of CH_3 produced through the reaction depends on the competition between H and N for C_2H_5 and that the formation of HCN is mainly due to the reaction of N with CH_3. This list of reactions is not meant to be inclusive. For instance, it does not account for the recombination of CH_3 which proceeds with a rate constant of 3.6×10^{-11} ml/molecure·s.[2)] This rate is so fast that, in order to produce HCN in Reaction 2, the rate constant, k_{N-CH_3}, between N and CH_3 needs to have a value greater than 10^{-11} ml/molecule·s. The value of k_{N-CH_3} has not been evaluated experimentally; however, 10^{-11} ml/molecule·s for k_{N-CH_3} seems to be too large.

In order to define the intermediate compounds and to determine the reaction mechanism, the reactions of N with C_2H_4 and C_2D_4 were reinvestigated.

Experimental

The apparatus and procedure were almost the same as those used by Herron and Klein.[3)] N was generated by a 2450 MHz electrodeless discharge in N_2. A reaction tube of Pyrex glass, 20 mm i.d. and 100 cm long, formed a part of the fast-flow system. C_2H_4 and C_2D_4 diluted with Ar were added through a movable central inlet tube in the reaction tube. At the end of the reaction tube, the sampling orifice of a mass spectrometer was located. The mass spectra were recorded on a quadrupole mass spectrometer. The pressure in the reaction tube was about 4 Torr and the linear velocity of the gas was 200 cm/s. The materials used in this experiment were research-grade. The observation was carried out at room temperature. The initial concentration of N was measured by means of a gas-phase titration with NO.[4)] The HCN was determined by titration with $AgNO_3$. The reaction time was calculated from the linear velocity of the gas and from the distance between the tip of the inlet of the hydrocarbon reactants and the sampling orifice.

The quantities of reactants and products were followed by the ion current with ionization by 23 eV. As to the intermediate products, assuming that they had the same mass spectrometric sensitivity as N, the quantities were determined. The measurements were done in both the N–C_2H_4 and N–C_2D_4 systems.

Results and Discussion

Substracting the background ion current from the observed value in the reaction, the detectable species and their concentrations are determined. The atoms and free radicals investigated in these observations are as follows:

m/e	14	15	16	27	29	30	34
Species	N,CH_2	CH_3	CD_2	HCN	C_2H_5	CD_2N,C_2H_6	C_2D_5

In the N–C_2H_4 system, the quantities of species of *m/e* 14, 15 and 27 are plotted as functions of the reaction time. They are shown in Fig. 1. In this figure, the quantity of species of *m/e* 14 shows a maximum at the beginning of the reaction, and the maximum moves in the direction of the increase in the reaction time with the decrease in the initial concentration of C_2H_4. This fact suggests that CH_2 is formed in the course of the reaction. The quantities of species of *m/e* 15 and 29 produced through the reactions are small and about equal in amount. The species of *m/e* 30 is not found as a product. The stoichiometry of the reaction (ΔN/HCN) is evaluated to be about 1.3.

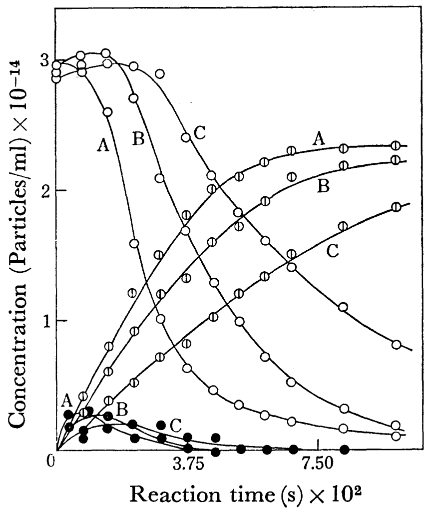

Fig. 1. Kinetics of the reaction of N with C_2H_4. ○: *m/e* 14, ⦶: *m/e* 27, ●: *m/e* 15.

Initial concentration

	$[N]_0\times10^{-14}$ atoms ml^{-1}	$[C_2H_4]_0\times10^{-14}$ molecules ml^{-1}
A	2.90	3.25
B	2.90	2.66
C	2·90	1.42

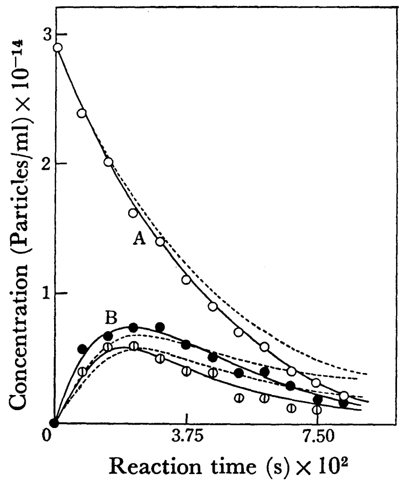

Fig. 2. Kinetics of the reaction of N with C_2D_4.
○: *m/e* 14, ●: *m/e* 16, ⦶: *m/e* 30.
Initial concentration
$[N]_0$: 2.90×10^{14} atoms ml^{-1},
$[C_2D_4]_0$: 2.66×10^{14} molecules ml^{-1}.
——: Experimental results, ……: calculated results.

As a supplementary method to determine the formation of CH_2, the reaction was studied in the N–C_2D_4 system. The results are shown in Fig. 2 in the same manner as in Fig. 1. In this case, the decrease in the quantity of the species of *m/e* 14 with the reaction time is shown by a monotonous curve, Curve A, and the concentrations of species of *m/e* 16 and 30 are varied with the time, having these maximum values in the course of the reaction, shown as Curve B. No species of *m/e* 34 was found.

At the same initial concentrations of reactions in the N–C_2H_4 and N–C_2D_4 systems, assuming that the quantity of N (*m/e* 14) in the N–C_2H_4 system represented as a function of the reaction time is equal to that in the N–C_2D_4 system, we can estimate the quantity of CH_2 produced in the N–C_2H_4 system. It is shown in Fig. 3. It is impossible, though, to measure the quantity of CH_2N produced in the reaction, because CH_2N has the same *m/e* value as N_2.

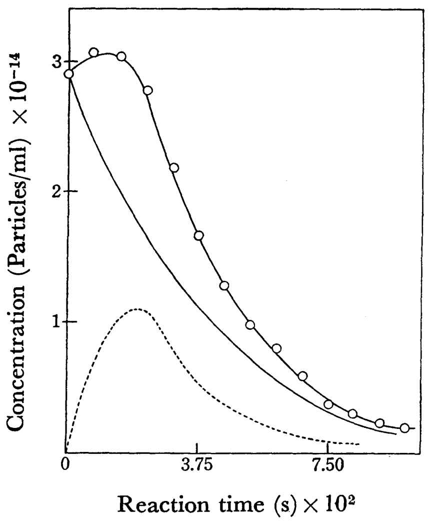

Fig. 3. Kinetics of the reaction of N with C_2H_4.
-○-: *m/e* 14, ——: *m/e* 14(N),
-----: *m/e* 14 (estimated value of CH_2).
Initial concentration
$[N]_0$: 2.90×10^{14} atoms ml^{-1},
$[C_2H_4]_0$: 2.66×10^{14} molecules ml^{-1}.

Comparing these results obtained in the N–C_2H_4 system with those in the N–C_2D_4 system, we can suggest that CH_2 and CH_2N are produced as intermediate compounds in the course of reactions in the N–C_2H_4 system.

In the N–C_2H_4 system, it seems possible that CH_2 and CH_2N might be formed at the beginning of the reaction:

$$N + C_2H_4 \longrightarrow CH_2 + CH_2N \quad (1)$$
$$N + CH_2 \longrightarrow CH_2N \quad (2)$$
$$CH_2N \longrightarrow HCN + H \quad (3)$$
$$N + CH_2N \longrightarrow N_2 + CH_2 \quad (4)$$
$$H + CH_2N \longrightarrow H_2 + HCN \quad (5)$$
$$CH_2 + CH_2 \longrightarrow C_2H_4 \quad (6)$$
$$N + N + M \longrightarrow N_2 + M \quad (7)$$
$$H + H + M \longrightarrow H_2 + M \quad (8)$$
$$CH_2 + \text{wall} \longrightarrow \frac{1}{2}C_2H_4 \quad (9)$$

In the N–C_2D_4 system, the reaction mechanism is almost the same as that considered in the N–C_2H_4 system. The main feature of the mechanism is the competition reaction between N and H for CH_2N in Steps 4 and 5. This competition roughly determines whether N will be detected as HCN or will remain undetected as N_2. An increase in the concentration of H would favor Reaction 5 relative to Reaction 4 and, hence, bring about a decrease in the ΔN/HCN ratio. It is known that the ΔN/HCN ratio approaches unity[1] with the introduction of H into the reactor.

Table 1. Evaluated rate constants in the N–C_2D_4 system (at room temperature)

Step	k ml molecule^{-1} s^{-1}	Step	k ml molecule^{-1} s^{-1}
1	1.0×10^{-13}	6	2.0×10^{-12}
2	5.0×10^{-14}	7	5.0×10^{-16}
3	6.0×10	8	5.0×10^{-16}
4	5.0×10^{-14}	9	3.0×10
5	1.0×10^{-14}		

In the N–C_2D_4 system, the rate constants are evaluated by a computer simulation of the experimental data. The rate constants for the reactions are listed in Table 1. With these values, the quantities of N, CD_2, and CD_2N are calculated as function of the reaction time. The results are shown by dotted lines in Fig. 2. The curves are seen to be identical within the limits of experimental uncertainty.

References

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