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Reactions of NH Radicals. I. Photolysis of HN_3 Vapor at 313 nm

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Photolysis of HN_3 vapor was studied at 313 nm as a function of HN_3 and Xe pressures, light intensity, and temperature. The photolysis of hydrazoic acid labeled with ^{15}N was also studied. The quantum yields of N_2, H_2, and NH_4N_3 as a product were 4.85, 0.494, and 0.842 at 30 °C and 6.7 kPa of HN_3, respectively. The mechanism for the main reactions was postulated as follows: $HN_3+h\nu(313\text{ nm})\rightarrow N_2+NH(a^1\Delta)$; $NH(a^1\Delta)+HN_3\rightarrow 2N_2+2H$ (2); $NH(a^1\Delta)+HN_3\rightarrow N_3+NH_2$ (3); $NH(a^1\Delta)+HN_3\rightarrow N_2+N_2H_2{}^*$ (4). The rate constant ratios of $k_3/k_2=0.746$ and $k_4/k_2=1.23$ were obtained at 30°C. $(k_3+k_4)/k_2$ decrease drastically with rising temperature. Xe is effective for the collisional deactivation, $NH(a^1\Delta)+Xe\rightarrow NH(X^3\Sigma^-)+Xe$ (15), and $k_{15}/(k_2+k_3+k_4)=0.187$ was obtained at 30 °C.

In order to study the reactions of various reactants with $NH(X^3\Sigma^-$ and $a^1\Delta)$ radicals that are in the same isoelectronic state as carbon, oxygen, and sulfur atoms and CH_2, SiH_2, and PH radicals, hydrazoic acid was chosen as a photochemical radical source.

The photolysis of HN_3 vapor at about 190 nm[1] and the mercury-photosensitized decomposition[2] were first investigated by Beckman and his co-workers. On the basis that the products are N_2, H_2, and NH_4N_3, and the quantum yield for the disappearance of HN_3 is about 3.6 in both cases, they have presented the following mechanism:

$$HN_3 + h\nu(\text{or Hg}^*) \longrightarrow NH + N_2$$
$$NH + HN_3 \longrightarrow H_2 + 2N_2 \quad (18\%)$$
$$NH + HN_3 \longrightarrow N_2H_2 + N_2 \quad (82\%)$$
$$N_2H_2 + HN_3 \longrightarrow NH_3 + 2N_2$$
$$NH_3 + HN_3 \longrightarrow NH_4N_3.$$

Thrush[3] has proposed the following mechanism from the identifications of NH, NH_2, and N_3 radicals in flash photolysis:

$$HN_3 + h\nu \longrightarrow NH + N_2$$
$$NH + HN_3 \longrightarrow NH_2 + N_3$$
$$NH_2 + HN_3 \longrightarrow NH_3 + N_3$$
$$N_3 + N_3 \longrightarrow 3N_2.$$

On the photolysis of HN_3 vapor in the vacuum-ultraviolet, Welge[4] has observed that $NH(c^1\Pi)$ and $NH(A^3\Pi_i)$ are produced below 160 nm. Okabe[5] has shown that the yield of the $NH(c^1\Pi)$ production is at most 2%, and $NH(A^3\Pi_i)$ may be formed largely by the reaction of electronically excited N_2, most probably $N_2(B^3\Pi_g)$, with HN_3.

Konar, Matsumoto, and Darwent[6] have investigated the photochemical decomposition of HN_3 at 214 nm, and reported that the primary processes are

$$HN_3 + h\nu(214\text{ nm}) \longrightarrow {}^1NH' + N_2' \quad (95\text{—}97\%)$$
$$\longrightarrow H + N_3 \quad (3\text{—}5\%)$$

and the vibrationally excited $^1NH'$ and N'_2 are capable of causig further decomposition of HN_3.

Paur and Bair[7,8] have studied the flash photolysis of HN_3 by coordinated time-resolved spectroscopic measurements of HN_3, $NH(a^1\Delta)$, $NH(X^3\Sigma^-)$, $NH(c^1\Pi)$, $NH(A^3\Pi)$, NH_2, and N_3. They have reported that the major reactive product is $NH(a^1\Delta)$ or states which quickly decay to $NH(a^1\Delta)$ above 200 nm. Disappearance of $NH(a^1\Delta)$ occurs predominantly by the process

$$NH(a^1\Delta) + HN_3 \longrightarrow NH_2 + N_3$$

with a rate constant of 9.3×10^{-11} cm³ molecule⁻¹ s⁻¹.[8]

Recently, Piper *et al.*[9] have studied the UV photolysis of HN_3 by observing the time dependent decay in the number density of the $NH(a^1\Delta)$ product following photolysis at about 290 nm. They have obtained 18×10^{-11} cm³ molecule⁻¹ s⁻¹ as a rate constant for the reaction

$$NH(a^1\Delta) + HN_3 \longrightarrow NH_2(\tilde{A}^2A_1) + N_3.$$

They also obtained 9.3×10^{-11} cm³ molecule⁻¹ s⁻¹ as a specific rate for the reaction of $NH_2(\tilde{A}^2A_1)$ with HN_3.

Although the photolysis of HN_3 has been investigated intensively, as cited above, the quantitative mechanism is not clear. Notably, the reaction mechanisms at short wavelengths are more complex than those at long wavelengths because of the appearance of highly excited species. On the other hand, an absorption edge on the longest absorption band of HN_3 is located at about 310 nm,[10] and the formation of the first excited singlet $NH(a^1\Delta)$ can be expected at this wavelength. Thus, the photolysis of HN_3 vapor at 313 nm had been carried out in this work, before the studies of reactions of $NH(a^1\Delta$ and $X^3\Sigma^-)$ with various reactants.

Experimental

Materials. Hydrazoic acid was prepared from the reaction of NaN_3 with sulfuric acid (H_2SO_4: $H_2O=1:2$ in volume ratio) at room temperature, dried by passing through columns packed with $CaCl_2$ and P_2O_5, and stored below a half atm in a reservoir protected from light to avoid explosion.

The UV absorption of HN_3 of 14.3 kPa at 25.7 °C was observed at wavelengths longer than 220 nm. The molecular extinction coefficients calculated from $\log_{10}(I/I_0)=-\varepsilon cl$ are illustrated in Fig. 1, and are slightly higher than those measured by McDonald and co-workers.[10] In the infrared region, two absorption peaks appear at 1.54 ($\varepsilon_{max}=1.79$) and 2.36 μm ($\varepsilon_{max}=1.34$ dm³ mol⁻¹ cm⁻¹). The former peak has been found in the spectrum of frozen HN_3.[11]

To elucidate the mechanism the photolysis was also carried out with hydrazoic acid labeled with nitrogen-15. For this purpose, potassium azide labeled with ^{15}N at the third nitrogen atom to the extent of 97% was obtained from Isomet Co. The hydrazoic acid was prepared from the azide in the same way

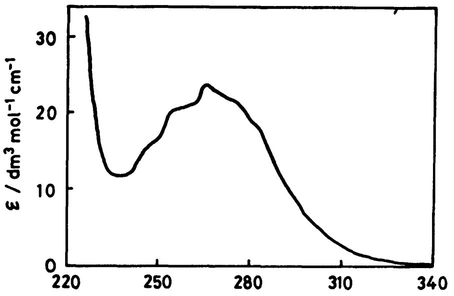

Fig. 1. UV absorption spectrum of HN_3 vapor.

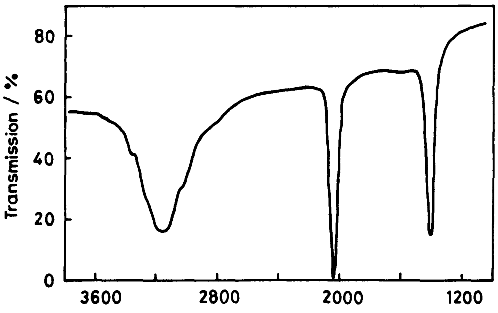

Fig. 2. Infrared spectrum of the white volatile powder condensed at the Dry Ice–acetone temperature.

as described above. It was presumably labeled at the first and third nitrogen atoms with the same probability, since the formation was due to the ionic processes:[12] $KNN^{15}N \xrightarrow{(H_2O)} K^+ + {}^{15}NNN^-$; $H^{15}NNN \longleftarrow H^+ + {}^{15}NNN^- \longrightarrow HNN^{15}N$.

Xe was obtained from Takachiho Chemical Co., and purified by vacuum distillation at liquid nitrogen temperature.

Apparatus. The photolysis was carried out at 313 nm obtained from a high pressure mercury lamp (Toshiba, SHL-100UV) of 100 W. As a filter for 313 nm, UV-D2 (Toshiba) was used. The light intensity was controlled by inserting screens between the light source and the reaction cell. The reaction cell was a quartz cylinder of 5.0 cm inner diameter and 10 cm length, with a volume of 196 cm³. It was inserted in an electric furnace to maintain a fixed temperature.

Procedure. Hydrazoic acid was purified each time before use by condensation and evacuation at −120 °C and at Dry Ice–acetone temperature, introduced into the reaction cell, and exposed to the light. The irradiation time was usually 20 min. The degree of conversion of HN_3, calculated from the relation[13] $(2[N_2]+4[NH_4N_3])/3[HN_3]_0$, was less than 7% for all runs except 12.8% at the lowest pressure (0.787 kPa).

The reaction products were only N_2, H_2, and NH_4N_3. The formation of NH_4N_3 was first reported by Beckman and Dickenson,[1] and was further confirmed by infrared spectroscopy in this work. The spectrum observed by the KBr method for the white volatile powder condensed at Dry Ice–acetone temperature is shown in Fig. 2, and is in accord with the main three peaks in the spectrum of solid NH_4N_3 at 90 K.[14] The formation of hydrazinium azide ($N_2H_5N_3$) is ruled out judging from the infrared spectrum of hydrazine vapor.[15]

Noncondensable gases (N_2 and H_2) at the liquid nitrogen temperature were introduced into a column of silica gel[16] (for gas chromatography) at −196 °C. Hydrogen was passing through the column and collected in a Toepler gauge, and its amount was determined. Nitrogen, trapped on silica gel at −196 °C, was collected in the gauge by warming the column, and its amount was also determined.

The following method was used for the quantitative analysis of NH_4N_3: Unconverted HN_3 was removed by evacuating at Dry Ice–acetone temperature. Ammonium azide, trapped at −78 °C, was warmed, introduced into a CuO column and burnt at about 550 °C. N_2, NO, N_2O, and H_2O were separated as combustion products[17] at −210, −196, and −110 °C, respectively. The amounts of N_2, NO, and N_2O were in turn determined by the Toepler gauge. The amount of NH_4N_3 was calculated from the equation, $NH_4N_3 = (N_2+N_2O)/2 + NO/4$. The expectation amount of NH_4N_3 can be estimated by the equation[18] $NH_4N_3 = N_2/4 - 3H_2/4$, and agreement between the experimental and expected amounts was very good.

The photolysis of HN_3 in the presence of Xe was also carried out by the same procedure.

Determination of Quantum Yield. Acetone was used as an actinometer, since the quantum yield of CO in photolysis of acetone at 313 nm is almost unity above 100 °C.[19] The quantum yield of nitrogen formation was 4.85 as an average value of three experiments at 30 °C, 313 nm, and 6.7 kPa of HN_3. The other quantum yields were calculated on the basis of the value for N_2.

Determination of Isotopic Composition. The isotopic composition of nitrogen formed in the photolysis of hydrazoic acid labeled by ^{15}N was analyzed by a mass spectrometer (Hitachi, RUM-5). The content of ^{15}N in NH_4N_3 was also determined by the mass spectrometric analysis of isotopic N_2, NO, and N_2O produced by the combustion.

Results

The results for photolysis of HN_3 of 6.7 kPa, measured as a function of the absorbed light intensity at 313 nm and 30 °C are shown in Fig. 3. It is found in Fig. 3 that the quantum yields, ϕ_{N_2}, ϕ_{H_2}, and $\phi_{NH_4N_3}$, are independent of the light intensity. The average values of ϕ_{N_2}, ϕ_{H_2}, and $\phi_{NH_4N_3}$ were 4.85, 0.494, and 0.842, respectively.

Figure 4 shows the results of photolysis, measured as a function of HN_3 pressure at 313 nm, 30 °C, and the incident light intensity of 2.0×10^{16} quanta s⁻¹. It is

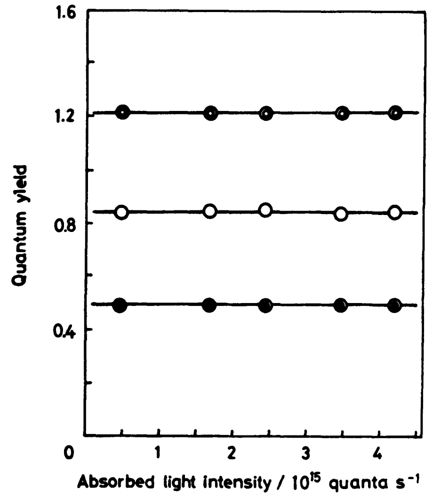

Fig. 3. Results of the photolysis of HN_3 of 6.7 kPa, measured as a function of the absorbed light intensity at 313 nm and 30 °C. ◎, $\phi_{N_2}/4$; ○, $\phi_{NH_4N_3}$; ⊙, ϕ_{H_2}.

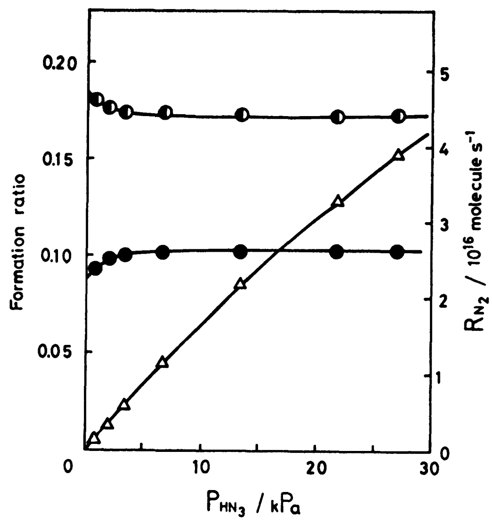

Fig. 4. Results of the photolysis, measured as a function of HN_3 pressure at 30 °C, 313 nm, and the incident light intensity of 2.0×10^{16} quanta s^{-1}. ◐, NH_4N_3/N_2; ●, H_2/N_2; △, R_{N_2}.

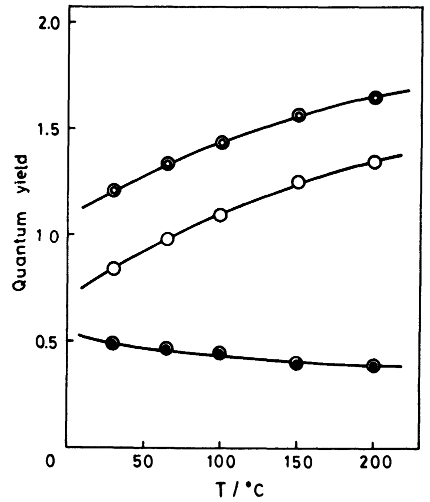

Fig. 5. Temperature dependence on the photolysis of HN_3 of 2.64 mmol dm^{-3} at 313 nm and the incident light intensity of 2.0×10^{16} quanta s^{-1}. ◎, $\phi_{N_2}/4$; ○, $\phi_{NH_4N_3}$; ⊙, ϕ_{H_2}.

seen in Fig. 4 that the relation of R_{N_2}, formation rate of N_2, *versus* P_{HN_3} changes slightly as is anticipated from Berr's law, H_2/N_2 decreases with lowering of the pressure, and NH_4N_3/N_2 increases in contrast with H_2/N_2.

The thermal decomposition of HN_3 has been studied at about 380[20] and 1000 °C,[21,22] but no decomposition was detected at least up to 200 °C in our system. Figure 5 shows the temperature dependence on the photolysis of HN_3 of 2.64×10^{-3} mol dm^{-3} (6.7 kPa at 30 °C) at 313 nm and the incident light intensity of 2.0×10^{16} quanta s^{-1}, where the quantum yields were estimated by assuming that the molecular extinction coefficient of HN_3 is independent of temperature. It is seen in Fig. 5 that ϕ_{N_2} and $\phi_{NH_4N_3}$ increase, but ϕ_{H_2} decreases with increase in temperature.

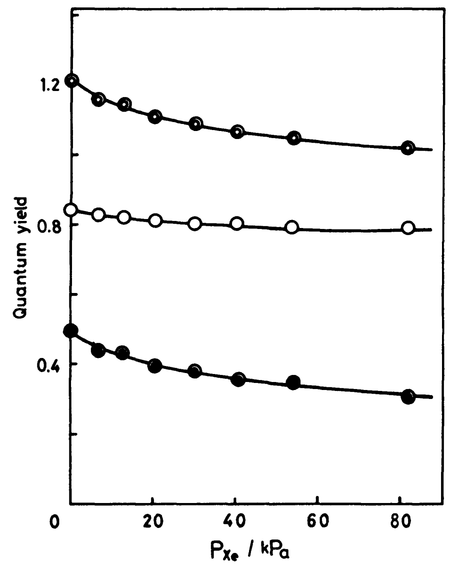

Fig. 6. Results of the photolysis of HN_3 of 6.7 kPa, measured as a function of Xe pressure at 313 nm, 30 °C, and the absorbed light intensity of 3.2×10^{15} quanta s^{-1}. ◎, $\phi_{N_2}/4$; ○, $\phi_{NH_4N_3}$; ⊙ ϕ_{H_2}.

The results for the photolysis of HN_3 of 6.7 kPa, measured as a function of Xe pressure at 313 nm, 30 °C, and an absorbed light intensity of 3.2×10^{15} quanta s^{-1}, are shown in Fig. 6. It is shown in Fig. 6 that all quantum yields decrease with an increase of Xe pressure.

On the photolysis of the labeled hydrazoic acid of 6.7 kPa at 313 nm and 30 °C, $^{14}N^{14}N/N_2$, $^{14}N^{15}N/N_2$, and $^{15}N^{15}N/N_2$ which mean the fractions of isotopic nitrogen molecules to total nitrogen molecules(N_2) were 44.5, 48.7, and 6.8%, respectively. The fraction of ^{15}N atoms to total N atoms in NH_4N_3 was 36.2%.

Discussion

Reaction Mechanism. It is difficult to determine the reaction scheme in this system, because only three kinds of products were obtained. However, we suggest the following reaction mechanism on the basis of the present results, our results in the photolysis of HN_3 in the presence of C_2H_6[23] and C_2H_4,[24] and the results obtained by previous investigators:

$$HN_3 + h\nu(313\text{ nm}) \longrightarrow N_2 + NH(a^1\Delta) \tag{1}$$

$$NH(a^1\Delta) + HN_3 \longrightarrow 2N_2 + 2H \tag{2}$$

$$NH(a^1\Delta) + HN_3 \longrightarrow N_3 + NH_2 \tag{3}$$

$$NH(a^1\Delta) + HN_3 \longrightarrow N_2 + N_2H_2{}^* \tag{4}$$

$$H + HN_3 \longrightarrow H_2 + N_3 \tag{5}$$

$$H + HN_3 \longrightarrow NH_2 + N_2 \tag{6}$$

$$N_2H_2{}^* \longrightarrow N_2H_2{}^{**} \tag{7}$$

$$N_2H_2{}^* + HN_3 \longrightarrow N_2 + H_2 + HN_3 \tag{8}$$

$$N_2H_2{}^* + HN_3 \longrightarrow NH_3 + 2N_2 \tag{9}$$

$$N_2H_2{}^{**} + HN_3 \longrightarrow NH_3 + 2N_2 \tag{10}$$

$$NH_2 + HN_3 \longrightarrow NH_3 + N_3 \tag{11}$$

$$NH_3 + HN_3 \longrightarrow NH_4N_3 \tag{12}$$

$$N_3 + HN_3 \longrightarrow HN_3\cdot N_3 \tag{13}$$

$$2HN_3\cdot N_3 \longrightarrow 3N_2 + 2HN_3. \tag{14}$$

Table 1. Selected heats of formation

	$\frac{\Delta H^\circ_{\mathrm{f},298}}{\mathrm{kJ\ mol^{-1}}}$	Ref.		$\frac{\Delta H^\circ_{\mathrm{f},298}}{\mathrm{kJ\ mol^{-1}}}$	Ref.
HN_3	299.8	a	*trans*-N_2H_2	175.7	i
$NH(X^3\Sigma^-)$	352.2	b	*cis*-N_2H_2	203.3	i
$NH(a^1\Delta)$	506.6	b,c	NH_4N_3	112.1	a
$NH(b^1\Sigma^+)$	612.8	b,d	$N(^4S_{3/2})$	474.1	e
$NH(A^3\Pi)$	711.2	b,d	$N(^2D_{5/2})$	703.7	e,j
$NH(c^1\Pi)$	873.1	b,d	HN_2	255.2	k
H	218.0	e	N_2H_3	278.9	l
N_3	468.6	f	N_2H_4	95.2	m
$NH_2(\tilde{X}^2B_1)$	171.5	g	NH_2–N=NH	274.1	n
$NH_2(\tilde{A}^2A_1)$	294.1	g,h	$N_2(A^3\Sigma_u^+)$	595.4	d
NH_3	−46.0	e	$N_2(B^3\Pi_g)$	709.2	d

a) P. Gray and T. C. Waddington, *Proc. R. Soc. London, Ser. A*, **235**, 106 (1956). b) L. G. Piper, *J. Chem. Phys.*, **70**, 3417 (1979). c) H. Okabe and M. Lenzi, *J. Chem. Phys.*, **47**, 5241 (1967). d) L. Wallace, *Astrophys. J. Suppl. Ser.*, **7**, 165 (1962). e) "JANAF Thermochemical Tables," ed by D. R. Stull, Dow Chemical Co., Midland, Mich. (1966). f) M. J. Pellerite, R. L. Jackson, and J. I. Brauman, *J. Phys. Chem.*, **85**, 1624 (1981). g) D. K. Sen Sharma and J. L. Franklin, *J. Am. Chem. Soc.*, **95**, 6562 (1973). h) K. Dressler and D. A. Ramsay, *Phil. Trans. R. Soc. London, Ser. A*, **251**, 553 (1959). i) N. W. Winter and R. M. Pitzer, *J. Chem. Phys.*, **62**, 1269 (1975). j) C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (1952). k) Ref. 25. l) A. A. Zavitsas, *J. Am. Chem. Soc.*, **94**, 2779 (1972). m) D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman, *J. Am. Chem. Soc.*, **71**, 2293 (1949). n) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 289 (1971).

In the photolysis of HN_3 in the presence of Xe, the following reactions were added to those listed above:

$$NH(a^1\Delta) + Xe \longrightarrow NH(X^3\Sigma^-) + Xe \qquad (15)$$

$$NH(X^3\Sigma^-) + HN_3 \longrightarrow H_2 + 2N_2 \qquad (16)$$

$$NH(X^3\Sigma^-) + HN_3 \longrightarrow NH_2 + N_3. \qquad (17)$$

Thermochemical considerations were taken into account using the standard heats of formation listed in Table 1.

For HN_3 excited by absorbing light of 313 nm, the photo-decomposition processes

$$\begin{aligned} HN_3 + h\nu(313\,\mathrm{nm}) &\longrightarrow H(^2S) + N_3(X^2\Pi) \\ &\longrightarrow N_2(X^1\Sigma_g^+) + N(^4S) + H(^2S) \\ &\longrightarrow N_2(X^1\Sigma_g^+) + N(^2D) + H(^2S) \\ &\longrightarrow HN_2 + N(^2D) \end{aligned}$$

to give H and N atoms are not possible energetically.[5,25] Reaction 1 is the only photochemical process which is energetically possible and spin allowed, except the process

$$HN_3 + h\nu(313\,\mathrm{nm}) \longrightarrow N_2(X^1\Sigma_g^+) + NH(b^1\Sigma^+)$$

However, the formation of $NH(b^1\Sigma^+)$ was not detected although $NH(a^1\Delta)$ was observed as a predominant primary product.[7–9] It seems that $NH(b^1\Sigma^+)$ decays quickly to $NH(a^1\Delta)$, even if $NH(b^1\Sigma^+)$ was formed. Therefore, reactions yielding $NH(b^1\Sigma^+)$ were excluded from the reaction mechanism.

The formation of $NH(X^3\Sigma^-)$ by the collisional spin relaxation process

$$NH(a^1\Delta) + HN_3 \longrightarrow NH(X^3\Sigma^-) + HN_3$$

is negative judging from the facts that McDonald *et al.*[26] were not able to observe any triplet NH formation when helium was introduced even at pressures as high as 12 kPa, and the relation of $[NH(X^3\Sigma^-)] \ll [NH(a^1\Delta)]$ was found by Piper *et al.*[9] While, $NH(X^3\Sigma^-)$ has been observed in flash photolysis.[3,7,8,27] It seems that the formation of $NH(X^3\Sigma^-)$ is due to an emission process, $NH(A^3\Pi) \rightarrow NH(X^3\Sigma^-) + h\nu$, and the collisional quenching of $NH(a^1\Delta)$ by diluent gases such as Reaction 15.

Reactions 2, 3 and 4 are highly exothermic and their enthalpy changes are −370, −166, and −631 kJ mol^{-1}, respectively. The formation of H atoms has been found in the flash photolysis[28] and the photolysis of HN_3 in inert and reactive matrices.[29,30] Reaction 2 is also supported by the fact that the reaction, $H + C_2H_4 \rightarrow C_2H_5$, occurs during the photolysis of HN_3 with C_2H_4.[24] NH_2 radicals have been observed in the flash photolysis of HN_3 vapor.[3,7–9]

The formation of N_2H_2 has been detected in the photolysis of HN_3 in frozen matrices.[12,29,31] Reaction 4 is also supported by the facts that the similar reaction, $CH_3N + CH_3N_3 \rightarrow CH_3N_2CH_3 + N_2$, was found in the photolysis of CH_3N_3 vapor[32] and the rapid hydrogenation reaction,[33] $N_2H_2 + C_2H_4 \rightarrow C_2H_6 + N_2$, takes place in the photolysis of HN_3 with C_2H_4.[24]

On the reaction to give nitrogen atoms,

$$NH(a^1\Delta) + HN_3 \longrightarrow N(^4S \text{ or } ^2D) + N_3H_2$$

the reaction to form $N(^4S)$ is rejected because of the spin forbidden reaction. The reaction to give $N(^2D)$ may also be excluded because the heat of formation of N_3H_2 seems to be higher than 102.7 kJ mol^{-1} judging from the heat of formation of NH_2–N=NH and the bond dissociation energies of NH_2NN–H and H–NHNNH. The reaction to give H_2 molecules,

$$NH(a^1\Delta) + HN_3 \longrightarrow H_2 + 2N_2$$

is excluded because the H_2 formation decreases drastically on adding C_2H_4 in small amount.[24] Baird[25] has predicted a value of 255 kJ mol^{-1} for the heat of formation of HN_2 radicals. Therefore, the reaction

$$NH(a^1\Delta) + HN_3 \longrightarrow 2HN_2$$

is energetically possible. However, the HN_2 will decompose immediately with large excess energy even if HN_2 were formed, and it results in Reaction 2.

On the reactions of H atoms with HN_3 molecules, only Reactions 5 and 6 are energetically possible processes. The reactions

$$\begin{aligned} H + HN_3 &\longrightarrow N(^4S \text{ or } ^2D) + N_2H_2 \\ &\longrightarrow NH(X^3\Sigma^- \text{ or } a^1\Delta) + HN_2 \end{aligned}$$

are excluded energetically. Reaction 5 is the hydrogen abstraction reaction from HN_3 by H, and is supported because HN_3 is a good hydrogen donor.[34] Reaction 6 is 337 kJ mol^{-1} exothermic, and the formations of N_3 and NH_2 radicals were confirmed in the flash photolysis.[3,7,8,35] Combourieu *et al.*[36] have obtained $k = 2.54 \times 10^{-11} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} as a rate constant of the reaction

$$H + HN_3 \longrightarrow \text{Products.}$$

Reactions 7 to 10 were introduced in order to explain the facts that NH_4N_3/N_2 increases and H_2/N_2 decreases with decrease of the HN_3 pressure, although the detail of these reactions are not clear. $N_2H_2^*$ formed by Reaction 4 is probably in an electronically excited state,[37] because Reaction 4 is very exothermic with 631 kJ mol^{-1}. If $N_2H_2^*$ is in an excited state, it may be possible that $N_2H_2^*$ transfers to a lower electronic state ($N_2H_2^{**}$) by internal conversion or intersystem crossing as Reaction 7, and $N_2H_2^{**}$ reacts to give NH_3 by Reaction 10. $N_2H_2^*$ may also possibly react with HN_3 by Reactions 8 and 9.

The bimolecular reactions as to N_2H_2,[38,39] $2N_2H_2 \rightarrow N_2H_4 + N_2$ and $2N_2H_2 \rightarrow N_2 + H_2 + N_2H_2$, are ruled out in our system, because the formation of N_2H_4 was not observed, and the quantum yields of N_2 and H_2 were independent of the light intensity. It means that the concentration of N_2H_2 in our system is much lower than those described in Refs. 38 and 39.

Reaction 11 is the hydrogen abstraction reaction by NH_2 from HN_3 which is a good hydrogen donor.[34] Piper *et al.*[9] have presented the mechanism

$$NH(a^1\Delta) + HN_3 \longrightarrow NH_2(\tilde{A}^2A_1) + N_3$$

$$NH_2(\tilde{A}^2A_1) \longrightarrow NH_2(X^2B_1) + h\nu$$

(α bands of ammonia[40])

$$NH_2(\tilde{A}^2A_1) + HN_3 \longrightarrow NH_2(X^2B_1) + HN_3$$

$$\longrightarrow NH_3 + N_3$$

to explain the formation and disappearance of $NH_2(\tilde{A}^2A_1)$, and obtained 9.3×10^{-11} cm^3 molecule^{-1} s^{-1} as a rate constant for the disappearance of $NH_2(\tilde{A}^2A_1)$ by HN_3. However, the HN_3 pressure dependence of NH_4N_3/N_2 in Fig. 4 can not be explained by their mechanism, provided that all $NH_2(X^2B_1)$ radicals disappear to give NH_3 as Reaction 11.

On the other hand, Kajimoto *et al.*[41] have observed the fluorescence from $NH_2(\tilde{A}^2A_1)$ formed by the reaction, $H + HN_3 \rightarrow N_2 + NH_2(\tilde{A}^2A_1)$. Thus, Reactions 2, 3, and 6 are supported in terms of both observations for the fluorescence from $NH_2(\tilde{A}^2A_1)$. Judging from the enthalpy changes of Reactions 3 and 6, it is surmised that the emission from $NH_2(\tilde{A}^2A_1)$ formed by Reaction 6 appears at shorter wavelength than that from $NH_2(\tilde{A}^2A_1)$ formed by Reaction 3.[41]

Basic NH_3 reacts rapidly in the vapor phase with acidic HN_3 to give NH_4N_3 as a white volatile powder[42] by Reaction 12.

Paur and Bair[7,8] have observed that the disappearance rate of N_3 radicals is faster than expected for reaction with other radicals at concentrations present in their system, and concluded that this rate most likely represents reaction with HN_3. Therefore, it seems that N_3 radicals disappear to give N_2 *via* an addition intermediate ($HN_3 \cdot N_3$) as Reactions 13 and 14. Addition intermediates of N_3 with C_2H_4 and *cis*-C_4H_8 having π bond are also found in the photolysis of HN_3 with C_2H_4[24] and *cis*-C_4H_8.

Finally, all of the Reactions 1 to 14 in the photolysis of HN_3 vapor are energetically possible and spin allowed. The reaction mechanism satisfy the experimental requirements that the quantum yields of N_2, H_2, and NH_4N_3 are independent of the light intensity, and NH_4N_3/N_2 increases but H_2/N_2 decreases with lowering of HN_3 pressure. Reactions 1 to 14 are also found as a common reaction pattern in the photolysis of HN_3 in the presence of C_2H_6[23] and C_2H_4.[24]

On the photolysis of HN_3 in the presence of Xe, Reaction 15 seems to be the only process for the reaction of $NH(a^1\Delta)$ with Xe as an inert gas. For reactions of $NH(X^3\Sigma^-)$, we do not have enough experimental evidence. In any case, $NH(X^3\Sigma^-)$ will disappear to give H_2 and NH_3 by reactions with HN_3 such as Reactions 16 and 17.[43]

Recently, Kajimoto *et al.*[22] have estimated 3.0×10^{11} $\exp(-805/T)$ cm^3 mol^{-1} s^{-1} as k_{17} and 2.5×10^{13} cm^3 mol^{-1} s^{-1} as a rate constant of the reaction, $2NH(X^3\Sigma^-) \rightarrow N_2 + 2H$, in the thermal decomposition of HN_3 in shock waves. However, the possibility of the reaction, $2NH(X^3\Sigma^-) \rightarrow$ Products, will be negligible, because the $NH(X^3\Sigma^-)$ concentration is low in our system.

Reaction Kinetics. On the basis of the mechanism of Reactions 1 to 17, the equation

$$\frac{1}{\phi_{H_2} + \phi_{NH_4N_3} - 1} = \frac{k_2 + k_3 + k_4}{k_2} + \frac{k_{15}[Xe]}{k_2[HN_3]}, \qquad (I)$$

can be derived for the formations of H_2 and NH_4N_3. From the intercept and slope in Fig. 7 and from $k_4/k_2 = 1.23$ obtained in the photolysis of HN_3 with C_2H_4,[24] $k_3/k_2 = 0.746$, $k_{15}/k_2 = 0.557$ and $k_{15}/(k_2+k_3+k_4) = 0.187$ are obtained.

Equation II can be derived for the formations of H_2 and N_2 in the absence of Xe.

$$\frac{1}{4/(1+R_{N_2}/R_{H_2}) - \alpha} = \frac{2k_2 + k_3 + k_4}{k_4}\left(1 + \frac{k_9}{k_8} + \frac{k_7}{k_8[HN_3]}\right), \qquad (II)$$

where

$$\alpha = \frac{k_2}{2k_2 + k_3 + k_4}\,\frac{2k_5}{k_5 + k_6}.$$

When α is 0.234, the best straight line is obtained as is seen in Fig. 8. From the intercept, the slope and $\alpha = 0.234$, $k_6/k_5 = 1.15$, $k_9/k_8 = 1.19$, and $k_7/k_8 = 2.27\times10^{-7}$ mol cm^{-3} are obtained.

On the formations of H_2 and N_2 in the presence of Xe, Equation III can be derived.

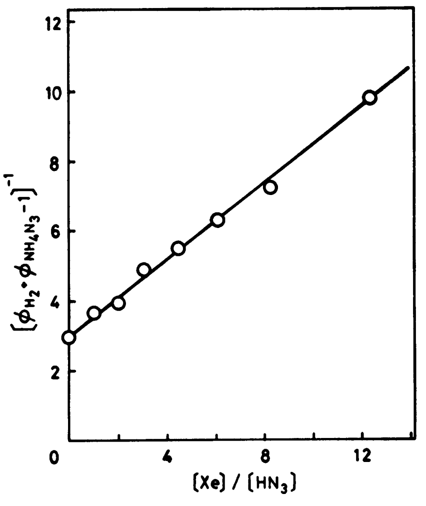

Fig. 7. Plot of $1/(\phi_{H_2}+\phi_{NH_4N_3}-1)$ *versus* $[Xe]/[HN_3]$.

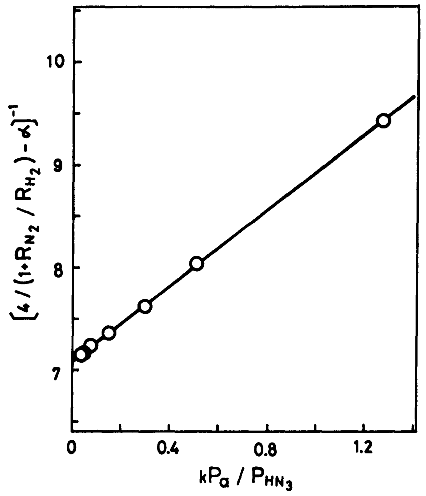

Fig. 8. Plot of $1/[4/(1+R_{N_2}/R_{H_2})-\alpha]$ against $1/P_{HN_3}$.

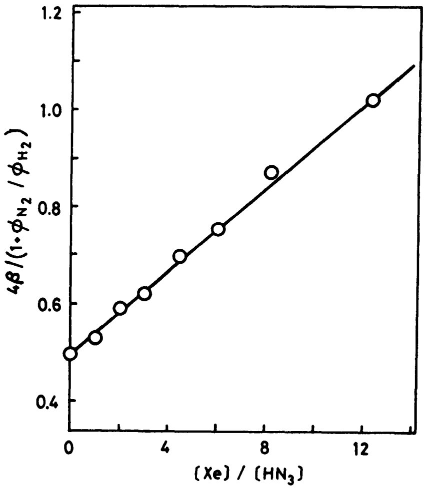

Fig. 9. Plot of $4\beta/(1+\phi_{N_2}/\phi_{H_2})$ *versus* $[Xe]/[HN_3]$.

$$\frac{4\beta}{1+\phi_{N_2}/\phi_{H_2}} = \alpha + \frac{k_4}{k_2+k_3+k_4}\,\frac{k_8[HN_3]}{k_7+(k_8+k_9)[HN_3]} + \frac{k_{15}}{k_2+k_3+k_4}\,\frac{k_{16}}{k_{16}+k_{17}}\,\frac{[Xe]}{[HN_3]}, \qquad \text{(III)}$$

where

$$\beta = 1 + \frac{k_2}{k_2+k_3+k_4}\left(1+\frac{k_{15}}{k_2}\,\frac{[Xe]}{[HN_3]}\right)$$
$$= 1.336 + 0.187[Xe]/[HN_3].$$

The plot of $4\beta/(1+\phi_{N_2}/\phi_{H_2})$ *versus* $[Xe]/[HN_3]$ at 6.7 kPa of HN_3 is shown in Fig. 9, and $k_{17}/k_{16}=3.22$ is obtained from the slope.

Equation I can be rewritten as

$$\frac{1}{\phi_{H_2}+\phi_{NH_4N_3}-1} - 1 = \frac{k_3+k_4}{k_2}, \qquad \text{(IV)}$$

in the absence of Xe. The temperature dependence is shown in Fig. 10. It is found in Fig. 10 that $(k_3+k_4)/k_2$ decreases drastically from 1.976 at 30 °C with increasing temperature.

Isotopic Considerations. In order to confirm the reaction mechanism obtained above, the experimental values of $^{14}N^{14}N/N_2$, $^{14}N^{15}N/N_2$, $^{15}N^{15}N/N_2$, and $^{15}N/NH_4N_3$ in the absence of Xe were compared with the values calculated by using Eqs. V to VIII.

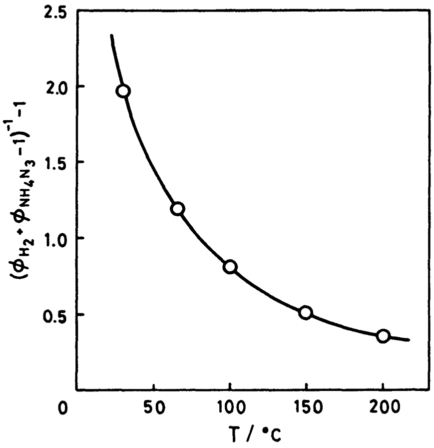

Fig. 10. Temperature dependence of $(k_3+k_4)/k_2$.

$$^{14}N^{14}N/N_2 = \sum_i S_i\alpha_i\phi_i/\phi_{N_2} \qquad \text{(V)}$$

$$^{14}N^{15}N/N_2 = \sum_i S_i\beta_i\phi_i/\phi_{N_2} \qquad \text{(VI)}$$

$$^{15}N^{15}N/N_2 = \sum_i S_i\gamma_i\phi_i/\phi_{N_2} \qquad \text{(VII)}$$

$$^{15}N/NH_4N_3 = 1.5/4 \qquad \text{(VIII)}$$

Here, ϕ_i is the quantum yield of i-th reaction, and can be calculated using the rate constant ratios obtained above. S_i is the stoichiometry of N_2 formed in i-th reaction. α_i, β_i and γ_i mean the fractions of $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ including in total N_2 formed by i-th reaction, respectively. The values needed for the calculations of Eqs. V to VII are listed in Table 2, where S_i values in Reactions 3, 5, 6, and 7 include additional N_2 formations by subsequent Reactions 10, 11, 13, and 14.

The calculated values of $^{14}N^{14}N/N_2$, $^{14}N^{15}N/N_2$, $^{15}N^{15}N/N_2$, and $^{15}N/NH_4N_3$ are 43.1, 50.0, 6.89, and 37.5%, respectively. These values are consistent with the experimental values of 44.5, 48.7, 6.8, and 36.2%. Slight discrepancies may be due to incomplete isotopic enrichment (97%) of ^{15}N in the labeled hydrazoic acid. The recovery of ^{15}N calculated from the equation $3[\phi_{^{14}N^{15}N}+2\phi_{^{15}N^{15}N}+4(^{15}N/NH_4N_3)\phi_{NH_4N_3}]/(2\phi_{N_2}+4\phi_{NH_4N_3})$ is 0.974, and in accord with the original (0.97).

On the other hand, if Beckman's[1,2] and Thrush's[3] mechanisms are applied to Eq. VII, the values of $^{15}N^{15}N/N_2$ become 6.55 and 8.33%, respectively. Papazian[44] has postulated the following mechanism in outline on the photolysis of HN_3 in frozen state: $HN_3 + h\nu \rightarrow NH + N_2$; $NH + HN_3 \rightarrow HN{=}N{-}N{=}NH \rightarrow 2HN_2$; $NH + HN_2 + HN_3 \rightarrow H_2N{-}N{=}NH + 3/2\, N_2$; $H_2N{-}N{=}NH \rightarrow NH_3 + N_2$; and $NH_3 + HN_3 \rightarrow NH_4N_3$. From the mechanism, we obtain $^{15}N^{15}N/N_2=7.30\%$. The value of $^{15}N^{15}N/N_2$ calculated from the reaction scheme proposed by Konar *et al.*[6] was 2.65% in the absence of forein gases. Of the various possible mechanisms, our mechanism of Reactions 1 to 14 gives the best agreement with the isotopic measurements.

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TABLE 2. VALUES USED TO CALCULATE THE ISOTOPIC COMPOSITIONS OF NITROGEN

Reaction No.	Quantum yield of i-th reaction	Stoichiometry of N_2 formation	Probability[a]		
			$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$
i	ϕ_i	S_i	α_i	β_i	γ_i
1	1	1	1/2	1/2	0
2	0.3360	2	3/8	1/2	1/8
3	0.2505	3	5/12	1/2	1/12
4	0.4135	1	1/2	1/2	0
5	0.3128	3/2	5/12	1/2	1/12
6	0.3592	5/2	9/20	1/2	1/20
7	0.0156[b]	2	3/8	1/2	1/8
8	0.1817[b]	1	1/4	1/2	1/4
9	0.2163[b]	2	3/8	1/2	1/8

a) The probabilities (α_i, β_i, and γ_i) were estimated assuming that the enrichment of ^{15}N in the labeled hydrazoic acid is 1.00. b) Values at 6.7 kPa of HN_3.

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17) The formation ratio of NO to N_2 was about two-tenths, and the formation of N_2O was trace.

18) The equation was derived from the relations of $[H]=2[H_2]+3[NH_4N_3]$, $[N]=2[N_2]+[NH_4N_3]$, and $[N]/[H]=3$.

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