

Reactions of NH Radicals. I. Photolysis of HN₃ Vapor at 313 nm

Sukeya KODAMA

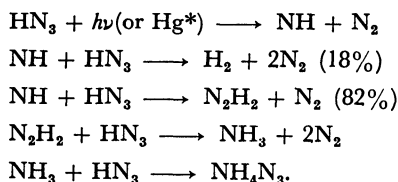
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591

(Received September 13, 1982)

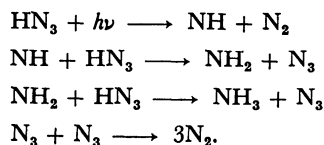
Photolysis of HN₃ vapor was studied at 313 nm as a function of HN₃ and Xe pressures, light intensity, and temperature. The photolysis of hydrazoic acid labeled with ¹⁵N was also studied. The quantum yields of N₂, H₂, and NH₄N₃ as a product were 4.85, 0.494, and 0.842 at 30 °C and 6.7 kPa of HN₃, respectively. The mechanism for the main reactions was postulated as follows: HN₃ + *hν* (313 nm) → N₂ + NH(^aΔ); NH(^aΔ) + HN₃ → 2N₂ + 2H (2); NH(^aΔ) + HN₃ → N₃ + NH₂ (3); NH(^aΔ) + HN₃ → N₂ + N₂H₂* (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(^aΔ) + Xe → NH(X³Σ⁻) + 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(X³Σ⁻ and ^aΔ) radicals that are in the same isoelectronic state as carbon, oxygen, and sulfur atoms and CH₂, SiH₂, and PH radicals, hydrazoic acid was chosen as a photochemical radical source.

The photolysis of HN₃ vapor at about 190 nm¹⁾ and the mercury-photosensitized decomposition²⁾ were first investigated by Beckman and his co-workers. On the basis that the products are N₂, H₂, and NH₄N₃, and the quantum yield for the disappearance of HN₃ is about 3.6 in both cases, they have presented the following mechanism:

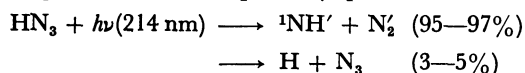


Thrush³⁾ has proposed the following mechanism from the identifications of NH, NH₂, and N₃ radicals in flash photolysis:



On the photolysis of HN₃ vapor in the vacuum-ultraviolet, Welge⁴⁾ has observed that NH(^cΠ) and NH(^AΠ₁) are produced below 160 nm. Okabe⁵⁾ has shown that the yield of the NH(^cΠ) production is at most 2%, and NH(^AΠ₁) may be formed largely by the reaction of electronically excited N₂, most probably N₂(^BΠ_g), with HN₃.

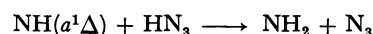
Konar, Matsumoto, and Darwent⁶⁾ have investigated the photochemical decomposition of HN₃ at 214 nm, and reported that the primary processes are



and the vibrationally excited ¹NH' and N'₂ are capable of causing further decomposition of HN₃.

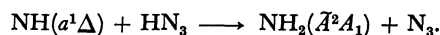
Paur and Bair^{7,8)} have studied the flash photolysis of HN₃ by coordinated time-resolved spectroscopic measurements of HN₃, NH(^aΔ), NH(X³Σ⁻), NH(^cΠ), NH(^AΠ), NH₂, and N₃. They have reported that the major reactive product is NH(^aΔ) or states which

quickly decay to NH(^aΔ) above 200 nm. Disappearance of NH(^aΔ) occurs predominantly by the process



with a rate constant of $9.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁸⁾

Recently, Piper *et al.*⁹⁾ have studied the UV photolysis of HN₃ by observing the time dependent decay in the number density of the NH(^aΔ) product following photolysis at about 290 nm. They have obtained $18 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as a rate constant for the reaction



They also obtained $9.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as a specific rate for the reaction of NH₂(²A₁) with HN₃.

Although the photolysis of HN₃ 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 HN₃ is located at about 310 nm,¹⁰⁾ and the formation of the first excited singlet NH(^aΔ) can be expected at this wavelength. Thus, the photolysis of HN₃ vapor at 313 nm had been carried out in this work, before the studies of reactions of NH(^aΔ and X³Σ⁻) with various reactants.

Experimental

Materials. Hydrazoic acid was prepared from the reaction of NaN₃ with sulfuric acid (H₂SO₄: H₂O = 1 : 2 in volume ratio) at room temperature, dried by passing through columns packed with CaCl₂ and P₂O₅, and stored below a half atm in a reservoir protected from light to avoid explosion.

The UV absorption of HN₃ of 14.3 kPa at 25.7 °C was observed at wavelengths longer than 220 nm. The molecular extinction coefficients calculated from $\log_{10} (I/I_0) = -\epsilon cl$ 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 ($\epsilon_{\text{max}} = 1.79$) and 2.36 μm ($\epsilon_{\text{max}} = 1.34 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The former peak has been found in the spectrum of frozen HN₃.¹¹⁾

To elucidate the mechanism the photolysis was also carried out with hydrazoic acid labeled with nitrogen-15. For this purpose, potassium azide labeled with ¹⁵N 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

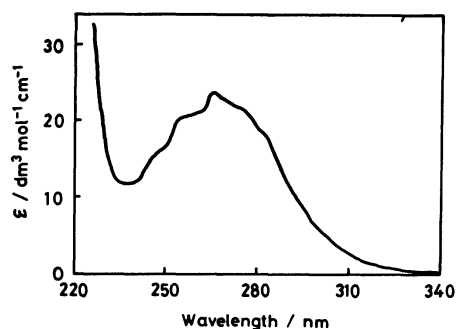
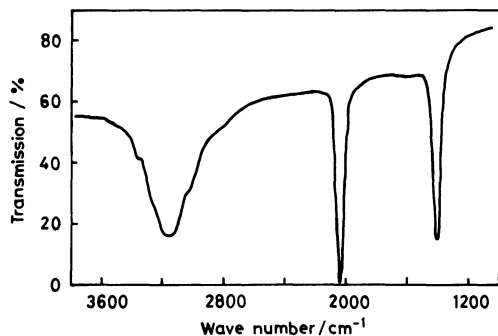
Fig. 1. UV absorption spectrum of HN_3 vapor.

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⁾ $\text{KNN}^{15}\text{N} \xrightarrow{(\text{H}_2\text{O})} \text{K}^+ + {}^{15}\text{NNN}^-$; $\text{H}^{15}\text{NNN} \leftarrow \text{H}^+ + {}^{15}\text{NNN}^- \rightarrow \text{HNN}^{15}\text{N}$.

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 cm^3 . 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 relation¹³⁾ $(2[\text{N}_2] + 4[\text{NH}_4\text{N}_3])/3[\text{HN}_3]_0$, 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 ($\text{N}_2\text{H}_5\text{N}_3$) 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 gel¹⁶⁾ (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 products¹⁷⁾ 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, $\text{NH}_4\text{N}_3 = (\text{N}_2 + \text{N}_2\text{O})/2 + \text{NO}/4$. The expectation amount of NH_4N_3 can be estimated by the equation¹⁸⁾ $\text{NH}_4\text{N}_3 = \text{N}_2/4 - 3\text{H}_2/4$, 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 $\phi_{\text{NH}_4\text{N}_3}$, are independent of the light intensity. The average values of ϕ_{N_2} , ϕ_{H_2} , and $\phi_{\text{NH}_4\text{N}_3}$ 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

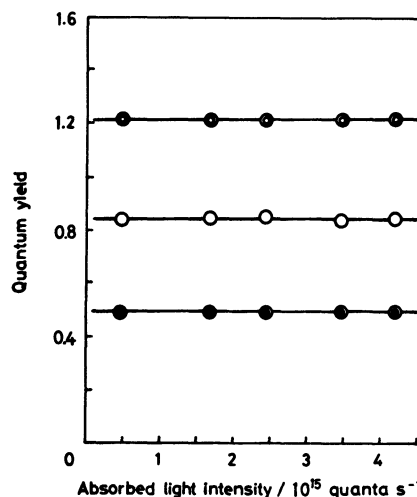


Fig. 3. Results of the photolysis of HN_3 of 6.7 kPa, measured as a function of the absorbed light intensity at 313 nm and 30°C . $\odot$, $\phi_{\text{N}_2}/4$; $\circ$, $\phi_{\text{NH}_4\text{N}_3}$; $\bullet$, ϕ_{H_2} .

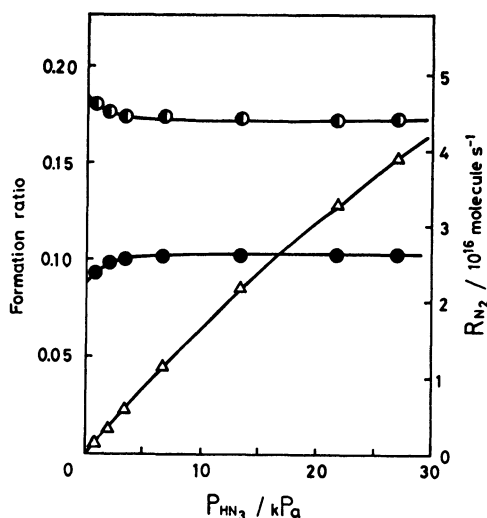


Fig. 4. Results of the photolysis, measured as a function of HN_3 pressure at 30 °C, 313 nm, and the incident light intensity of 2.0×10^{16} quanta s^{-1} . $\odot$, $\text{NH}_4\text{N}_3/\text{N}_2$; $\bullet$, H_2/N_2 ; $\triangle$, R_{N_2} .

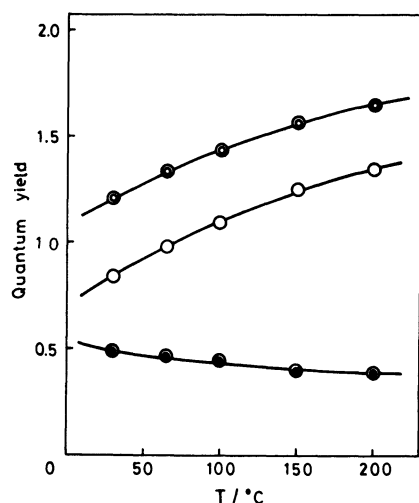


Fig. 5. Temperature dependence on the photolysis of HN_3 of $2.64 \text{ mmol dm}^{-3}$ at 313 nm and the incident light intensity of 2.0×10^{16} quanta s^{-1} . $\odot$, $\phi_{\text{N}_2}/4$; $\circ$, $\phi_{\text{NH}_4\text{N}_3}$; $\bullet$, ϕ_{H_2} .

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 $\text{NH}_4\text{N}_3/\text{N}_2$ increases in contrast with H_2/N_2 .

The thermal decomposition of HN_3 has been studied at about 380²⁰⁾ 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 $2.64 \times 10^{-3} \text{ mol dm}^{-3}$ (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 $\phi_{\text{NH}_4\text{N}_3}$ increase, but ϕ_{H_2} decreases with increase in temperature.

The results for the photolysis of HN_3 of 6.7 kPa,

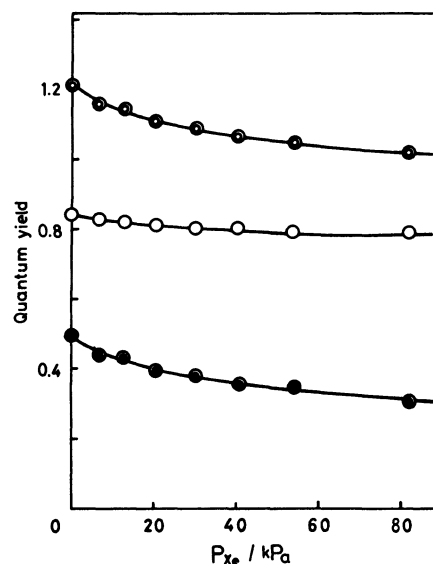


Fig. 6. Results of the photolysis of HN_3 of 6.7 kPa, measured as a function of Xe pressure at 313 nm, 30 °C, and the absorbed light intensity of 3.2×10^{15} quanta s^{-1} . $\odot$, $\phi_{\text{N}_2}/4$; $\circ$, $\phi_{\text{NH}_4\text{N}_3}$; $\bullet$, ϕ_{H_2} .

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, $^{14}\text{N}^{14}\text{N}/\text{N}_2$, $^{14}\text{N}^{15}\text{N}/\text{N}_2$, and $^{15}\text{N}^{15}\text{N}/\text{N}_2$ 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:

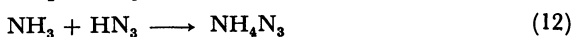
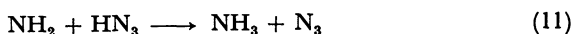
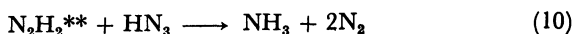
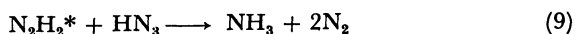
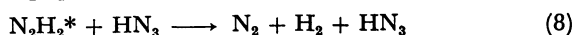
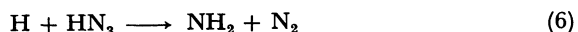
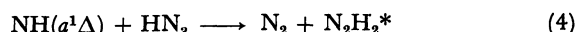
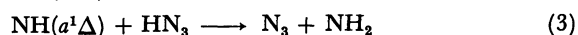
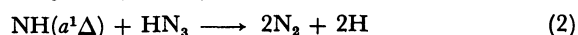
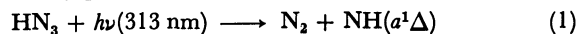
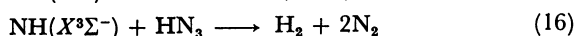
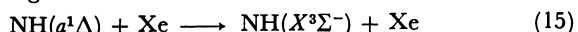


TABLE 1. SELECTED HEATS OF FORMATION

	$\Delta H_{f,298}^{\circ}$ kJ mol ⁻¹	Ref.		$\Delta H_{f,298}^{\circ}$ kJ mol ⁻¹	Ref.
HN ₃	299.8	a	<i>trans</i> -N ₂ H ₂	175.7	i
NH(<i>X</i> ³ Σ ⁻)	352.2	b	<i>cis</i> -N ₂ H ₂	203.3	i
NH(<i>a</i> ¹ Δ)	506.6	b,c	NH ₄ N ₃	112.1	a
NH(<i>b</i> ¹ Σ ⁺)	612.8	b,d	N(⁴ S _{3/2})	474.1	e
NH(<i>A</i> ³ Π)	711.2	b,d	N(² D _{5/2})	703.7	e,j
NH(<i>c</i> ¹ Π)	873.1	b,d	HN ₂	255.2	k
H	218.0	e	N ₂ H ₃	278.9	l
N ₃	468.6	f	N ₂ H ₄	95.2	m
NH ₂ (<i>X̃</i> ² B ₁)	171.5	g	NH ₂ -N=NH	274.1	n
NH ₂ (<i>Ã</i> ² A ₁)	294.1	g,h	N ₂ (<i>A</i> ³ Σ _u ⁺)	595.4	d
NH ₃	-46.0	e	N ₂ (<i>B</i> ³ Π _g)	709.2	d

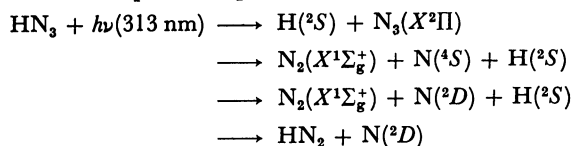
a) P. Gray and T. C. Waddington, *Proc. R. Soc. London, Ser. A*, **235**, 106 (1956). b) L. G. Piper, *J. Chem. Phys.*, **70**, 3417 (1979). c) H. Okabe and M. Lenzi, *J. Chem. Phys.*, **47**, 5241 (1967). d) L. Wallace, *Astrophys. J. Suppl. Ser.*, **7**, 165 (1962). e) "JANAF Thermochemical Tables," 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 HN₃ in the presence of Xe, the following reactions were added to those listed above:

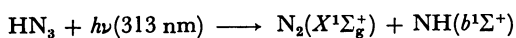


Thermochemical considerations were taken into account using the standard heats of formation listed in Table 1.

For HN₃ excited by absorbing light of 313 nm, the photo-decomposition processes



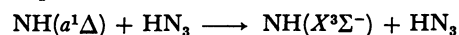
to give H and N atoms are not possible energetically.^{5,25} Reaction 1 is the only photochemical process which is energetically possible and spin allowed, except the process



However, the formation of NH(*b*¹Σ⁺) was not detected although NH(*a*¹Δ) was observed as a predominant primary product.⁷⁻⁹ It seems that NH(*b*¹Σ⁺) decays quickly to NH(*a*¹Δ), even if NH(*b*¹Σ⁺) was formed. Therefore, reactions yielding NH(*b*¹Σ⁺) were excluded from the reaction mechanism.

The formation of NH(*X*³Σ⁻) by the collisional spin

relaxation process

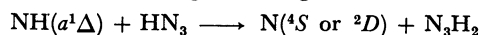


is negative judging from the facts that McDonald *et al.*²⁶ were not able to observe any triplet NH formation when helium was introduced even at pressures as high as 12 kPa, and the relation of [NH(*X*³Σ⁻)] ≪ [NH(*a*¹Δ)] was found by Piper *et al.*⁹ While, NH(*X*³Σ⁻) has been observed in flash photolysis.^{3,7,8,27} It seems that the formation of NH(*X*³Σ⁻) is due to an emission process, NH(*A*³Π) → NH(*X*³Σ⁻) + *hν*, and the collisional quenching of NH(*a*¹Δ) by diluent gases such as Reaction 15.

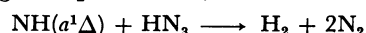
Reactions 2, 3 and 4 are highly exothermic and their enthalpy changes are -370, -166, and -631 kJ mol⁻¹, respectively. The formation of H atoms has been found in the flash photolysis²⁸ and the photolysis of HN₃ in inert and reactive matrices.^{29,30} Reaction 2 is also supported by the fact that the reaction, H + C₂H₄ → C₂H₅, occurs during the photolysis of HN₃ with C₂H₄.²⁴ NH₂ radicals have been observed in the flash photolysis of HN₃ vapor.^{3,7-9}

The formation of N₂H₂ has been detected in the photolysis of HN₃ in frozen matrices.^{12,29,31} Reaction 4 is also supported by the facts that the similar reaction, CH₃N + CH₃N₃ → CH₃N₂CH₃ + N₂, was found in the photolysis of CH₃N₃ vapor³² and the rapid hydrogenation reaction,³³ N₂H₂ + C₂H₄ → C₂H₆ + N₂, takes place in the photolysis of HN₃ with C₂H₄.²⁴

On the reaction to give nitrogen atoms,



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 N₃H₂ seems to be higher than 102.7 kJ mol⁻¹ judging from the heat of formation of NH₂-N=NH and the bond dissociation energies of NH₂NN-H and H-NHNNH. The reaction to give H₂ molecules,

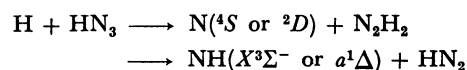


is excluded because the H₂ formation decreases drastically on adding C₂H₄ in small amount.²⁴ Baird²⁵ has predicted a value of 255 kJ mol⁻¹ for the heat of formation of HN₂ radicals. Therefore, the reaction

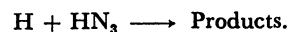


is energetically possible. However, the HN₂ will decompose immediately with large excess energy even if HN₂ were formed, and it results in Reaction 2.

On the reactions of H atoms with HN₃ molecules, only Reactions 5 and 6 are energetically possible processes. The reactions



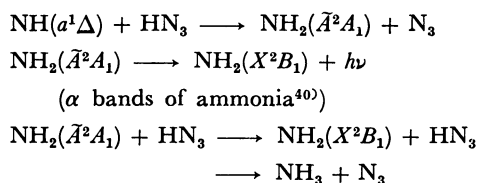
are excluded energetically. Reaction 5 is the hydrogen abstraction reaction from HN₃ by H, and is supported because HN₃ is a good hydrogen donor.³⁴ Reaction 6 is 337 kJ mol⁻¹ exothermic, and the formations of N₃ and NH₂ radicals were confirmed in the flash photolysis.^{3,7,8,35} Combourieu *et al.*³⁶ have obtained *k* = 2.54 × 10⁻¹¹ exp(-2300/*T*) cm³ molecule⁻¹ s⁻¹ as a rate constant of the reaction



Reactions 7 to 10 were introduced in order to explain the facts that $\text{NH}_4\text{N}_3/\text{N}_2$ 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 ($\text{N}_2\text{H}_2^{**}$) by internal conversion or intersystem crossing as Reaction 7, and $\text{N}_2\text{H}_2^{**}$ 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)} $2\text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}_4 + \text{N}_2$ and $2\text{N}_2\text{H}_2 \rightarrow \text{N}_2 + \text{H}_2 + \text{N}_2\text{H}_2$, 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



to explain the formation and disappearance of $\text{NH}_2(\bar{A}^2A_1)$, and obtained 9.3×10^{-11} cm³ molecule⁻¹ s⁻¹ as a rate constant for the disappearance of $\text{NH}_2(\bar{A}^2A_1)$ by HN_3 . However, the HN_3 pressure dependence of $\text{NH}_4\text{N}_3/\text{N}_2$ in Fig. 4 can not be explained by their mechanism, provided that all $\text{NH}_2(X^2B_1)$ radicals disappear to give NH_3 as Reaction 11.

On the other hand, Kajimoto *et al.*⁴¹⁾ have observed the fluorescence from $\text{NH}_2(\bar{A}^2A_1)$ formed by the reaction, $\text{H} + \text{HN}_3 \rightarrow \text{N}_2 + \text{NH}_2(\bar{A}^2A_1)$. Thus, Reactions 2, 3, and 6 are supported in terms of both observations for the fluorescence from $\text{NH}_2(\bar{A}^2A_1)$. Judging from the enthalpy changes of Reactions 3 and 6, it is surmised that the emission from $\text{NH}_2(\bar{A}^2A_1)$ formed by Reaction 6 appears at shorter wavelength than that from $\text{NH}_2(\bar{A}^2A_1)$ 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 powder⁴²⁾ 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 ($\text{HN}_3 \cdot \text{N}_3$) 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 $\text{NH}_4\text{N}_3/\text{N}_2$ 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 $\text{NH}(\bar{A}^1\Delta)$ with Xe as an inert gas. For reactions of $\text{NH}(X^3\Sigma^-)$, we do not have enough experimental evidence. In any case, $\text{NH}(X^3\Sigma^-)$ 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*) cm³ mol⁻¹ s⁻¹ as k_{17} and 2.5×10^{13} cm³ mol⁻¹ s⁻¹ as a rate constant of the reaction, $2\text{NH}(X^3\Sigma^-) \rightarrow \text{N}_2 + 2\text{H}$, in the thermal decomposition of HN_3 in shock waves. However, the possibility of the reaction, $2\text{NH}(X^3\Sigma^-) \rightarrow \text{Products}$, will be negligible, because the $\text{NH}(X^3\Sigma^-)$ concentration is low in our system.

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

$$\frac{1}{\phi_{\text{H}_2} + \phi_{\text{NH}_4\text{N}_3} - 1} = \frac{k_2 + k_3 + k_4}{k_2} + \frac{k_{15}[\text{Xe}]}{k_2[\text{HN}_3]}, \quad (\text{I})$$

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.

$$\frac{1}{4/(1 + R_{\text{N}_2}/R_{\text{H}_2}) - \alpha} = \frac{2k_2 + k_3 + k_4}{k_4} \left(1 + \frac{k_9}{k_8} + \frac{k_7}{k_8[\text{HN}_3]} \right), \quad (\text{II})$$

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 $k_7/k_8 = 2.27 \times 10^{-7}$ mol cm⁻³ are obtained.

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

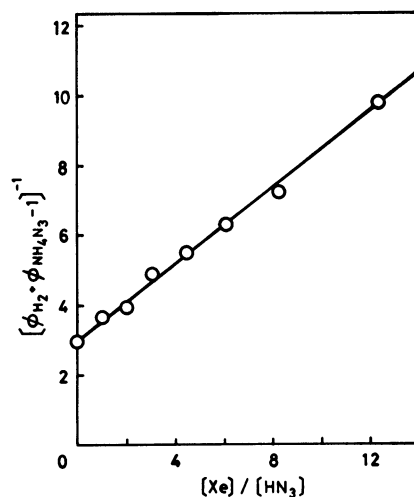
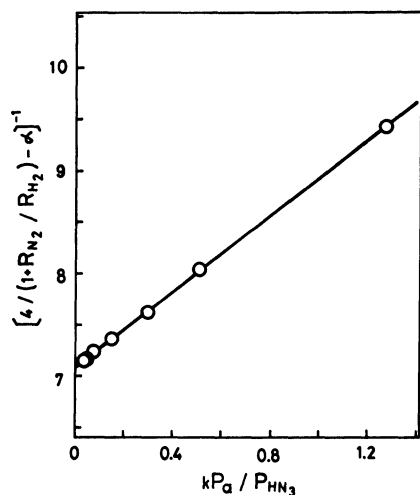
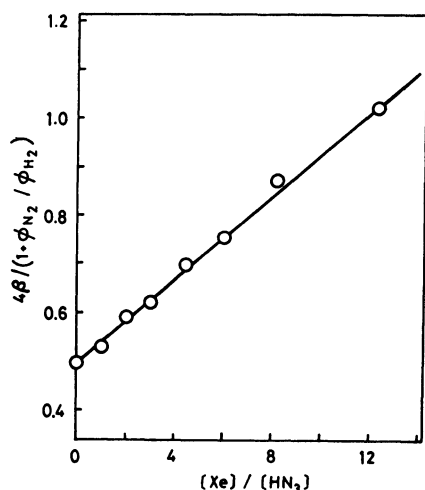


Fig. 7. Plot of $1/(\phi_{\text{H}_2} + \phi_{\text{NH}_4\text{N}_3} - 1)$ versus $[\text{Xe}]/[\text{HN}_3]$.

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 $[Xe]/[HN_3]$.

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

where

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

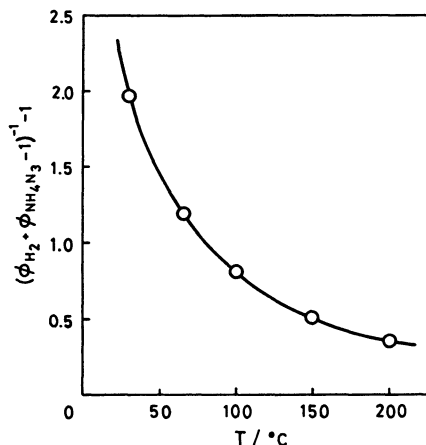
The plot of $4\beta/(1+\phi_{N_2}/\phi_{H_2})$ versus $[Xe]/[HN_3]$ at 6.7 kPa of HN₃ is shown in Fig. 9, and $k_{17}/k_{16}=3.22$ is obtained from the slope.

Equation I can be rewritten as

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

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

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

values calculated by using Eqs. V to VIII.

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

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

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

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

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 N₂ 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 N₂ 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 N₂ 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's³⁾ mechanisms are applied to Eq. VII, the values of $^{15}N^{15}N/N_2$ become 6.55 and 8.33%, respectively. Papazian⁴⁴⁾ has postulated the following mechanism in outline on the photolysis of HN₃ in frozen state: $HN_3+h\nu \rightarrow NH+N_2$; $NH+HN_3 \rightarrow HN=N-NH \rightarrow 2HN_2$; $NH+HN_2+HN_3 \rightarrow H_2N-N-NH+3/2 N_2$; $H_2N-N-NH \rightarrow NH_3+N_2$; 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 foreign gases. Of the various possible mechanisms, our mechanism of Reactions 1 to 14 gives the best agreement with the isotopic measurements.

I would like to thank Emeritus Professor Osamu Toyama and Professor Shigeru Yamashita of University of Osaka Prefecture for their helpful discussions. I would also like to thank Dr. Sotaro Esho and Mr.

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

Reaction No. <i>i</i>	Quantum yield of <i>i</i> -th reaction ϕ_i	Stoichiometry of N ₂ formation <i>S_i</i>	Probability ^{a)}		
			¹⁴ N ¹⁴ N α_i	¹⁴ N ¹⁵ N β_i	¹⁵ N ¹⁵ N 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 ¹⁵N in the labeled hydrazoic acid is 1.00. b) Values at 6.7 kPa of HN₃.

Hidetoshi Hori for support of this work.

References

- 1) A. O. Beckman and R. G. Dickinson, *J. Am. Chem. Soc.*, **50**, 1870 (1928); **52**, 124 (1930).
- 2) A. E. Myers and A. O. Beckman, *J. Am. Chem. Soc.*, **57**, 89 (1935).
- 3) B. A. Thrush, *Proc. R. Soc. London, Ser. A*, **235**, 143 (1956).
- 4) K. H. Welge, *J. Chem. Phys.*, **45**, 4373 (1966).
- 5) H. Okabe, *J. Chem. Phys.*, **49**, 2726 (1968).
- 6) R. S. Konar, S. Matsumoto, and B. DEB. Darwent, *Trans. Faraday Soc.*, **67**, 1698 (1971).
- 7) R. J. Paur and E. J. Bair, *J. Photochem.*, **1**, 255 (1973).
- 8) R. J. Paur and E. J. Bair, *Int. J. Chem. Kinet.*, **8**, 139 (1976).
- 9) L. G. Piper, R. H. Krech, and R. L. Taylor, *J. Chem. Phys.*, **73**, 791 (1980).
- 10) J. R. McDonald, J. W. Rabalais, and S. P. McGlynn, *J. Chem. Phys.*, **52**, 1332 (1970).
- 11) F. O. Rice and R. B. Ingalls, *J. Am. Chem. Soc.*, **81**, 1856 (1959).
- 12) K. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, **43**, 507 (1965).
- 13) The equation was derived from the material balance as to nitrogen atoms. [HN₃]₀ is the initial amount of HN₃.
- 14) D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1475 (1955).
- 15) P. A. Giguère and I. D. Liu, *J. Chem. Phys.*, **20**, 136 (1952).
- 16) The separation of H₂ from mixtures of H₂, O₂, N₂, CH₄, NO, and CO by this method was very favorable.
- 17) The formation ratio of NO to N₂ was about two-tenths, and the formation of N₂O was trace.
- 18) The equation was derived from the relations of [H] = 2[H₂] + 3[NH₄N₃], [N] = 2[N₂] + [NH₄N₃], and [N]/[H] = 3.
- 19) D. S. Herr and W. A. Noyes, *J. Am. Chem. Soc.*, **62**, 2052 (1940).
- 20) W. C. Richardson and D. W. Setser, *Can. J. Chem.*, **47**, 2725 (1969).
- 21) F. O. Rice and M. Freamo, *J. Am. Chem. Soc.*, **73**, 5529 (1951); F. O. Rice and C. Grelecki, *ibid.*, **79**, 1880 (1957); F. O. Rice and T. A. Luckenbach, *ibid.*, **82**, 2681 (1960).
- 22) O. Kajimoto, T. Yamamoto, and T. Fueno, *J. Phys. Chem.*, **83**, 429 (1979).
- 23) S. Kodama, *Bull. Chem. Soc. Jpn.*, **56**, 2355 (1983).
- 24) S. Kodama, *Bull. Chem. Soc. Jpn.*, **56**, 2363 (1983).
- 25) N. C. Baird, *J. Chem. Phys.*, **62**, 300 (1975).
- 26) J. R. McDonald, R. G. Miller, and A. P. Baronavski, *Chem. Phys. Lett.*, **51**, 57 (1977).
- 27) D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.*, **88**, 544 (1966).
- 28) F. Stuhl, dissertation, The University of Bonn, Bonn, Germany (1966).
- 29) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **41**, 2838 (1964).
- 30) P. H. H. Fischer, S. W. Charles, and C. A. McDowell, *J. Chem. Phys.*, **46**, 2162 (1967).
- 31) M. V. Thiel and G. C. Pimentel, *J. Chem. Phys.*, **32**, 133 (1960).
- 32) C. L. Currie and B. DEB. Darwent, *Can. J. Chem.*, **41**, 1552 (1963).
- 33) S. K. Vidyarthi, C. Willis, R. A. Back, and R. M. McKittrick, *J. Am. Chem. Soc.*, **96**, 7647 (1974).
- 34) R. S. Konar and B. DEB. Darwent, *Can. J. Chem.*, **48**, 2280 (1970).
- 35) A. E. Douglas and W. J. Jones, *Can. J. Phys.*, **43**, 2216 (1965).
- 36) J. Combourieu, G. Le Bras, and J. Barassin, *Bull. Soc. Chim. Fr.*, **1970**, 1271; G. Le Bras and J. Combourieu, *Int. J. Chem. Kinet.*, **5**, 559 (1973).
- 37) N. C. Baird and J. R. Swenson, *Can. J. Chem.*, **51**, 3097 (1973).
- 38) C. Willis and R. A. Back, *Can. J. Chem.*, **51**, 3605 (1973).
- 39) C. Willis, R. A. Back, and J. G. Purdon, *Int. J. Chem. Kinet.*, **9**, 787 (1977).
- 40) W. B. Rimmer, *Proc. R. Soc. London*, **103**, 696 (1923); A. Fowler and J. S. Badami, *ibid.*, **133**, 325 (1931); G. Herzberg and D. A. Ramsay, *Discuss. Faraday Soc.*, **14**, 11 (1953); D. A. Ramsay, *Mem. Soc. R. Sci. Liege Collect.*, **4**, **18**, 471 (1957); J. W. C. Johns, D. A. Ramsay, and S. C. Ross, *Can. J. Phys.*, **54**, 1804 (1976).
- 41) O. Kajimoto, T. Kawajiri, and T. Fueno, *Chem. Phys. Lett.*, **76**, 315 (1980).
- 42) E. D. Miller, Ph. D. Dissertation, Catholic University of America, Catholic University of America Press, Washington, D. C. (1961).
- 43) S. Tsunashima, J. Hamada, M. Hotta, and S. Sato, *Bull. Chem. Soc. Jpn.*, **53**, 2443 (1980); T. Kitamura, S. Tsunashima, and S. Sato, *ibid.*, **54**, 55 (1981).
- 44) H. A. Papazian, *J. Chem. Phys.*, **32**, 456 (1960).