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The Rate Constants of the Reactions of the Metastable Nitrogen Atoms, ^2D and ^2P, and the Reactions of $N(^4S)+NO \rightarrow N_2+O(^3P)$ and $O(^3P)+NO+M \rightarrow NO_2+M$

Ko-ichi Sugawara, Yo-ichi Ishikawa, and Shin Sato*
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The pulse-radiolysis technique was used for the measurement of the quenching rates of the metastable nitrogen atoms, ^2D and ^2P, both in nitrogen and in helium. The rate constants obtained for $N(^2D)$ were $(1.3\pm0.2)\times10^{-14}$ cm^3 molecule^{-1} s^{-1} (1 cm^3 molecule^{-1} s$^{-1}=6.022\times10^{17}$ m^3 mol^{-1} s^{-1}) in nitrogen and $(4.6\pm0.4)\times10^{-17}$ in helium; these values were larger than those for the higher energy metastable nitrogen atoms, $N(^2P)$, $(3.3\pm0.3)\times10^{-17}$ in nitrogen and $(4.2\pm1.3)\times10^{-18}$ in helium. The room temperature rate constants of the reactions of these atoms with nitrogen monoxide and with ethylene were also measured. All of these rate constants were found to be of the order of 3×10^{-11} cm^3 molecule^{-1} s^{-1}. The rate constants of the reactions, $N(^4S)+NO\rightarrow N_2+O(^3P)$ and $O(^3P)+NO+M\rightarrow NO_2+M$, were also measured and compared with literature values.

Recently we used a pulse-radiolysis technique combined with the resonance absorption method for the measurement of the rate constants of the reactions of the ground state-nitrogen atoms with several olefins.[1] In that experiment, we recognized that the metastable nitrogen atoms, ^2D and ^2P, generated together with the ground state-nitrogen atoms, ^4S, decayed very rapidly in a high pressure nitrogen gas. Since then, our technique was improved, so that the measurement of the reactions of these metastable atoms could be attempted.

The quenching of the metastable nitrogen atoms by simple molecules and atoms is attracting the attention of many researchers. This is not only because of their occurrence in discharge systems, but also because of the significant roles which these atoms play in the chemistry of the upper atmosphere.[2-7]

A number of investigations have been reported on the reaction of the NO-titration for $N(^4S)$ atoms.[8-22] Since our apparatus can easily be applied for the measurement of this reaction, we have measured the rate constants of the reactions of $N(^4S)+NO\rightarrow N_2+O(^3P)$ and $O(^3P)+NO+M\rightarrow NO_2+M$, where M stands for N_2 or He.

Experimental

The apparatus, the set-up of which is shown schematically in Fig. 1, has been described previously.[23] To measure the time dependence of the concentration of $N(^2D)$ and $N(^2P)$ atoms, the emission lines at around 149.3 and 174.3 nm, respectively, were used; these were excited in flowing He containing a trace of N_2. Although both lines consisted of fine structures (149.262, 149.267, and 149.467 for the $^2P_J\rightarrow{}^2D$ transition and 174.272, 174.273, 174.526, and 174.527 for the $^2P_J\rightarrow{}^2P$ transition), they were not resolved for the measurement of the concentration of the atoms. For $N(^4S)$ and $O(^3P)$ atoms, the resonace lines were used.[1,23]

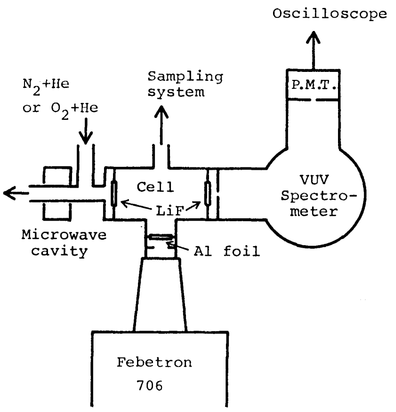

Fig. 1. Schematic diagram of the experimental apparatus. P.M.T., Photomultiplier.

Figures 2, 3, and 4 show the optical densities for $N(^2D)$, $N(^2P)$, and $N(^4S)$ atoms generated immediately after the irradiation of the high-energy electrons, the peak energy

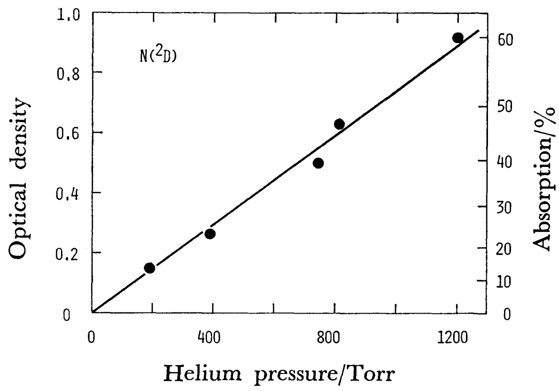

Fig. 2. The optical densities of $N(^2D)$ atoms generated immediately after the electron irradiation in the mixture of 2.0 Torr N_2 and He as a function of the He pressure.

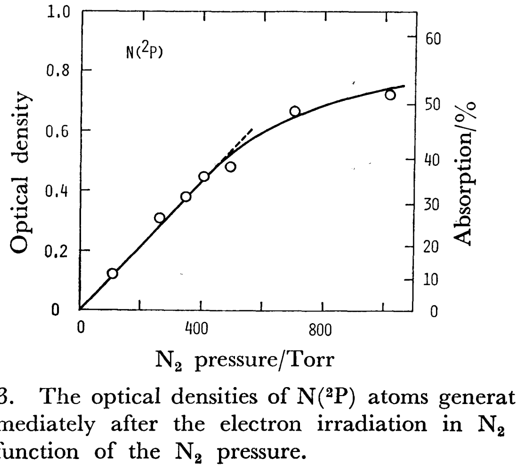

Fig. 3. The optical densities of $N(^2P)$ atoms generated immediately after the electron irradiation in N_2 as a function of the N_2 pressure.

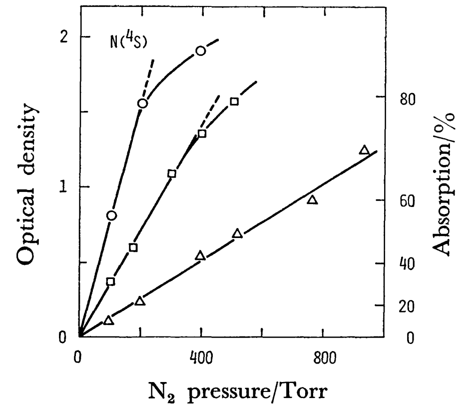

Fig. 4. The optical densities of $N(^4S)$ atoms generated immediately after the electron irradiation in N_2 as a function of the N_2 pressure. The d.c. charging voltages of Febetron 706 were set at 20 (△), 25 (□), and 28 (○) kV.

being 600 keV, from Febetron 706 as functions of the pressure of nitrogen or helium in the reaction cell. Since the penetration length of 600 keV-electrons is longer than 1 m in the atmosphere, probably most of the electrons ejected from Febetron 706 discharge at the wall of the reaction cell after having penetrated the reactant gas. Consequently, the energy transfer from the electrons to the gas should be proportional to the pressure of the gas in the cell.

The spectral lines used for the measurement of the optical densities of $N(^2P)$ and $N(^4S)$ atoms are not completely isolated from other spectral lines; therefore, some contamination could not be avoided. This is probably the reason for the apparent saturation of the optical densities for $N(^2P)$ and $N(^4S)$ atoms shown in Figs. 3 and 4. In the present experiments, optical densities less than 0.5 were always used for the measurement of the relative concentrations of atoms. Even if the light intensity of the contaminated spectral lines is 40%, the errors introduced in the estimation of the decay rate do not exceed 10%, since the first-order decay plots are always made in the optical density of 0.5—0.05.

The high-purity dried He (Nihon Helium Co.) and N_2 (Nihon Sanso Co.) were passed through traps filled with molecular sieve 4A at 77 K before use. The research grade NO and C_2H_4 (Takachiho Shoji Co.) were used without further purification.

Results

Figure 5 shows a typical example of the oscillograms obtained for the decay of $N(^2D)$ atoms in the mixture of He and N_2. The decay rate may be expressed as follows:

$$k = k_{He}[He] + k_{N_2}[N_2] + k_{dif}.$$

Here, k is the apparent decay rate, k_{He} and k_{N_2} are the rate constants of the quenching by He and N_2, and k_{dif} is the decay rate due to the diffusion of $N(^2D)$ atoms from the optical path. The last term may be ignored in the present experiment, since the k_{dif} value of the ground-state $N(^4S)$ atoms in N_2 at one atmosphere is only 0.3 s^{-1},[1] and k_{dif} is known to be roughly proportional to the reciprocal of the pressure of the solvent gas. In Fig. 6, the apparent decay rates are plotted as a function of the nitrogen pressure. The slope of this linear relation corresponds to the quenching rate constant of $N(^2D)$ atoms by N_2, while the intercept corresponds to the quenching rate by He at 800 Torr (1 Torr=133.3 Pa). Figure 7 shows the helium pressure-dependence of the quenching rate. The slope of this linear relation gives the quenching rate constant of $N(^2D)$ atoms by He.

Similar measurements were carried out for the decay rates of $N(^2P)$ atoms. Table 1 summarizes the quenching rate constants thus obtained, where the error limits are the standard deviation. It is noticeable

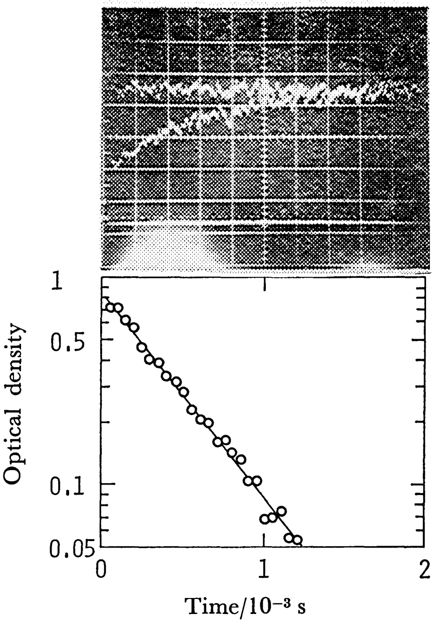

Fig. 5. The oscillogram and the first-order plot for the decay of $N(^2D)$ atoms in the mixture of 2.00 Torr N_2 and 1200 Torr He.

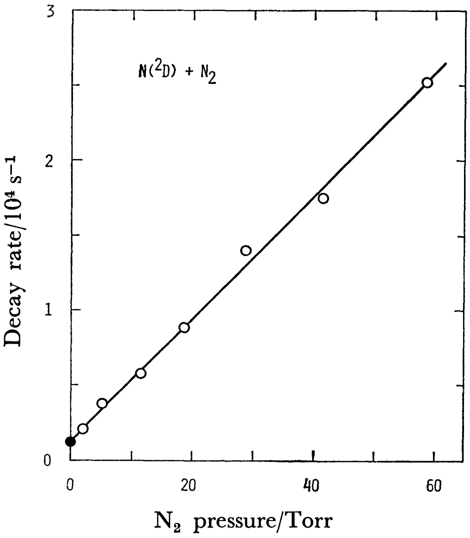

Fig. 6. The decay rates of $N(^2D)$ atoms in the mixture of 800 Torr He and N_2 as a function of the N_2 pressure. The filled circle corresponds to the quenching rate by He at 800 Torr, which has been calculated from the data shown in Fig. 7. This plot is not included for the estimation of the quenching rate constant by N_2.

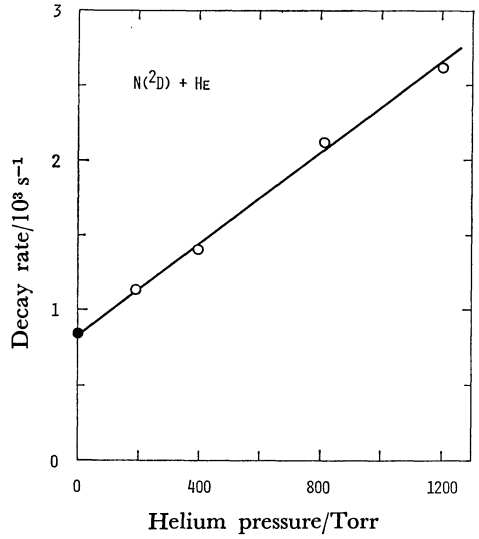

Fig. 7. The decay rates of N(^{2}D) atoms in the mixture of 2.0 Torr N_2 and He as a function of the He pressure. The filled circle corresponds to the quenching rate by N_2 at 2.0 Torr, which has been calculated from the data shown in Fig. 6. This plot is not included for the estimation of the quenching rate constant by He.

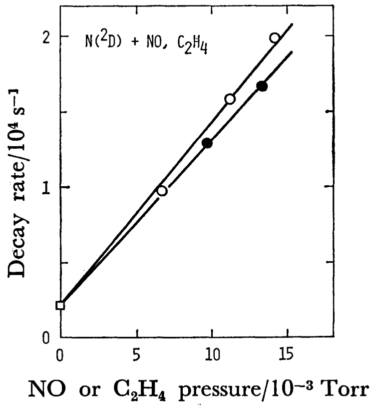

Fig. 8. The decay rates of N(^{2}D) atoms as functions of the NO (●) or C_2H_4 (○) pressure. The N_2 pressure is 2.0 Torr and the He pressure, 800 Torr.

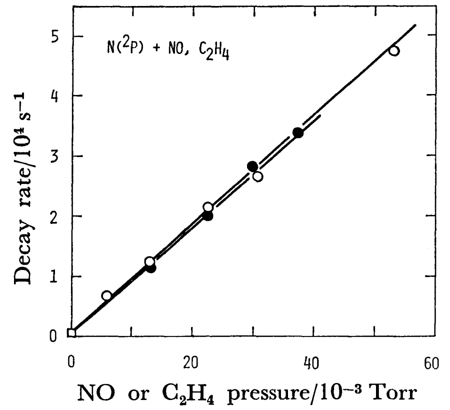

Fig. 9. The decay rates of N(^{2}P) atoms as functions of the NO (●) or C_2H_4 (○) pressure. The N_2 pressure is 700 Torr.

Table 1. Quenching rate constants of N(^{2}D) and N(^{2}P) in N_2 and in He at room temperature

	k/cm^3 molecule^{-1} s^{-1}		Ref.
	N(^{2}D)	N(^{2}P)	
N_2	$\leq 6\times10^{-15}$		2
	$(1.6\pm0.7)\times10^{-14}$		3
	$(2.3\pm1.1)\times10^{-14}$	$\leq 3\times10^{-16}$	4
	$(1.5\pm0.1)\times10^{-14}$	10^{-16}	5
	$(1.6\pm0.25)\times10^{-14}$		7
	$(1.3\pm0.2)\times10^{-14}$	$(3.3\pm0.3)\times10^{-17}$	This work[a]
He	$\leq 2\times10^{-16}$		2
	$\leq 1.6\times10^{-16}$		3
	$(4.6\pm0.4)\times10^{-17}$	$(4.2\pm1.3)\times10^{-18}$	This work[a]

a) 298±2 K.

Table 2. Rate constants of the reactions of N(^{2}D) and N(^{2}P) with NO and C_2H_4 at room temperature

	k/10^{-11} cm^3 molecule^{-1} s^{-1}		Ref.
	N(^{2}D)	N(^{2}P)	
NO	18±5		2
	7±2.5		3
	6.1±3.7	3.4±1.1	4
	5.9±0.4	3.2±0.1	5
		2.8±0.6	6
	3.5±0.3	2.7±0.2	This work[a]
C_2H_4	12±3		2
	3.7±0.3	2.8±0.2	This work[a]

a) 298±2 K.

that the ^{2}P state, which is higher than the ^{2}D state by 1.20 eV, is quenched more slowly than the ^{2}D state. Since the energy level of the ^{2}P state is higher than that of the ^{2}D state, the quenching of the ^{2}P state might produce the ^{2}D state; therefore, we carefully observed the decay of the ^{2}D state in the long time-range. But no indication of the production of the ^{2}D state by the quenching of the ^{2}P state could be observed in any case.

When a small amount of NO or C_2H_4 was added in the systems studied above, the rapid decays of both metastable states could be observed. The experimental results are shown in Figs. 8 and 9, and the quenching rate constants calculated from these figures are summarized in Table 2. The four rate constants are all of the order of 3×10^{-11} cm^3 molecule^{-1} s^{-1}. About a quarter of all collisions are efficient for the quenching.

Among the reactions of the ground state-nitrogen atoms with molecules, the reaction with nitrogen monoxide has been well established. In order to ascertain whether our apparatus works properly, we have measured the rate constant of this reaction. Figure 10 shows one of the combined oscillograms; one of the traces is for the decay of N(^{4}S) atoms and the other for the formation and decay of O(^{3}P) atoms. The measurement of the concentration of the O(^{3}P)

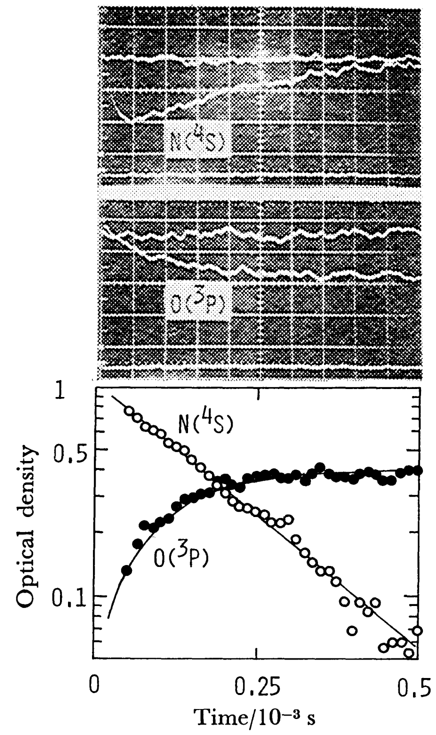

Fig. 10. The oscillograms and the plots of the logarithm of the optical densities for the decay of N(^{4}S) atoms and for the formation and decay of O(^{3}P) atoms. The NO pressure is 10.5 mTorr and the N_2 pressure, 198 Torr.

atoms has been discussed previously.[23] These traces correspond to the following reactions:

$$N(^4S) + NO \longrightarrow N_2 + O(^3P), \qquad (1)$$

$$O(^3P) + NO + N_2 \longrightarrow NO_2 + N_2. \qquad (2)$$

The solid curve for the time dependence of the concentration of O(^{3}P) atoms was calculated by using the rate constants obtained below.

According to Reactions 1 and 2, the time dependence of the concentration of O(^{3}P) atoms should be expressed as follows:

$$I_t = I_0[\exp(-k_2[NO][N_2]t) - \exp(-k_1[NO]t)].$$

Here, I_t is the time dependent variable proportional to the concentration of O(^{3}P) atoms, I_0 is a constant, k_1 and k_2 are the rate constants of Reactions 1 and 2, and [NO] and [N_2] are the concentrations of NO and N_2. When the solid curve for the O(^{3}P) atoms shown in Fig. 10 was drawn by substituting the rate constants into the above equation, the constant I_0 was adjusted so as to fit the plot obtained at 0.50 ms.

Figure 11 shows the decay rates of N(^{4}S) atoms as a function of the NO pressure. Here, three different nitrogen pressures and two different charging voltages of Febetron 706 were used; however, as shown in Fig. 11, all the decay rates obtained gave a consistent value. From this linear plot, the rate constant of Reaction 1 was estimated. In this estimation, the reaction of N(^{4}S) atoms with NO_2, which is the product of Reaction 2, was ignored, since the reaction of N+NO_2 is known to be slower than that of N+NO ($k(N+NO_2) = (1.4\pm0.2)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}),[13] and the concentration of NO_2 produced does not exceed 5% of that of NO. Table 3 compares the present result with those previously reported.

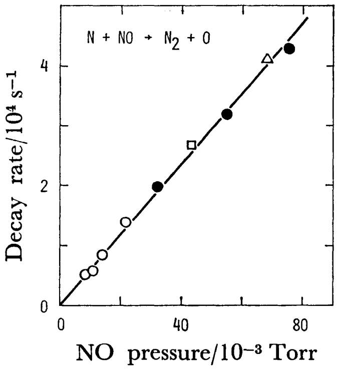

Fig. 11. The decay rates of N(^{4}S) atoms as a function of the NO pressure. The N_2 pressures are 200 (□), 600 (○,●), and 1000 (△) Torr. The filled symbols denote 20 kV for the d.c. charging voltage of Febetron 706, while the open symbols, 25 kV.

Table 3. Rate constant of the reaction of $N+NO \rightarrow N_2+O$ at room temperature

Author[a]	Method[b]	Pressure/Torr	$k/10^{-11}$ cm^3 s^{-1}
CT	DF/CL	1.5—6.5	3.6[c]
H	DF/MS	0.33—0.87	1.7±0.8
PS	DF/MS	0.026—0.31	2.2±0.6
LPK	DF/RA	1.1—2.7	3±1
CM	DF/MS	≤5	2.2±0.2
LMPS	DF/RF	1.12—2.61	2.7±0.4
LMPS	FP/RF	20—70	4.0±0.2
This work[d]	PR/RA	200—1000	1.9±0.2

a) CT: Clyne and Thrush, Refs. 8 and 9; H: Herron, Ref. 10; PS: Phillips and Schiff, Ref. 11; LPK: Lin, Parkes, and Kaufman, Ref. 12; CM: Clyne and McDermid, Ref. 13; LMPS: Lee, Michael, Payne, and Stief, Ref. 14. b) DF: Discharge flow; CL: chemiluminescence; MS: mass spectrometry; RA: resonance absorption; RF: resonance fluorescence; FP: flash photolysis; PR: pulse radiolysis. c) Calculated from the Arrhenius expression. d) 298±2 K.

Since Reactions 2 and 3 were much slower than Reaction 1 under the conditions of the present experiments,

$$O(^3P) + NO + He \longrightarrow NO_2 + He, \qquad (3)$$

the concentration of NO was increased in the measurement of the rate constants of Reactions 2 and 3. In the time-range used for the measurement of the data shown in Figs. 12 and 13, Reaction 1 is already finished.

Figure 12 shows the decay rates of O(^{3}P) atoms as functions of the pressures of NO and N_2. From these two linear relations, the rate constant of Reaction 2 can be derived. It is known that the rate constant of the reaction between O(^{3}P) and NO_2 is comparable to that of Reaction 1 ($k(O+NO_2) = (9.5\pm1.1)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}).[24] Consequently, the NO_2 produced in Reaction 2 might disturb the estimation of the rate constant of Reaction 2. However, as will be shown later, the concentration of NO_2 produced cannot exceed 2×10^{13} molecules cm^{-3}; therefore, the

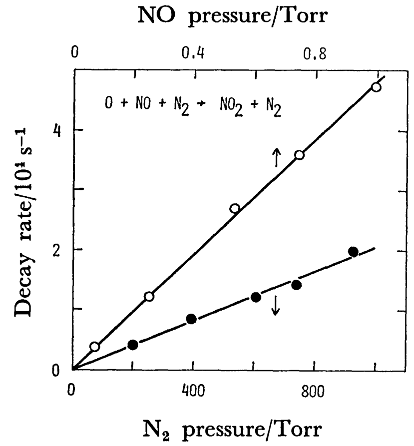

Fig. 12. The decay rates of O(^{3}P) atoms as functions of the NO (○) or N_2 (●) pressure. When the NO pressure was varied, the N_2 pressure was fixed at 600 Torr, while when the N_2 pressure was varied, the NO pressure was fixed at 0.25 Torr.

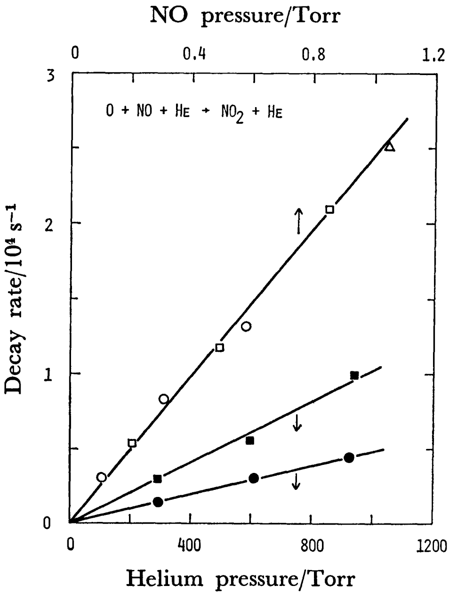

Fig. 13. The decay rates of O(^{3}P) atoms as functions of the NO or He pressure. The symbols, ○ and ● stand for the mixture of 2.0 Torr O_2, He, and NO; □ and ■ for the mixture of 10 Torr N_2, He, and NO; △ for the mixture of NO and He. The open symbols denote that the He pressure is 600 Torr, while the filled ones denote that the NO pressures are fixed at 0.10 (●) and 0.20 (■) Torr.

disappearance of O(^{3}P) atoms due to the reaction with NO_2 is less than 10% of that due to Reaction 2, even if the reactant gas consists of 0.25 Torr NO and 200 Torr N_2.

Figure 13 shows the experimental results which can be used for the estimation of the rate constant of Reaction 3. In order to establish the rate constant, various experimental conditions were used, as stated in the figure caption. In six measurements, oxygen was used as the source of oxygen atoms. Since NO is reactive with O_2, the experiments were performed immediately after the mixture of O_2 and He was introduced in the reaction cell containing a known amount of NO.

TABLE 4. RATE CONSTANTS OF THE REACTIONS OF $O+NO+M \rightarrow NO_2+M$ ($M=N_2$, He) AT ROOM TFMPERATURE

Author[a)]	Method[b)]	Pressure/Torr	$k/10^{-32}$ cm^6 s^{-1}
	$O+NO+N_2 \rightarrow NO_2+N_2$		
KV	DF/MS	~2	13
FE	P/PA		5.0
K	DF/CL	~0.5	6.9
CT	DF/CL	2	8.6±1.2
KH	DF/MS	2—3	10.3±0.4
This work[c)]	PR/RA	200—1000	7.7±0.5
	$O+NO+He \rightarrow NO_2+He$		
OS	DF/IC	1.21—3.21	5.10±0.28
CT	DF/CL	2	5.0±0.9
SN	FP/CL	~10	6.7±1.4
SN	FP/CL	0.3—31	6.65±0.67
This work[c)]	PR/RA	300—1000	4.2±0.5

a) KV: Kistiakowsky and Volpi, Ref. 15; FE: Ford and Endow, Ref. 16; K: Kaufman, Ref. 17; CT: Clyne and Thrush, Ref. 18; KH: Klein and Herron, Ref. 19; OS: Ogryzlo and Schiff, Ref. 20; SN: Stuhl and Niki, Refs. 21 and 22. b) P: photolysis; PA: product analysis; IC: isothermal calorimetry. c) 298±2 K.

The apparent decay rate of O(^{3}P) atoms in this case may be expressed as follows:

$$k = k_{NO}[NO][M] + k_{O_2}[O_2][M].$$

Here, k_{NO} and k_{O_2} are the rate constants of the third-order reactions for the disappearance of O(^{3}P) atoms, and $[M]=[He]+[NO]+[O_2]$. Since the He pressure is much higher than those of NO and O_2, the following equations may hold: $[M]=[He]$, $k_{NO}=k_3$, and $k_{O_2}=k_4$.

$$O(^3P) + O_2 + He \longrightarrow O_3 + He. \qquad (4)$$

Using the rate constant of Reaction 4, which was determined in the previous paper,[23)] the decay rate due to Reaction 3 can be estimated. These calculated results are plotted in Fig. 13. All the data obtained under different experimental conditions were found to be consistent with each other. The rate constants calculated from the slopes of the linear relations shown in Figs. 12 and 13 are compared with previous measurements in Table 4.

Discussion

In the previous paper,[23)] we estimated the initial concentration of oxygen atoms generated in the mixture of 3 Torr oxygen and 900 Torr He to be about 3×10^{13} molecules cm^{-3}, when the d.c. charging voltage of Febetron 706 was set at 25 kV. In that calculation, the *G*-value of oxygen atoms was assumed to be 12.8. According to a theoretical calculation,[25)] the *G*-value of nitrogen atoms under similar conditions is about 9; therefore, the initial concentration of nitrogen atoms at 25 kV of the d.c. charging voltage may be in the order of 2×10^{13} molecules cm^{-3}. The concentration of nitrogen atoms is not so high that the quenching of the metastable N(^{2}D) and N(^{2}P) atoms by N(^{4}S) atoms may be ignored. If the quenching by $N(^4S)$ atoms is an important process, the decay rates shown in Figs. 6 and 7 should not be linearly dependent upon the pressure of the solvent gas.

As Table 1 shows, the $N(^2D)$ atoms are quenched by N_2 or He more easily than the higher state $N(^2P)$ atoms, while it is known that the radiative lifetime of $N(^2D)$ is longer than that of $N(^2P)$.[26] Such a reverse order can also be found between $O(^1D)$ and $O(^1S)$ atoms.[27] The quenching rate constants for the metastable oxygen atoms, however, are generally much larger than those for the metastable nitrogen atoms.

The rate constants of the reactions of $N(^2D)$ and $N(^2P)$ with NO and C_2H_4 obtained in the present experiments are a little smaller than those reported previously. One possible reason is that some other reactions contaminate the process; they might participate in the formation of $N(^2D)$ and $N(^2P)$ atoms in the present system. The neutralization reactions such as $N^+ + e^- + M \rightarrow N(^2D \text{ or } ^2P) + M$, however, may be ignored, since the time-range used for the measurement of $N(^2D)$ and $N(^2P)$ atoms is 20 μs–10 ms, while it is believed that the neutralization is completed within 10 μs.[28] If the metastable states higher than ^2P state are produced and if they are quenched to the ^2D and ^2P states in the time-range of ms, the discrepancy stated above may be explained, but it is difficult to imagine that the irradiation of high energy electrons is considerably different from the microwave discharge, which was used by previous investigations in producing the metastable atoms.

The rate constant obtained for the reaction $N(^4S) + NO \rightarrow N_2 + O(^3P)$ is in good agreement with the literature value. Since the rate constant of this reaction is comparable to those of the quenching reactions of $N(^2D)$ and $N(^2P)$ atoms by NO, the following reactions might affect the estimation of k_1:

$$N(^2D \text{ or } ^2P) + NO \longrightarrow N_2 + O \qquad (5)$$

$$\longrightarrow N(^4S) + NO. \qquad (6)$$

In the present experiments, we can measure only the time dependence of the relative concentrations of N or O atoms, but not the absolute concentrations; therefore, we cannot eliminate the possibility of the participation of Reaction 6 in the formation of $N(^4S)$ atoms. If Reaction 6 is a predominant process compared to Reaction 5, the data shown in Table 3, probably including the results reported from other investigations, need serious corrections. Further studies are obviously necessary.

As Fig. 11 shows, the initial concentration of $N(^4S)$ atoms, which is controlled by the charging voltage of Febetron 706, does not affect the observed rate constant; this fact seems to suggest that the active species such as $N_2(^3\Sigma_u^+)$ state produced by the pulse-irradiation have no effect on the reaction between $N(^4S)$ and NO.

The reaction between $O(^3P)$ atoms and NO is important in the chemistry of the atmosphere. So far, the rate constant of this famous third-order reaction has been measured mainly at low pressures. It may be worthwhile to mention that the present result, which was obtained at higher pressures, is in good agreement with the values obtained at low pressures. In other words, the reaction between $O(^3P)$ atoms and NO does not reach its high pressure limit even at 1000 Torr.

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