COLLISION ENERGY DEPENDENCE OF THE OVERALL RATE CONSTANT FOR THE REACTION $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$

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The overall rate constant for the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ has been determined by the laser photolysis of hydrogen azide (HN_3) at 266 nm and 193 nm. The visible emission from vibrationally excited $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ was dispersed and its time-dependent profiles were measured at several wavelengths. The rate constants are dependent not only on the photolysis wavelengths but also on the vibrational levels of the $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ produced in the reaction. The intermolecular potential between $\text{NH}(\text{a}^1\Delta)$ and HN_3 was determined to be the form $V(R) = -C/R^s$ ($2 < s < 4$, C: constant) from the analysis with a long-range potential approximation. The interaction between $\text{NH}(\text{a}^1\Delta)$ and HN_3 is mainly governed by the dipole-dipole interaction in the initial stage of the reaction.

KEY WORDS: Chemiluminescence, Rate constant, NH , NH_2 , HN_3 .

INTRODUCTION

Chemiluminescence is due to the reactions which produce emissive excited states. Such highly reactive species as atoms and radicals are frequently related with the production of the electronically excited states. Chemiluminescence was observed in many reaction systems; nevertheless, most of the mechanisms have not completely been resolved yet. The goal of the present study is not only to make clear the reaction mechanism but also to investigate the effect of a collision energy on a chemiluminescent reaction. Spectroscopic information reveals a source of the emission and a kinetic study gives the reaction mechanism of the chemiluminescence. The visible emission in the HN_3 photolysis system was studied in the present work.

There have been a few reports on the chemiluminescence in the photodissociation of hydrogen azide HN_3 . Okabe¹ first observed the emission over the range of 430–800 nm in the photolysis of HN_3 with rare gas lamps (Xe and Kr). He assigned the source of the emission to the transition of N_2 first-positive band ($\text{B}^3\Pi_g - \text{A}^3\Sigma_u^+$). McDonald and co-workers,^{2–4} who performed pioneering works on the photolysis of HN_3 , observed visible emission in the 266 nm photolysis. They proposed that the emission was due to the transition of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{B}_1)$ only by comparing with its

absorption wavelength. They also proposed a reaction $\text{NH}(a^1\Delta, v = 0) + \text{HN}_3 \rightarrow \text{NH}_2(\tilde{A}^2A_1) + \text{N}_3$ for the mechanism on the basis of the heat of reaction.

Piper *et al.*⁵ observed temporal profiles not only of the visible emission but also of the laser-induced fluorescence (LIF) of $\text{NH}(c^1\Pi-a^1\Delta)$. They reported that both profiles were consistent with the mechanism proposed by McDonald *et al.*, although their rate constant was about two times larger than that measured by McDonald *et al.* The mechanism had been accepted with little doubt since then and no study showed the direct information on the origin of the emission by more reliable spectroscopic technique. The overall rate constant for the reaction $\text{NH}(a^1\Delta, v = 0) + \text{HN}_3$ has also been reported using various techniques;⁶⁻¹⁰ however, there have been few studies on the reaction products, particularly on the electronically excited states.

In our previous study,¹¹ we reported a direct evidence for the source of the emission [$\text{NH}_2(\tilde{A}^2A_1-\tilde{X}^2B_1)$] and for how the emissive species are produced in the HN_3 photolysis at 266 nm. We observed dispersed fluorescence spectra that were not necessarily consistent with the mechanism accepted before and gave a modified reaction mechanism including internally excited $\text{NH}(a^1\Delta)$.

In the present study, the overall rate constant for the reaction $\text{NH}(a^1\Delta) + \text{HN}_3$ has been determined using different photolysis wavelengths (266 nm and 193 nm) and given information on the reaction dynamics. The rate constants were found to be dependent not only on the photolysis wavelength but also on the vibrational levels of the $\text{NH}_2(\tilde{A}^2A_1)$ produced in the reaction. The rate constants reduce with an increase in the energy of photodissociation and with a decrease in the vibrational energy of the product $\text{NH}_2(\tilde{A}^2A_1)$. The results are rationalized by the generation of centrifugal potential barrier due to the large translational energy of $\text{NH}(a^1\Delta)$. The relation between the rate constant and collision energy will be discussed.

EXPERIMENTAL

The experiments were carried out in a quasistatic laser photolysis system.¹¹ Photolysis of HN_3 at two different wavelengths were performed: 266 nm from Nd^{3+} :YAG laser (Continuum YG660-20, 0.2–5 mJ pulse⁻¹) and 193 nm from ArF excimer laser (Lambda Physik Lextra-50SL, 1–5 mJ pulse⁻¹). Typical repetition rate was 4–10 Hz. Both laser beams were trimmed with an aperture to 6 mm in diameter. The cell made of Pyrex tube has two ports for observation with quartz window of 22 mm in diameter and was evacuated with a rotary pump (ULVAC D-950). The pressure of the sample gas was monitored with a capacitance manometer (Baratron 122AA).

Emission from the observation region was collected through a long-pass filter (Toshiba Y-43) and was focused with a lens ($f = 80$ mm) on the entrance slit of a monochromator (Nikon P-250). Spectral resolution was 3 nm (FWHM). The signal from a photomultiplier (Hamamatsu R928) mounted on the exit slit was sent to a home-made amplifier ($\times 10$) and then fed into a gated integrator (Stanford Research Systems SR-250). The signals of 30 pulses were averaged. In order to correct for the shot-to-shot laser fluctuations, undispersed emission was focused with a lens ($f = 60$ mm) on another photomultiplier (Hamamatsu 1P28) through a filter (Toshiba

0–54) at the opposite side of the monochromator. The signal from the 1P28 was amplified ($\times 10$) and inverted with a home-made amplifier and then averaged with a home-made gated integrator. Both dispersed and undispersed emission signals were fed into an A/D interface and sent to a computer.

When the temporal behavior of the emission intensity was observed, the signal from the photomultiplier was amplified ($\times 300$) and digitized with a home-made transient memory whose time resolution was 40 ns. Signals of 15000–30000 pulses were averaged to obtain a good S/N ratio. The relative laser fluence was monitored with a photodiode and averaged with a gated integrator. Data acquisition system was the same as that described in the spectroscopic study.

Hydrogen azide, HN_3 , was synthesized *in vacuo* by the reaction between sodium azide and stearic acid according to the procedure in ref. 12.

RESULTS AND DISCUSSION

Spectroscopic Study

Figure 1 shows a dispersed emission spectrum that was observed in the 266 nm photolysis of HN_3 (ref. 11). Significant progression appears along with a broad background. Since the overall sensitivity of the detection system was not corrected, the decrease in the intensity at longer wavelengths does not show the correct intensity distribution but reflects the sensitivity of the detection system. Moreover, the filter used (Toshiba Y-43) was transparent only at longer wavelength than 420 nm; the

Figure 1 Dispersed emission spectrum observed in the $\text{HN}_3/266\text{nm}$ photolysis. Pressure of HN_3 was 150 mTorr with no buffer gas; spectral resolution was 3 nm (FWHM). The assignments are appropriate to the linear configuration for the $\tilde{A}^2A_1$ state (ref. 13). The onset about 420 nm is due to the filter used.

Figure 2 Dispersed emission spectrum observed in the $\text{HN}_3/193\text{ nm}$ photolysis. The pressure of HN_3 was 18 mTorr with no buffer gas; the spectral resolution was 3 nm (FWHM).

onset of the spectrum at short wavelength is due to the transmission of the filter. Most of the peaks were assigned to the transition $\text{NH}_2(\tilde{A}^2A_1(0, v_2', 0) - \tilde{X}^2B_1(0, 0, 0))$. The broad background results from rotational excitation of $\text{NH}_2(\tilde{A}^2A_1)$ and/or congestion of many weak vibronic sub-bands.^{13–15} The spectrum shows the excitation of the v_2 -bending vibrational levels up to at least $v_2' = 15$. Figure 2 shows a dispersed emission spectrum in the $\text{HN}_3/193\text{ nm}$ photolysis recorded under the same detection system. The envelope of the spectrum is very similar to that of 266 nm photolysis and the peaks can also be assigned to the transition of $\text{NH}_2(\tilde{A}^2A_1 - \tilde{X}^2B_1)$.

The spectra observed with 266 nm and 193 nm are essentially the same each other. The fact suggests that the temporally averaged vibrational distributions are not different in both photolyses.

McDonald *et al.*^{2–4} proposed that $\text{NH}_2(\tilde{A}^2A_1)$ was produced in the reaction $\text{NH}(a^1\Delta, v = 0) + \text{HN}_3 \rightarrow \text{NH}_2(\tilde{A}^2A_1) + \text{N}_3$. The maximum vibrational quantum number can be estimated from the heats of formation of all species related to the reaction on the assumption that all the exothermicity of the reaction is deposited into NH_2 . The $\Delta H_{f,0}^\circ$ values, for $\text{HN}_3(\tilde{X}^1A')$, $\text{NH}(\tilde{X}^3\Sigma^-)$, and $\text{NH}_2(\tilde{X}^2B_1)$ have been determined precisely: $300.5 \pm 0.3\text{ kJ mol}^{-1}$,¹⁶ $357 \pm 1\text{ kJ mol}^{-1}$,¹⁷ $192 \pm 1\text{ kJ mol}^{-1}$,¹⁷ respectively. The 0-0 transition energies are known for $\text{NH}(a^1\Delta - \tilde{X}^3\Sigma^-)$ and $\text{NH}_2(\tilde{A}^2A_1 - \tilde{X}^2B_1)$: 12589 cm^{-1} ,¹⁸ 10249 cm^{-1} .¹⁹ For N_3 , unfortunately, an accurate heat of formation is not available. Although $\Delta H_{f,0}^\circ(\text{N}_3) = 417 \pm 21\text{ kJ mol}^{-1}$ ²⁰ has been adopted for a long time, recent reliable reports using various techniques recommended higher values: $469 \pm 21\text{ kJ mol}^{-1}$ from ion cyclotron resonance of N_3^- ,²¹ $<475.3\text{ kJ mol}^{-1}$ in the study of the reaction $\text{F} + \text{HN}_3 \rightarrow \text{HF}(v \leq 4) + \text{N}_3$,²² 457.1 kJ mol^{-1} from quantum-mechanical calculation;²³ 451.5 kJ mol^{-1} from the dissociation energy of $\text{H}-\text{N}_3$

bond.²⁴ These values give the maximum vibrational quantum number $v_2'_{\max} = 0-5$, <2 , 4 and 5, respectively. Therefore, the production of highly excited vibrational levels at lowest $v_2' \geq 10$ of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ cannot be ascribed to only the reaction between $\text{NH}(\text{a}^1\Delta, v = 0) + \text{HN}_3$.

Since the rotational motion of nascent $\text{NH}(\text{a}^1\Delta)$ produced in the uv photolysis is not highly excited at any wavelength,²⁵ there are two possible sources to produce the high vibrational levels of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ in the reaction. One is a vibrational energy and the other is a translation energy of $\text{NH}(\text{a}^1\Delta)$. There have been many works on the energy partitioning in the $\text{NH}(\text{a}^1\Delta)$ produced in the HN_3 photolysis,^{10, 26-31} whereas the vibrational distribution of nascent $\text{NH}(\text{a}^1\Delta, v)$ is still a matter of controversy. Nelson and McDonald²⁶ have reported the energy partition in the HN_3 photolysis at 266 nm. According to their summary, the vibrational distribution of nascent $\text{NH}(\text{a}^1\Delta, v)$ is $1.0/(1.1 \pm 0.3)/(0.8 \pm 0.3)/(0.9 \pm 0.5)$ for $v = 0/1/2/3$. Hawley et al.³¹, however, have recently reported a totally different distribution: $1.0/0.3/0.02$ for $v = 0/1/2$. These data were obtained in the same laboratory; the reason for the discrepancy is unclear. The 193 nm photolysis has not been concluded, either. Misra and Dagdigian²⁹ reported the vibrational distribution to be $1.0/(0.66 \pm 0.05)/(0.09 \pm 0.05)$ for $v = 0/1/2$. Bohn and Stuhl,³⁰ on the other hand, reported more highly excited distribution: $1.0/(0.48 \pm 0.11)/(0.21 \pm 0.07)/(0.13 \pm 0.05)$ for $v = 0/1/2/3$.

A translational energy of $\text{NH}(\text{a}^1\Delta)$, on the other hand, has been determined by Nelson and McDonald²⁶ to be $6000-7000 \text{ cm}^{-1}$ from Doppler-broadening in the 266 nm photolysis. Rohrer and Stuhl²⁷ have reported that the nascent $\text{NH}(\text{a}^1\Delta)$ has a translational energy of 26000 cm^{-1} in the 193 nm photolysis.

The emission spectra observed in the 266 nm and 193 nm photolysis are almost the same in the present study. If translational energy is effective to produce highly excited $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$, there must be a difference in the spectra owing to the large difference in the translational energy of $\text{NH}(\text{a}^1\Delta)$ colliding with HN_3 . Thus we tentatively conclude that the vibrational energy in the $\text{NH}(\text{a}^1\Delta)$ is more effective to produce highly excited $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ than the translational energy.

Time resolved emission intensity should be observed to obtain information on the difference in kinetics.

Kinetic Study

In the photolysis at 266 nm, a laser fluence dependence and temporal profiles of dispersed emission were measured at 520, 600 and 660 nm, where the emissions were due mainly to the transitions from $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1) v_2' = 12, 9$, and 7 to $\tilde{\text{X}}^2\text{B}_1 v_2'' = 0$, respectively. The emission intensities are linearly dependent on the laser fluence irrespective of the observation wavelengths. Linear dependence does not necessarily correspond to a one-photon process because two-photon process shows the first-order dependence if the first excitation is not effective and there is no process competing with the second absorption. This is not the case because HN_3 on the upper potential undergoes fast predissociation.¹² Consequently, the dependence observed shows that an only photon is associated with the production of single $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ molecule.

In the photolysis at 193 nm, the emission of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1-\tilde{\text{X}}^2\text{B}_1)$ was observed at 520, 600 and 630 nm, where the emission due to the transitions from the $v_2' = 12$, 9, and 8 levels of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ state. Typical profiles observed are shown in Figure 3. The emission intensity also varied linearly with laser fluence as the same as that observed in the 266 nm photolysis.

The reaction mechanism established in our previous work is as follows:¹¹

where the “products” denotes all the possible species produced in quenching and/or reactions. It should be noted that a faster process always governs the rise and a slower one relates to the fall (Fig. 3). In the present experiment, the rise must be related to deactivation of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ because of its extraordinary large quenching rate constant,^{32,33} for example, $1.45 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ even by helium and

Figure 3 Time resolved emission of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1-\tilde{\text{X}}^2\text{B}_1)$ in the $\text{HN}_3/193 \text{ nm}$ photolysis observed at 520 nm (a) and at 630 nm (b). Pressure of HN_3 was 30 mTorr with no buffer gas. The dots denote the observed data and the solid line is the results of simulation.

short radiative lifetime $k_5 = 1.0 \times 10^5 \text{ s}^{-1}$.^{32,34} Accordingly, the fall corresponds to the overall decay of the reactions [$k_2 (= k_{2a} + k_{2b})$] for $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ and radiation or diffusion (k_3) of $\text{NH}(\text{a}^1\Delta)$.

The absorption cross-sections of HN_3 at 266 nm and at 193 nm are $7.4 \times 10^{-20} \text{ cm}^2$ and $1.7 \times 10^{-18} \text{ cm}^2$, respectively.¹² From the laser fluences and the sizes of the laser beams, the densities of photons at 266 nm and 193 nm were estimated to be 3.6×10^{15} and $1.3 \times 10^{15} \text{ photons cm}^{-2}$. The ratios of the initial concentration of $\text{NH}(\text{a}^1\Delta)$ to that of HN_3 are about to be 2.0×10^{-4} at 266 nm photolysis and 2.1×10^{-2} in the 193 nm photolysis with the quantum yield for the formation of $\text{NH}(\text{a}^1\Delta)$.³⁵ Therefore, the pseudo-first-order reaction conditions are always satisfied in both the reactions (3) and (5), thus there is little change in the concentration of HN_3 during the reaction.

In addition to the double-exponential fitting, the Simplex optimization method coupled with the Runge-Kutta-Gill numerical integration of the rate equations was adopted in the analysis of the temporal profiles. The overall rate constants $k_2 (= k_{2a} + k_{2b})$ measured at different wavelengths are $k_2(520 \text{ nm}) = (1.2 \pm 0.1) \times 10^{-10}$, $k_2(600 \text{ nm}) = (0.97 \pm 0.1) \times 10^{-10}$, and $k_2(660 \text{ nm}) = (0.84 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 266 nm photolysis and $k_2(520 \text{ nm}) = (0.92 \pm 0.2) \times 10^{-10}$, $k_2(600 \text{ nm}) = (0.61 \pm 0.2) \times 10^{-10}$, and $k_2(630 \text{ nm}) = (0.35 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 193 nm photolysis as listed in Table 1. The errors denote 2σ in the analysis. The order of the rate constants is the same as that recently measured by $\text{NH}(\text{c}^1\Pi - \text{a}^1\Delta)$ LIF [$(1.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]⁸ and much different from that for $\text{H} + \text{HN}_3 \rightarrow \text{NH}_2(\tilde{\text{A}}^2\text{A}_1) + \text{N}_2$ reaction ($1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).³⁶ Therefore, the $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ is produced by the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ also in the 193 nm photolysis.

Table 1 The overall rate constants for the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ determined by the analysis of temporal profiles of the emission from $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$. The rate constants are in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The errors denote 2σ .

Photolysis wavelength	Observed wavelength			
	520 nm	600 nm	630 nm	660 nm
266 nm	1.2 ± 0.1	0.97 ± 0.1	–	0.84 ± 0.1
193 nm	0.92 ± 0.2	0.61 ± 0.2	0.35 ± 0.2	–

The dependence of the first-order decay rate on the pressure of buffer gas (He and Xe) was measured in the study on the 266 nm photolysis. The temporal profiles of the emission were observed through a cut-off filter (Toshiba R-61) which is transparent for the light longer than 610 nm. Thus, the emission observed was mainly due to the transition from $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1, v_2' < 8)$. Since Xe is known to be a fast quencher of $\text{NH}(\text{a}^1\Delta)$ ($1.28 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),^{29,37–39} the apparent first-order decay rate should increase under the presence of Xe. On the other hand, He has much less effective quencher ($< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),¹⁰ and can hardly affect the decay rate. Figure 4 shows the dependence of the first-order decay rate on the pressure of the buffer gas. The first-order decay rate is affected by Xe but little by He. Since

Figure 4 Dependence of the first-order decay rate (k_{decay}) on the buffer gas pressure (P_M). Pressure of HN_3 was 20 mTorr. The time resolution was 1 μs . Closed circle ● denotes the results of He and open circle ○ denotes the effect of Xe.

the dependence was measured with low time resolution (1 μs) under the static conditions, the data shows a qualitative result. Nevertheless, the difference between Xe and He also supports the mechanism that the $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ is produced by the reaction between $\text{NH}(\text{a}^1\Delta)$ and HN_3 .

The overall rate constants obtained for the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ apparently depend on the photolysis wavelength. The rate constants in the 193 nm photolysis are smaller than those in the 266 nm photolysis. Since no buffer gas was used in the present study, the translational energy of $\text{NH}(\text{a}^1\Delta)$ is not relaxed until the first collision with HN_3 . Therefore, collision energies for the $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ reaction are very different between the 266 nm and the 193 nm photolysis: translational energy of the nascent $\text{NH}(\text{a}^1\Delta)$ is 6000–7000 cm^{-1} ²⁶ and 26000 cm^{-1} ²⁷ in the 266 nm and 193 nm photolysis, respectively. The overall rate constant of the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ determined by $\text{NH}(\text{c}^1\Pi-\text{a}^1\Delta)$ LIF was independent of temperature,⁴⁰ hence the reaction proceeds with no barrier. However, the apparent decrease in the rate constants was shown in the present study with an increase in the translational energy. Note that buffer gas of about 10–20 Torr was added in the LIF experiment and that no buffer gas was used in the present experiment. Since the $\text{NH}(\text{a}^1\Delta)$ has a large translational energy without buffer gas, the centrifugal potential barrier on the reaction coordinate must be taken into account.

Relation between reaction rate constant and collision energy is expressed by the next equation [Eq. (A-5) in Appendix]:⁴¹

$$k \propto E_T^{(s-4)/2s},$$

where E_T is a collision energy of the system and s is a parameter in the function of the potential ($V(R) \propto -1/R^s$). The overall rate constants in the present study decrease with an increase in the translational energy (Table 1); as a result, the parameter s for the potential energy at long distance must be less than 4. Potential energies whose radial distributions are consistent with our result ($2 < s < 4$) are those for charge-quadrupole ($s = 3$) and dipole-dipole interactions ($s = 3$) in a specific intermolecular orientation. No electrostatic interactions have the dependence, $2 < s < 4$, when being averaged over possible orientation under Boltzmann distribution. Since there is no charged reactants, the $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ reaction system is governed mainly by dipole-dipole interaction at a specific orientation of the molecules. Hydrogen azide HN_3 has relatively large dipole moment: $\mu_a = 0.84$ and $\mu_b = 1.48$ Debye, where μ_a and μ_b denote the dipole moments along principle axes of inertia. Although the dipole moment of $\text{NH}(\text{a}^1\Delta)$ has not been reported, the ground state $\text{NH}(\text{X}^3\Sigma^-)$ has $\mu = 0.98$ Debye. Accordingly, it can be concluded that the interaction potential between $\text{NH}(\text{a}^1\Delta)$ and HN_3 is mainly governed by the dipole-dipole interaction.

The overall rate constants for the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$ depends not only on the photolysis wavelength but also on the observation wavelength. As seen in Table 1, the smaller rate constants are obtained at longer observation wavelengths. The difference is more apparent in the 193 nm photolysis than that in the 266 nm photolysis. In other words, a large translational energy suppresses the production of lower vibrational states of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$. There has been no information as to whether the reaction goes through a complex mechanism or a direct mechanism in terms of the reaction dynamics. It is reasonable that the period of interaction is short in the collisions with high translational energy. If the structure of H-N-H cannot relax to quasi-linear configuration during the interaction time, $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ with low vibrational energy is not likely to be produced. (The equilibrium structure is quasi-linear ($\angle\text{HNH} = 144^\circ$ in the $\tilde{\text{A}}^2\text{A}_1$ state and bent in the $\tilde{\text{X}}^2\text{B}_1$ state).⁴² Further experiments are needed into the problem, for example, the decay of $\text{NH}(\text{a}^1\Delta)$ produced by the photolysis without buffer gas must be directly measured.

CONCLUSION

The visible emission following the ultraviolet photolysis of HN_3 originates from the vibronically excited $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$. All the vibrational levels of $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ are produced in the reaction of $\text{NH}(\text{a}^1\Delta)$ with HN_3 , and highly vibrationally excited $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ is produced from vibrationally excited $\text{NH}(\text{a}^1\Delta)$. From the measurement of the photolysis wavelength dependence of the overall rate constants for the reaction $\text{NH}(\text{a}^1\Delta) + \text{HN}_3$, a long-range potential between the reactants was determined to be the form:

$$V(R) = -\frac{C}{R^s}, \quad (2 < s < 4, C: \text{constant})$$

The value of s indicates that the potential between reactants at long distance is mainly governed by the dipole-dipole interaction. The overall rate constants for the reaction

$\text{NH}(\text{a}'\Delta) + \text{HN}_3$ depend also on the observed wavelengths, which suggests that $\text{NH}_2(\tilde{\text{A}}^2\text{A}_1)$ with low vibrational energy is not likely to be produced when $\text{NH}(\text{a}'\Delta)$ has large translational energy.

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APPENDIX

The relation between rate constant and collision energy is derived according to the formulation of ref. 41. The total energy E_T of the reaction system is expressed by

$$E_T = \frac{1}{2}\mu\dot{R}^2 + \frac{E_T b^2}{R^2} + V(R), \quad (\text{A-1})$$

where μ denotes reduced mass, R distance between colliding molecules, b impact parameter, and $V(R)$ potential energy. An effective potential $V_{\text{eff}}(R)$ is defined by the sum of the potential energy and the centrifugal energy:

$$V_{\text{eff}}(R) = V(R) + \frac{E_T b^2}{R^2} \quad (\text{A-2})$$

Since the reaction $\text{NH}(\text{a}'\Delta) + \text{HN}_3$ has no threshold energy, the only barrier during approach of the reactants is the centrifugal barrier due to the large translational energy of $\text{NH}(\text{a}'\Delta)$.

A parameter b_{max} is defined as the maximum impact parameter with which colliding molecules can approach within R_{max} . R_{max} is the distance where the centrifugal barrier takes its maximum. It is now defined that the reaction occurs whenever the radial distance R is smaller than R_{max} . A rate constant k is expressed by the product of the reaction-cross section and the relative velocity:

$$k = \sigma_R u = \pi b_{\text{max}}^2 u. \quad (\text{A-3})$$

Large rate constant ($1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction $\text{NH}(\text{a}'\Delta) + \text{HN}_3$ corresponds to a large reaction cross section. The fact means that the reactants interact even at long distance and the initial stage of the reaction is governed by a long-range attractive force. The potential between the reactants can be assumed to be the form:

$$V(R) = -\frac{C}{R^s}, \quad (\text{A-4})$$

The rate constant is expressed by

$$k = \pi q(s) C^{1/2} \left(\frac{2}{\mu} \right)^{2/s} E_T^{(s-4)/2s} \quad (\text{A-5})$$

where s and C are constants.

$$q(s) = (s/2)[(s-2)/2]^{-(s-2)/s} \quad (\text{A-6})$$

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