Bull. Chem. Soc. Jpn., 59, 1671—1674 (1986)

Phase-Shift Studies of the Quenching of NH($c^1\Pi$) by HN_3, NO, CO, and CO_2

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(Received December 26, 1985)

Absolute cross sections for quenching NH($c^1\Pi$) by the use of several inorganic molecules were determined at room temperature by using a phase-shift method. The NH($c^1\Pi$) radicals were produced by the photolysis of HN_3 using an amplitude-modulated Xe-resonance lamp. The results obtained were as follows: 0.01(He), 12(HN_3), 48(NO), 49(CO), and 30(CO_2) in units of 10^{-16} cm^2. In the case of NO, the 336 nm emission was enhanced, which suggests that NO quenches NH($c^1\Pi$) to NH($A^3\Pi$). From the phase difference between the 325 and 336 nm emissions, the quenching cross-section of NO for NH($A^3\Pi$) was estimated to be 60×10^{-16} cm^2.

A number of emission and absorption bands of NH radicals have been investigated by using the photolysis or electron impact of HN_3, NH_3, and HNCO.[1] The spectroscopic properties of NH radicals in the lower excited states are now well-known.[2] The energy-level diagram of the NH radical is shown in Fig. 1. The reactivities of these different states of NH radicals are, however, not well understood yet. Recently, we showed that the reactions of NH($a^1\Delta$) with hydrocarbons are very much similar to those of the isoelectronic species, O(^1D) and $CH_2(^1A_1)$: The NH($a^1\Delta$) radical inserts into the C–H bond and adds to the double bond of hydrocarbons.[3]

The quenching of the NH($b^1\Sigma^+$) state by various molecules was studied by Zetsch and Stuhl[4] and by Gelernt et al.[5] The rate constants of the quenching of NH($c^1\Pi$) and NH($A^3\Pi$) states by rare gases, H_2, and N_2 have been measured by Kawasaki et al., using the vuv photolysis of NH_3.[6] The quenching rates were estimated from the pressure dependence of the fluorescence intensities at 325 and 336 nm. On the other hand, the radiative lifetime of NH($c^1\Pi$) has been estimated to be 0.43[7] or 0.48[8] μs by the phase-shift method using a modulated electron beam. Since the bombardment of high-energy electrons produces not only NH($c^1\Pi$) but also the higher excited states of NH, the effect of the "cascading" from these excited states was taken into account.[7,8] Clerc et al. also estimated the lifetime of the NH($c^1\Pi$) state to be 0.50 μs from the decay rate of the fluorescence at 325 nm in the pulse radiolysis of NH_3.[9] Similar values were obtained in the studies of the pulse vuv photolysis of HNCO[10] and the 193-nm laser photolysis of HN_3.[11]

In the present study, a phase-shift method is used to determine the rate constants of the quenching of the NH($c^1\Pi$) state by several molecules, using an amplitude-modulated Xe resonance lamp. Here, the effect of the "cascading" may be ignored.

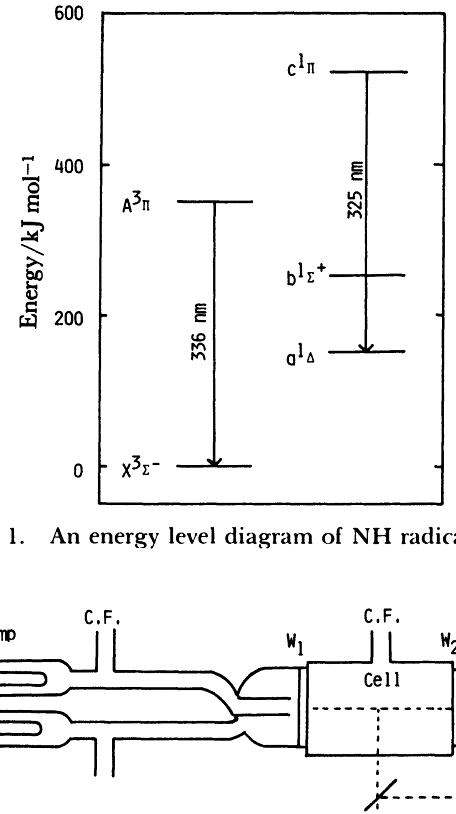

Fig. 1. An energy level diagram of NH radical.

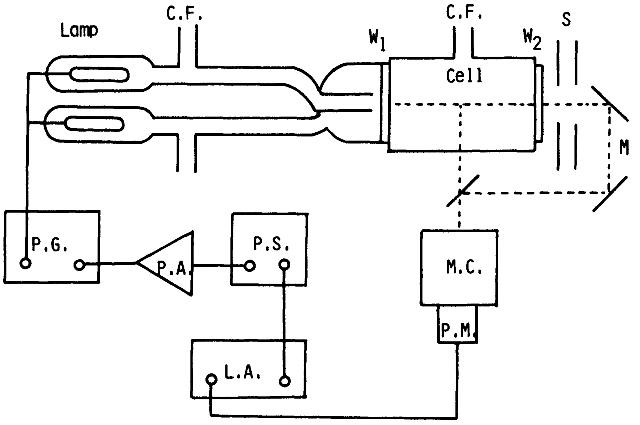

Fig. 2. A block diagram of the experimental apparatus: M; mirror, S; slit, W_1; LiF window, W_2; LiF window coated with sodium salicylate, C.F.; to circulating fan, M.C.; monochromator, P.M.; photomultiplier, L.A.; lock-in amplifier, P.S.; phase shifter, P.A.; pre-amplifier, P.G.; power generator.

Experimental

A block diagram of the experimental arrangement is shown in Fig. 2. The light source used was a home-made Xe-discharge lamp. The power of the lamp was supplied by a home-made power generator which had been used for previous studies of the mercury photosensitized luminescence.[12] The intensities were modulated at a frequency of 100 or 120 kHz, using the reference signal of a lock-in amplifier (NF Circuit Design Block Co., LI 573). A mixture of He (≈20 Torr; 1 Torr=133.3 Pa) and Xe

(≈0.06 Torr) was circulated in the lamp by means of an all-glass-made fan. This mixture was found to be suitable for effective modulation at high frequencies. The light from the lamp illuminated a Pyrex fluorescence cell, 50 mm in length and 30 mm o.d., through a LiF window. In order to detect the transmitted light, another LiF window coated with sodium salicylate was attached to the opposite side of the cell.[13] The emission from sodium salicylate was measured at 415.5 nm with a photomultiplier (Hamamatsu Photonics, 1P28) through a monochromator (Japan Spectroscopic Co., CT-25N). The signal from the photomultiplier was fed into the lock-in amplifier, and its phase angle was measured relative to the internal signal of the lock-in amplifier. Since the radiative lifetime of sodium salicylate is about 10 ns,[13] the phase angle thus measured can be considered to be equal to that of the excitation light from the lamp.

The fluorescence cell had two side arms for circulating the reaction mixture by means of an all-glass-made fan. The reaction mixture was diluted with He, typically 20 or 13 Torr. The fluorescence from the cell was measured at right angles to the excitation light using the same monochromator and photomultiplier as were used for the measurement of the emission from sodium salicylate. The phase angle of the fluorescence was also measured relative to that of the internal signal of the lock-in amplifier.

The phase-control dial of the lock-in amplifier was calibrated with a phase shifter (NF Circuit Design Block Co., UP 725), while the phase shifter was calibrated by drawing a Lissajous figure on an oscilloscope (Iwatsu Co., SS-5100). The phase shifter was also used to shift the phase angle of the reference signal so that the measured phase angle was kept in the linearly changing region of the phase-control dial.

The HN_3 was synthesized and purified by the method described in a previous paper.[3] The He (Suzuki Shokan Co.) was used after having been passed through a column packed with reduced copper at 300 °C and a trap packed with molecular sieve 4A at −196 °C. The NO, CO, CO_2, and Xe (Takachiho Shoji Co.) were used after having been distilled at low temperatures.

Results

When 0.1 Torr of HN_3 diluted with 20 Torr of He was irradiated with the Xe lamp, fluorescence was observed at about 325 nm. The spectrum was the same as that observed by Okabe,[14] and it was identified as the emission from $NH(c^1\Pi)$. The phase angle of the fluorescence was measured within the initial few minutes of irradiation, since a long irradiation caused a decrease in the emission intensity and its phase angle.

The difference in the phase angle between the 415.5 and 326 nm emissions, ϕ_1, was measured at the modulation frequencies of 100 and 120 kHz, and at various pressures of HN_3 and He. From the measurements of ϕ_1, the decay rate of $NH(c^1\Pi)$, R_1, was estimated by means of this relation: $R_1 = 2\pi f / \tan\phi_1$, where f denotes the frequency of the modulation (for details, see below). The decay rates thus determined are plotted in Figs. 3 and 4 as functions of the pressures of HN_3 and He respectively. The plots shown in Fig. 3 give a straight line with an intercept of $(2.2\pm0.1)\times10^6\,s^{-1}$ and a slope of $(5.2\pm0.7)\times10^{13}\,cm^3\,mol^{-1}\,s^{-1}$. The intercept and the slope of the straight line in Fig. 4 were $(2.8\pm0.1)\times10^6\,s^{-1}$ and $(1.1\pm0.1)\times10^{11}\,cm^3\,mol^{-1}\,s^{-1}$ respectively. All error limits quoted in this paper correspond to one standard deviation.

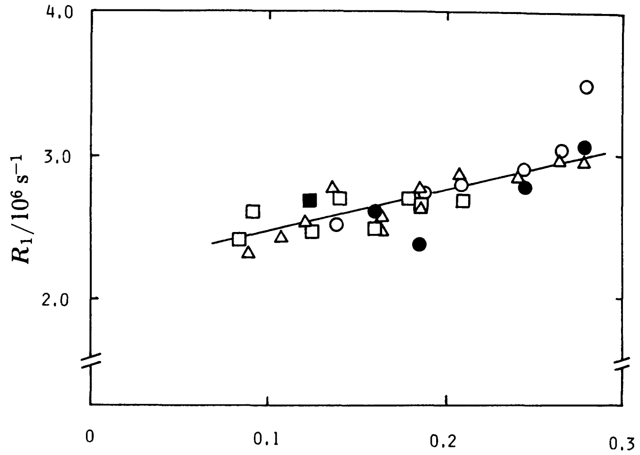

Fig. 3. Plots of R_1 against the pressure of HN_3: open symbols; f=100 kHz and closed symbols; f=120 kHz, [He]=20(○), 13.3(△), and 8.8(□) Torr.

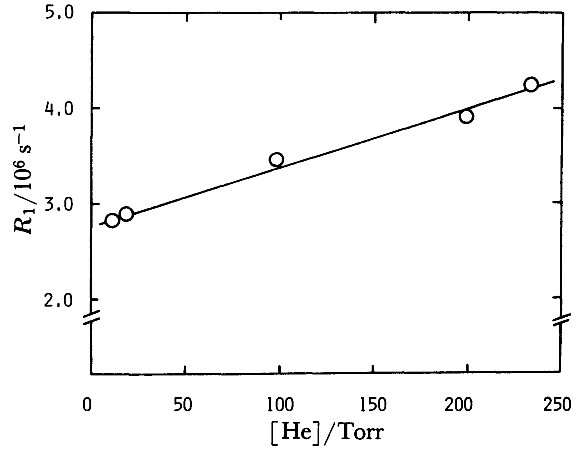

Fig. 4. Plots of R_1 against the pressure of He obtained at f=120 kHz and $[HN_3]$=0.244 Torr.

When a quencher, such as NO, CO, or CO_2, was added to a mixture of HN_3 (0.123 Torr) and He (20 Torr), the decay rate, R_1, increased. The decay rates are plotted as functions of the pressures of the quenchers in Fig. 5. The plots show straight lines for every quencher examined. The slopes and the intercepts of the straight lines are summarized in Table 1.

In the case of NO, a fluorescence at 336 nm was observed in addition to the 325-nm fluorescence. The spectrum was the same as that identified as the emission from $NH(A^3\Pi)$.[14] The phase difference between the 325 and 336-nm fluorescences, ϕ_3, was determined at various pressures of NO and HN_3. The $2\pi f/\tan\phi_3$

Table 1. The Intercepts and the Slopes of the Straight Lines Shown in Fig. 5 and the Quenching Cross-Sections

Quencher	Intercept	Slope	Cross-section[a)]	
Q	$10^6\,s^{-1}$	$10^{14}\,cm^3\,mol^{-1}\,s^{-1}$	Obsd.	Ref.
CO_2	2.30±0.07	1.34±0.20	30	
CO	2.23±0.11	2.37±0.38	49	27,[b)] 61[c)]
NO	2.25±0.09	2.31±0.34	48	21[b)]

a) In units of $10^{-16}\,cm^2$. b) Private communication from M. Kawasaki. c) Ref. 14.

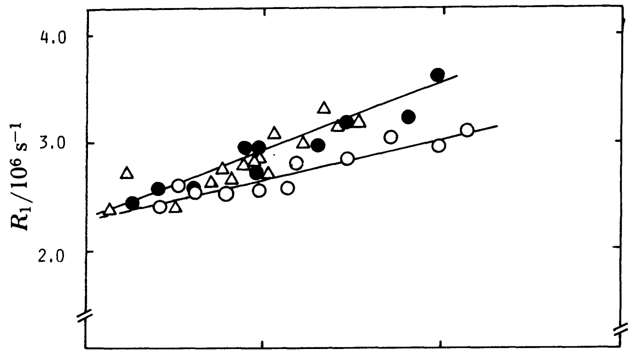

Fig. 5. Plots of R_1 against the pressure of CO(●), NO(△), and CO_2(○). For detail, see text.

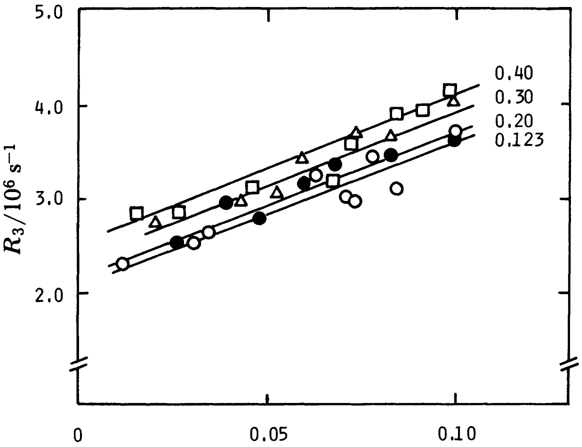

Fig. 6. Plots of R_3 against the pressure of NO. The values show the initial pressure of HN_3 in units of Torr.

Table 2. The Intercepts and the Slopes of the Straight Lines in Fig. 6

$[NH_3]$	Intercept	Slope	Cross-section
Torr	$10^6\,s^{-1}$	$10^{14}\,cm^3\,mol^{-1}\,s^{-1}$	$10^{-16}\,cm^2$
0.123	2.16±0.21	2.59±0.58	54
0.20	2.20±0.13	2.70±0.38	57
0.30	2.27±0.13	3.24±0.37	68
0.40	2.43±0.15	2.97±0.42	62
	Average	2.88±0.53	60±11

(=R_3) values are plotted in Fig. 6 as a function of the pressure of NO. The plots showed straight lines for every pressure of HN_3 examined. The values of the intercepts, R_{30}, and the slopes are summarized in Table 2.

Discussion

Photolysis of HN_3. The fluorescence of the NH ($c^1\Pi$) radicals appears at 325 nm. In order to explain the observed phase difference between the excitation light and the fluorescence at 325 nm, ϕ_1, the following reaction mechanism was considered:

$$HN_3 + h\nu \longrightarrow NH(c^1\Pi) + N_2 \tag{1}$$

$$NH(c^1\Pi) \longrightarrow NH(a^1\Delta) + h\nu(325) \quad k_{10} \tag{2}$$

$$NH(c^1\Pi) + HN_3 \longrightarrow \text{products} \quad k_{1a} \tag{3}$$

$$NH(c^1\Pi) + He \longrightarrow \text{products} \quad k_{1h} \tag{4}$$

Assuming the above mechanism, the decay rate, R_1, can be expressed as follows:

$$R_1 = 2\pi f/\tan\phi_1 = k_{10} + k_{1a}[HN_3] + k_{1h}[He] \tag{5}$$

Here, f denotes the frequency of the modulation. According to Eq. 5, the plots of the decay rates against the pressure of HN_3 will give a straight line with an intercept of $k_{10}+k_{1h}[He]$ and a slope of k_{1a}. Under a constant pressure of HN_3, the plots of the decay rates against the pressure of He will give a straight line with an intercept of $k_{10}+k_{1a}[HN_3]$ and a slope of k_{1h}. From the values of the intercepts and the slopes of the straight lines in Figs. 3 and 4, the values of k_{10}, k_{1a}, and k_{1h} are estimated to be $(2.2\pm0.2)\times10^6\,s^{-1}$, $(5.2\pm0.7)\times10^{13}$, and $(1.1\pm0.1)\times10^{11}\,cm^3\,mol^{-1}\,s^{-1}$ respectively. The radiative lifetime of NH($c^1\Pi$), the reciprocal of k_{10}, was estimated to be (0.48±0.03) μs. The value obtained here agreed well with those estimated by the various other methods.[7)–11)] The quenching by He was about two orders of magnitude smaller than that of HN_3 and agreed with that obtained by Kawasaki et al.[6)] Recently, Haak and Stuhl estimated k_{1a} to be $4.4\times10^{14}\,cm^3\,mol^{-1}\,s^{-1}$ by using the ArF-laser photolysis of HN_3; this value is about one order of magnitude larger than the present value.[11)] The reaction mechanism may not be simple in their laser-photolysis system, since they observed that (a) products were formed in an appreciable concentration, (b) the intensities of the fluorescence of NH($A^3\Pi$) varied from 1.4 to 1.9 powers of the laser intensities, and (c) the decay rate of NH($A^3\Pi$) was not a single exponential. Thus, the quenching process can be considered to be disturbed by the side reactions.

If NH($c^1\Pi$) is formed via a long-lived intermediate, such as an excited HN_3 molecule, the observed decay rate should be dependent on the frequency of the modulation. This is, however, not the case, as is shown in Fig. 3.

Quenching of NH($c^1\Pi$). In the presence of a quencher, such as NO, CO, or CO_2, Eq. 5 should be changed:

$$R_1 = k_{10} + k_{1h}[\mathrm{He}] + k_{1a}[\mathrm{HN_3}] + k_{1q}[\mathrm{Q}] \tag{6}$$

Here, k_{1q} represents the rate constant for the quenching of NH($c^1\Pi$) by a quencher, Q:

$$\mathrm{NH}(c^1\Pi) + \mathrm{Q} \longrightarrow \text{products} \quad k_{1q} \tag{7}$$

When the pressures of HN_3 and He are kept constant, the plots of R_1 against the pressure of a quencher will give a straight line with a slope of k_{1q} and an intercept of $k_{10}+k_{1h}[\mathrm{He}]+k_{1a}[\mathrm{HN_3}]$ (see Fig. 5). Using the values of k_{10}, k_{1a}, and k_{1h} estimated in this study, the intercept was calculated to be $2.5\times10^6\,s^{-1}$, a value which agreed well with the observed values of the intercepts shown in Table 1; i.e., the slopes shown in Table 1 can be considered to represent k_{1q}. The quenching cross-sections, σ_{1q}, were estimated by the use of Eq. 8 and are listed in the fourth column of Table 1:

$$\sigma_{1q} = k_{1q}(\pi\mu/8kT)^{1/2} \tag{8}$$

The symbols in Eq. 8 represent their usual meanings. In the fifth column of Table 1, the literature values are also listed. The NO, CO, and CO_2 efficiently quench the NH($c^1\Pi$) state.

Quenching by NO. In the case of NO, the formation of NH($A^3\Pi$) was detected by the fluorescence at 336 nm. The following reactions can be considered to explain the results:

$$\mathrm{NH}(c^1\Pi) + \mathrm{NO} \longrightarrow \mathrm{NH}(A^3\Pi) + \mathrm{NO}^* \quad \alpha \tag{9}$$

$$\longrightarrow \text{other reactions} \quad 1-\alpha \tag{10}$$

$$\mathrm{NH}(A^3\Pi) \longrightarrow \mathrm{NH}(X^3\Sigma^-) + h\nu(336) \quad k_{30} \tag{11}$$

$$\mathrm{NH}(A^3\Pi) + \mathrm{NO} \longrightarrow \text{products} \quad k_{3n} \tag{12}$$

$$\mathrm{NH}(A^3\Pi) + \mathrm{HN_3} \longrightarrow \text{products} \quad k_{3a} \tag{13}$$

where α denotes the branching ratio for the formation of NH($A^3\Pi$). In the above reactions, the quenching by He is neglected. Assuming the above reactions, the decay rates of the NH($A^3\Pi$), R_3, can be expressed as follows:

$$R_3 = 2\pi f/\tan\phi_3 = k_{30} + k_{3a}[\mathrm{HN_3}] + k_{3n}[\mathrm{NO}] \tag{14}$$

The slopes of the straight lines in Fig. 6 correspond to k_{3n}. The values of the slopes shown in Table 2 are almost constant for every pressure of HN_3 examined. From the value of k_{3n}, the quenching cross-section of NO was calculated to be $60\times10^{-16}\,cm^2$. Recently, Hofzumahaus and Stuhl have estimated the cross section of NO for quenching rotationally hot NH($A^3\Pi$) to be $17\times10^{-16}\,cm^2$.[15] They pointed out that rotation of NH radicals reduces the effect of the quencher. The present result corresponds to the quenching rate for rotationally relaxed NH radicals.

The branching ratio, α, could not be determined from the phase-shift studies, because no formation rate of NH($A^3\Pi$), k_9, appeared in Eq. 14. Since the energy difference between NH($c^1\Pi$) and NH($A^3\Pi$) is 167 kJ mol^{-1}, the NO* formed by Reaction 9 is probably not an electronically excited one. Reaction 9, however, is a spin-allowed process for NO. For CO and CO_2, similar quenching reactions are spin-forbidden processes unless CO or CO_2 is excited to a triplet state. No triplet states of these molecules, however, are assigned in such a low energy region. This explains why only the NO molecule can quench NH($c^1\Pi$) to NH($A^3\Pi$).

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