Reactions of Nitrogen Atom with Methane and with Ethylene

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Recent works on the reactions of nitrogen atom with methane and with ethylene have shown that these can not be discussed adequately by the simple mechanisms.[1] However, the appearent over-all rate constants of these reactions can be defined respectively as follows[2];

$$N + CH_4 \xrightarrow{k_1} HCN + 3/2 H_2 , \quad (1)$$

$$N + 1/2\, C_2H_4 \xrightarrow{k_2} HCN + 1/2 H_2 . \quad (2)$$

In this paper, we evaluate the values of k_1 and k_2 at room temperature from the measurements of decay rate of afterglow intensity in the mixture of nitrogen atom and a reactant.

Experimental

The investigations were made with conventional flow techniques.[3] The afterglow was monitored by an RCA 6217 photomultiplier tube. The nitrogen was activated by a microwave discharge. Only a few percent of nitrogen molecules were decomposed into nitrogen atoms. The reactant was introduced between the discharge and entry of the quartz observation tube. The afterglow intensity was observed at a selected level. The observed lights were in the regions of 1st and 2nd positive bands of the nitrogen molecule.

In order to take a picture of the decay rate of afterglow intensity a single sweep from a synchroscope was used.

The concentration of nitrogen atom at the observation level was determined by nitric oxide titration.

Results and Discussion

Rate of Recombination of Nitrogen Atom. For the reaction

$$N + N + N_2 \xrightarrow{k_3} N_2 + N_2 + h\nu , \quad (3)$$

the differential form of the rate equation is

$$-\frac{d[N]}{dt} = k_3[N]^2[N_2] .$$

It may be considered that the concentration of nitrogen keeps an approximately constant value through the reaction. In this case, if the concentration of nitrogen atom is equal to the half of its initial concentration, $a/2$, after time τ, the following equation is obtained:

$$k_3 = 1/[N_2]\tau a . \quad (4)$$

Table 1 lists values of [N] or a, τ, $[N_2]$, flow rate and evaluated value of k_3.

Rate Constant of Reaction of Nitrogen Atom with Methane. At room temperature, a few percent of methane reacts with nitrogen atom.[4] Hydrogen cyanide is the only product of the reaction obtained in measurable quantities.

For competitive reaction

$$N + N + N_2 \xrightarrow{k_3} N_2 + N_2 + h\nu , \quad (3)$$

$$N + CH_4 \xrightarrow{k_1} HCN + 3/2 H_2 , \quad (1)$$

the differential form of the rate equation is

$$-\frac{d(a-x)}{dt} = k_3[N_2](a-x)^2 + k_1[CH_4](a-x).$$

Since the concentrations of methane and nitrogen may be considered to keep an approximately constant values through the reaction, when t is τ, x is equal to $a/2$, the following equation is obtained;

1) P. A. Gartaganis and C. A. Winkler, *Can. J. Chem.*, **34**, 1457 (1956); J. T. Herron, *J. Phys. Chem.*, **69**, 2736 (1965).
2) D. A. Armstrong and V. A. Winkler, *Can. J. Chem.*, **33**, 1649 (1955).
3) M. A. A. Clyne and D. H. Stedman, *Trans. Faraday Soc.*, **62**, 2164 (1966).

TABLE 1. RATE DATA FOR THE EVALUATION OF RATE CONSTANT k_3

Flow rate cm/sec	$[N_2]\times 10^{-17}$ molecule/cc	$[N]\times 10^{-15}$ atom/cc	$\tau\times 10$ sec	$k_3\times 10^{32}$ cc^2/molecule^2 sec
		1 st positive band		
42	1.41	4.33	1.20	1.37
38	1.41	4.16	1.22	1.40
35	1.41	3.82	1.25	1.49
32	1.41	3.62	1.30	1.51
27	1.41	3.72	1.35	1.41
		2 nd positive band		
45	1.41	4.31	1.13	1.46
45	1.41	4.31	1.12	1.47
39	1.41	3.79	1.21	1.57
35	1.41	3.46	1.30	1.58
26	1.41	3.06	1.51	1.54

TABLE 2. RATE DATA FOR THE EVALUATION OF RATE CONSTANT k_1

Flow rate cm/sec	$[N_2]\times 10^{-17}$ molecule/cc	$[CH_4]\times 10^{-17}$ molecule/cc	$[N]\times 10^{-15}$ atom/cc	$\tau\times 10$ sec	$k_1\times 10^{16}$ cc/molecule sec
		1 st positive band			
51	1.04	0.37	1.77	1.08	1.07
47	1.12	0.29	2.16	1.10	1.21
40	1.09	0.32	2.00	1.17	1.05
33	1.04	0.37	1.92	1.30	0.84
29	1.18	0.23	2.32	1.35	1.09
		2 nd positive band			
47	1.11	0.29	3.02	0.56	2.72
42	1.25	0.15	3.62	0.78	2.95
38	1.16	0.24	3.02	0.76	2.12
33	1.04	0.37	2.60	0.75	1.54
27	1.24	0.17	3.15	1.09	1.79

TABLE 3. RATE DATA FOR THE EVALUATION OF RATE CONSTANT k_2

Flow rate cm/sec	$[N]\times 10^{-15}$ atom/cc	$[C_2H_4]\times 10^{-15}$ molecule/cc	$\tau\times 10^2$ sec	$k_2\times 10^{14}$ cc/molecule sec
		1 st positive band		
39	0.96	6.06	2.09	0.58
38	1.85	3.52	2.58	0.82
33	0.60	7.05	2.08	0.47
26	0.45	7.75	2.08	0.43
25	1.50	3.52	3.07	0.68
		2 nd positive band		
37	1.59	1.74	1.00	4.58
33	0.97	2.37	0.70	4.47
32	3.57	1.50	1.94	3.81
25	0.90	3.02	0.78	3.09
24	4.74	1.55	2.77	3.31

$$1+\frac{k_1[CH_4]}{a\,k_3([N_2]+[CH_4])}=\frac{1}{2(0.6723-k_1[CH_4]\tau)}\,. \qquad (5)$$

Inserting the observed values into Eq. (5), the rate constant k_1 is evaluated. The results are listed in Table 2.

Rate Constant of Reaction of Nitrogen Atom with Ethylene. In the reaction of nitrogen atom with ethylene, it is found that the reaction proceeds rapidly with a low activation energy and hydrogen cyanide is the only gas product.[4]

4) C. A. Winkler and H. I. Schiff, " The reactivity of free radical " General discussion of Faraday Society, 63 (1953).

TABLE 4. RATE CONSTANTS FOR SOME REACTIONS OF NITROGEN ATOM

Reaction	Rate constant	Reference
$N + N + N_2 \rightarrow N_2 + N_2$	1.5×10^{-32} cc^2/molecule^2 sec	5
	2.2×10^{-32} cc^2/molecule^2 sec	6
	$1.4-1.5 \times 10^{-32}$ cc^2/molecule^2 sec	This paper
$N + 1/2C_2H_4 \rightarrow HCN + 1/2H_2$	1.6×10^{-13} cc/molecule sec	7
	9.7×10^{-14} cc/molecule sec	8
	$2.4-0.8 \times 10^{-14}$ cc/molecule sec	9
	$3.8-0.6 \times 10^{-14}$ cc/molecule sec	This paper
$N + CH_4 \rightarrow HCN + 3/2H_2$	$1.0-2.2 \times 10^{-16}$ cc/molecule sec	This paper

For competitive reactions

$$N + N + N_2 \xrightarrow{k_3} N_2 + N_2 + h\nu\,,$$

$$N + \tfrac{1}{2}C_2H_4 \xrightarrow{k_2} HCN + \tfrac{1}{2}H_2\,,$$

it is quite plausible to assume that the rate of recombination of nitrogen atom is negligible, compared to the rate of reaction of nitrogen atom with ethylene. In this case, the following differential form of the rate equation is obtained;

$$-\frac{d(a-x)}{dt} = k_2(a-x)(b-x/2)$$

where b is the initial concentration of ethylene and $(b-x/2)$ is the concentration of ethylene at time t. From this equation, when t is τ, x is equal to $a/2$, the following equation is derived;

$$\frac{2}{(2b-a)} \ln \frac{4b-a}{2b} = k_2\tau\,. \qquad (6)$$

Table 3 lists the observed values and the evaluated value of k_2.

Our measured values of rate constants are listed in Table 4 along with the values measured by other workers. It is known that the results obtained in this paper are in agreement with them.

5) P. Harteck, R. R. Reeves and G. G. Manella, *J. Chem. Phys.*, **29**, 608 (1958).
6) K. M. Evenson and D. S. Burch, *ibid.*, **45**, 2450 (1966).
7) E. R. V. Milton and H. B. Dunford, *ibid.*, **34**, 51 (1961).
8) H. G. V. Evan, G. R. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).
9) J. Herron, *J. Phys. Chem.*, **70**, 2803 (1966).