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Mechanism of the Reaction of $NH(^1\Delta)$ with NO in Argon Matrix

Keiichi Yokoyama, Hiroshi Kitaike, and Takayuki Fueno*
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560
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Matrix-isolated hydrazoic acid HN_3 admixed with NO was photolyzed by a low-pressure mercury discharge lamp. Product analysis based on the FTIR spectroscopy has revealed the formations of NH, N_2O, OH, HNO, and HONO as photoproducts. From the comparisons of the amount of HN_3 consumed with that of N_2O produced, we conclude that the reaction of $NH(^1\Delta)$ with NO proceeds mainly through the process $NH(^1\Delta)+NO \rightarrow N_2O+H$. The quantum yield of N_2O is found to be $\phi_1=0.7\pm0.1$. The conclusion is in line with our previous results of the gas phase experiments at room temperature.

We have previously investigated the gas-phase reaction of $NH(^1\Delta)$ with NO both theoretically and experimentally.[1] The theoretical studies have shown that the reaction should proceed through an intermediacy of the HNNO adduct and that two channels are open for the unimolecular decomposition of the HNNO adduct:

$$NH(^1\Delta)+NO \longrightarrow [HNNO] \begin{array}{ll} \longrightarrow N_2O+H & \quad (1a) \\ \longrightarrow N_2+OH & \quad (1b) \end{array}$$

The entire reaction is expected to be essentially collision-controlled, and the HNNO decompositions as the product-determining step have energy barrier heights lower than the heat of the adduct formation, with a marginal advantage of reaction (1a) over reaction (1b). The expectation that the primary product of the reaction should be N_2O was borne out by the experimental determination of the quantum yield of N_2O being ca. 0.7, under the assumption that the quantum yield of $NH(^1\Delta)$ in the photodissociation is 1.0.

$$HN_3 \xrightarrow{h\nu} NH(^1\Delta)+N_2 \qquad \phi=1 \text{ at } 2537\,\text{Å} \qquad (2)$$

It is feared, however, that in the gas phase N_2O might well be formed by some routes other than the direct process (1a). Hack et al. carried out laser photolysis of HN_3 in the presence of NO in the gas phase at room temperature.[2] On the basis of the laser-induced fluorescence signal intensity of OH, they concluded that the primary product is $OH(X^2\Pi)$ to be formed by reaction (1b). They suggested the possibility that the formation of N_2O was rather a consequence of subsidiary reactions as follows:

$$NH(^1\Delta)+HN_3 \longrightarrow NH_2+N_3 \qquad (3)$$

$$N_3+NO \longrightarrow N_2O+N_2 \qquad (4)$$

In the present work, we have undertaken studies of the photo-induced reaction of HN_3 with NO in argon matrix. Our principal purpose here is to examine whether our previous gas-phase product determination study has indeed reflected the kinetics of reaction (1a). In a matrix there are not only isolated monomers but also dimers, polymers, and complexes with other molecular species, but generally there are little mobilities for isolated molecules except for the H atom. Thus, photoinduced reactions are thought to be completed within single cages of argon matrix. Contributions of subsidiary processes to the overall reaction could be examined more closely in this study.

Experimental

The cryogenic apparatus used in the matrix experiments is schematically shown in Fig. 1. A Cryomini D310 closed-cycle helium system (Iwatani Cryo-Techno Inc.) was used to refrigerate the deposition target made of CsI of 20 mm in diameter and 2 mm in thickness. An indium gasket was inserted between the CsI disk and the copper sample holder mounted on the cold head. Two Pylex nozzles of 0.5 mm in internal diameter were placed at a distance of 3 cm from the target in the direction orthogonal to each other to spray sample gases onto the target. Only one of these nozzles was used in the present experiments. A thermocouple of Chromel vs. Au–0.07% Fe was embedded on the sample holder. The ordinary operating temperature was measured to be 12 K. A liquid nitrogen trap and an oil diffusion pump were used to evacuate all of these devices placed within a stainless steel envelope.

IR spectra were measured through two KRS-5 windows located on both sides of the target on the envelope. In the direction perpendicular to the IR beam, there were two quartz

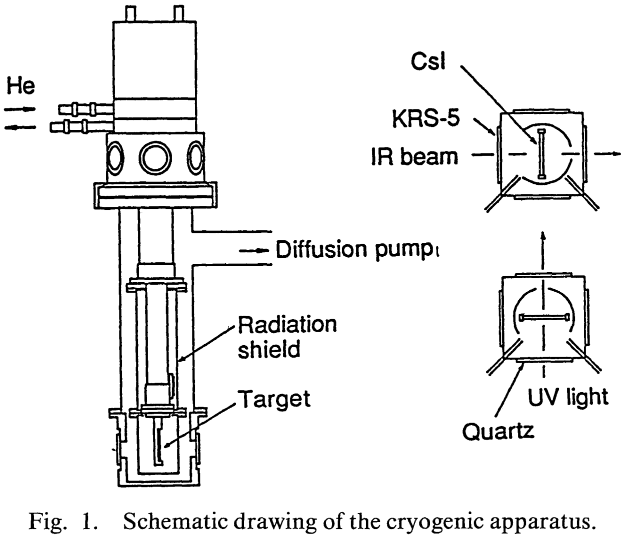

Fig. 1. Schematic drawing of the cryogenic apparatus. Top right, target alignment for IR measurement. Bottom right, that for deposition of the sample gases and UV photolyses.

windows for UV irradiation. The target was rotatable on a horizontal plane for IR measurement and UV irradiation. The UV light source used was a 22W low-pressure mercury discharge lamp (Ultra Violet Prod. Inc.) placed just in front of the quartz window of 2 mm in thickness without lens nor filter. This alignment provided homogeneous exposure of the target to the 2537 Å UV light. It is thought that another mercury line 1849 Å will little influence the measurements because of the absorption by the quartz window (not suprasil) at this wavelength. A Fourier-transform infrared spectrometer FT/IR-5000 (Japan Spectroscopic Co., Ltd.) was operated with a resolution of 4 cm^{-1} and the spectra were calculated from the coaddition of 100 interferograms. The deposition rates of sample gases were controlled with a teflon needle valve and a capacitance manometer CMLB-1000 (Vacuum General Inc.).

HN_3/NO/Ar(=0.1—1/0.08—1/100) gas mixtures were sprayed out through the nozzle at a rate of 2 mmol h^{-1} for ca. 3.5 h. After measurements of IR spectra for deposited samples, UV irradiation was started. Photolyzed matrix spectra were measured at the irradiation times of 0.5, 1, 2, 4, 6, 10, 20, 30, 60, and 120 min. A single measurement took about 4 min. The matrix temperature was monitored to be maintained at 12 K during irradiation. A relative intensity of the N_2O ν_3 (2224 cm^{-1}) to the HN_3 ν_2 (2138 cm^{-1}) band was evaluated on the basis of the matrix spectra of N_2O/HN_3/Ar of known compositions.

HN_3 was synthesized by the reaction of NaN_3 with excess stearic acid at 80—90 °C in a vacuum glass line. After the purification by means of trap-to-trap distillations at −80 °C, HN_3 gas was stored in a 6-l Pyrex bulb. NO (99.99%), Ar (99.9999%), and N_2O (99.999%) (Takachiho Kagaku Inc.) were used without further purification. Gas mixtures diluted in argon were kept in a 6-l Pyrex bulb overnight for mixing.

Results

(A) Assignment of Complexes. The HN_3/NO/Ar matrix spectra have exhibited, in the vicinity of the HN_3 ν_2 band (2138 cm^{-1}), a perturbed ν_2 band at 2150 cm^{-1} due to the hydrogen-bonded HN_3 dimer.[3] More highly aggregated molecules may also contribute to this peak since annealing experiments broadened the ν_2 band. By contrast, the ν_2 band was not resolved by possible complexation of HN_3 with NO, which might reflect a weaker hydrogen bonding between the two components.

A new peak was observed at 1882 cm^{-1} near the isolated NO stretching (1874 cm^{-1}). It is assigned essentially to the HN_3–NO complex on the basis of the following observations. First, this peak is observed in the HN_3/NO/Ar spectra but is absent in either of the HN_3/Ar and NO/Ar matrix spectra. Second, as can be seen in Fig. 2, the relative peak heights of the complexes vs. NO remain constant, irrespective of the molar fraction of NO in the sample gas used. It is possible, however, that the assigned peak is actually overlaped with that of the $(HN_3)_2$–NO complex, as will be considered later.

(B) Photoproducts. Figure 3 shows a difference spectrum of an HN_3/NO/Ar matrix after photolysis for 1 h. The irradiation diminishes HN_3 and the complexes and gives rise to NH($X^3\Sigma^-$), N_2O, OH, HNO, HONO, and NO_2. Little change was observed in absorbance of the peak due to the isolated NO monomer

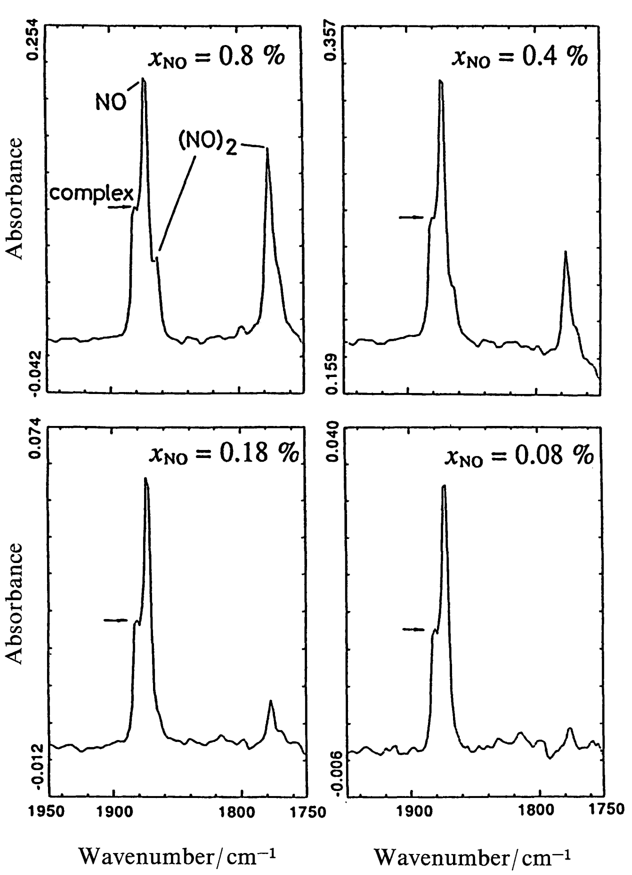

Fig. 2. Absorbance changes for the NO stretching bands of the NO monomer and dimer and for the complexes in the spectra of the HN_3/NO/Ar=1/0.08—0.8/100 matrices.

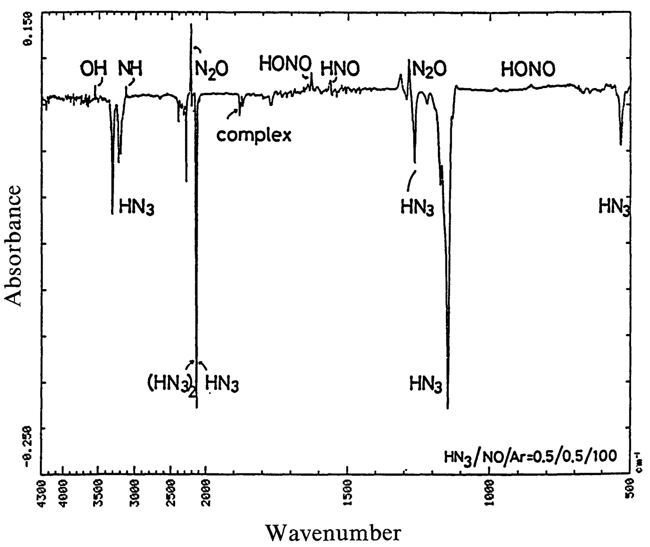

Fig. 3. FTIR difference spectrum of the HN_3/NO/Ar=0.5/0.5/100 matrix at 12 K after 1 h photolysis.

Table 1. Infrared Absorption Frequencies for the Products Formed in the Photolyses of the HN_3/NO/Ar Matrices

Frequency cm^{-1}	Assignment	Lit. value cm^{-1}	Ref.
3554	OH	3548.2	10
3136	NH	3133	12
2744			
2718	HNO	2717	13
2224	N_2O	2221	14
1758			
1686	*trans*-HONO	1690	15
1644			
1630	*cis*-HONO	1633	15
1609	NO_2	1610	15
1566	HNO	1563	13
1510			
1503			
1499[a)]	NH_2	1499	6
1317			
1286	N_2O	1284.9	14
1215			
856	*cis*-HONO	850	15
800	*trans*-HONO	800	15
719			
661			
588	N_2O	588	14

a) Observed in the photolysis of the HN_3/Ar matrix.

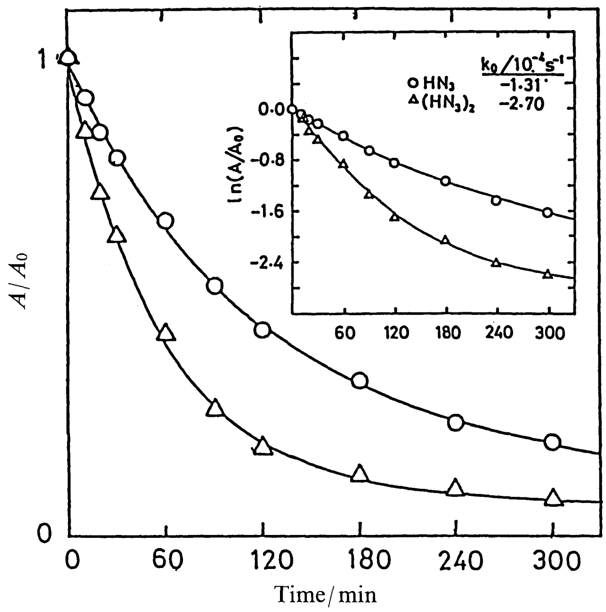

Fig. 4. Differernce between relative decay curves for the HN_3 monomer (2138 cm^{-1}) and dimer (2150 cm^{-1}) in the spectrum of HN_3/NO/Ar=0.5/0.5/100. Solid curve is obtained from biexponential fitting. Insert is log plots of the decays. Note that initial slope ratio is about 1 : 2 (monomer : dimer).

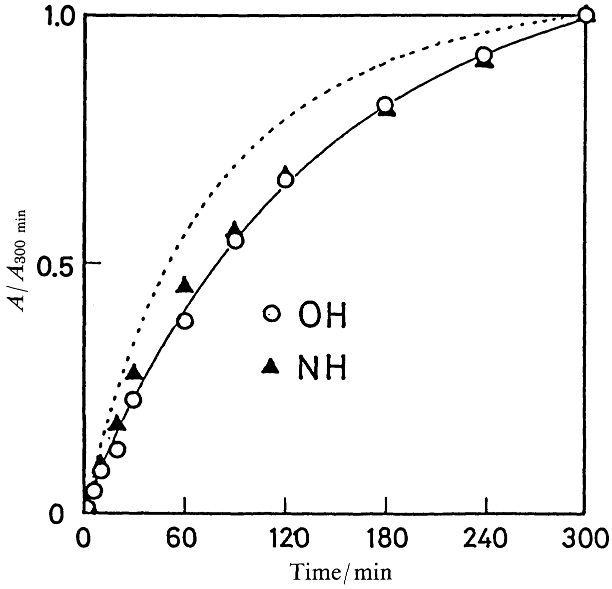

Fig. 5. Comparisons of the OH (3554 cm^{-1}) or the NH (3136 cm^{-1}) production profile with the HN_3 monomer and dimer decay profiles. The solid and dashed curves provide decrements in absorbance at the HN_3 (2138 cm^{-1}) and $(HN_3)_2$ (2150 cm^{-1}) ν_2 bands, respectively. HN_3/NO/Ar=1/1/100.

(1874 cm^{-1}). Assignments of the product peaks are listed in Table. 1, together with the literature values. In the vicinity of the NH_2 ν_2 band (1499 cm^{-1}), no significant peak was observed.

Evidently, N_2O is the primary product of the present matrix experiments also. As we believe, it has arisen from reaction (1a) directly, even though the mechanism proposed by Hack et al.,[2] i.e., the succession of reactions (3) and (4), cannot wholly be negated at this stage. Importantly, the concurrent formation of HNO lends strong support to our belief. Namely, the H atom which should have been formed together with N_2O by reaction (1a) could migrate in argon matrix cages to undergo recombination with NO:

$$NO + H + M \longrightarrow HNO + M \qquad (5)$$

Reaction (1a) followed by reaction (5) seems to be the only route for the formation of HNO under our experimental conditions.

(C) Time Evolution. The HN_3 ν_2 band absorbances for monomer (2138 cm^{-1}) and dimer (2150 cm^{-1}) are plotted in Fig. 4 as the functions of irradiation time. Two curves have apparently different time constants. Log plots of these decay curves manifest that the dimer is photodecomposed nearly twice as rapidly as is the monomer; the initial slope ratio for dimer to monomer is about 2. The results indicate that the dimerization does not perturb the IR intensity of the ν_2 band nor the UV dissociation cross section of HN_3. In addition, it seems that highly aggregated HN_3 molecules, if any, hardly contribute to the absorption at 2150 cm^{-1} because they should be photodecomposed further more rapidly.

Figure 5 shows the increases in the OH (3554 cm^{-1}) and NH (3136 cm^{-1}) absorbances with the elapsing irradiation time. For the purpose of comparisons in shape, measured absorbances have been arbitrarily normalized to a constant value at 300 min. Shown by the solid and dotted curves are the *decrements* in absorbance of HN_3 (2138 cm^{-1}) and $(HN_3)_2$ (2150 cm^{-1}), respectively, as the functions of time (Fig. 4). It can be seen that both the OH and NH increment curves fit the HN_3 monomer decrement curve. The results suggest that NH arises from the photolysis of the HN_3 monomer and that the precursor for OH is the 1 : 1 HN_3-NO complex.

The absorbance of N_2O ν_2 band (2224 cm^{-1}) was also found to increase with time but to be fitted with neither of the HN_3 and $(HN_3)_2$ decay curves. The time profile showed a somewhat faster saturation curve. This is presumably due to a photodecomposition process of N_2O itself.[4]

$$N_2O \xrightarrow{h\nu} N_2 + O(^1\Delta) \quad \lambda < 2300\,\text{Å} \tag{6}$$

Under such circumstances, we have decided to examine the initial rate of the formation of N_2O relative to that of the consumption of HN_3 monomer as the function of the molar fraction χ_{HN_3} of HN_3 present in the sample gas deposited. Note that the word "initial" used here means such an early time region that the secondary photodecomposition does not affect $[N_2O]$, normally less than 4 min.

Figure 6 shows the initial production rate of N_2O (2224 cm^{-1}), $d[N_2O]/dt$ (t=0), relative to the initial decay rate of HN_3 monomer (2138 cm^{-1}), i.e., $-d[HN_3]/dt$ (t=0), at the varying initial molar fraction χ_{HN_3}. It can be seen in Fig. 6 that the relative initial rate $-d[N_2O]/d[HN_3]$ (t=0), is constant at 0.52, irrespective of χ_{HN_3}. The results indicate that N_2O is produced from the HN_3 monomer complexes; i.e. $HN_3\text{-}(NO)_{1,2}$.

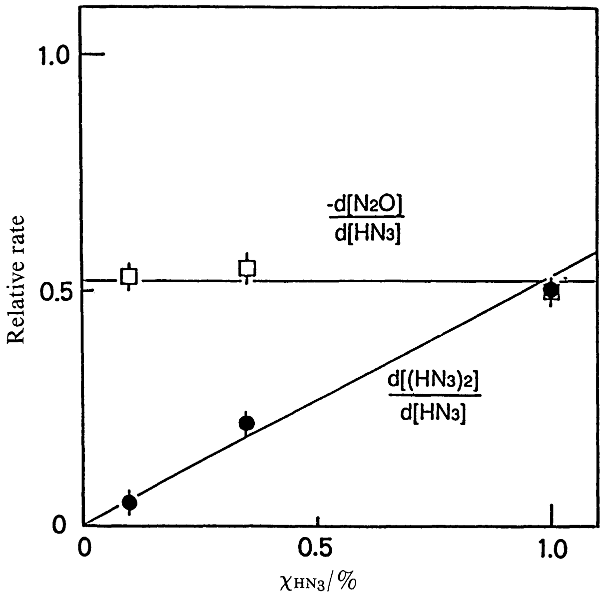

Fig. 6. Dependence of the production of N_2O on the fraction of HN_3. Dependence of the monomer: dimer ratio of HN_3 is also shown.

In addition, the initial rate of the consumption of $(HN_3)_2$ (2150 cm^{-1}) was measured relative to $-d[HN_3]/dt$ (t=0). The relative rate $d[(HN_3)_2]/d[HN_3]$ (t=0) was confirmed to be proportional to χ_{HN_3}. Therefore, if the photolysis of $(HN_3)_2\text{-}(NO)_{1,2}$ had given rise to N_2O, the plots of $-d[N_2O]/d[HN_3]$ against χ_{HN_3} would have shown a significant positive slope. Constancy of $-d[N_2O]/d[HN_3]$ indicates that the photolysis of the 2 : 1 or 2 : 2 complex $(HN_3)_2\text{-}(NO)_{1,2}$ has hardly contributed to the N_2O production. The results entirely negate the contribution of the succession of reactions (3) and (4) in the N_2O production under the present conditions.

(D) Yield of N_2O. We have evaluated the yield of N_2O formed by the photolysis of the 1 : 1 complex. In the measurements of the yield, there are two complexities. One is that N_2O may be formed by the photolysis of the 1 : 2 complex as well. The other is that the absorption at 1882 cm^{-1}, which was used to measure the amount of the 1 : 1 complex, may have overlaped with that of the 2 : 1 complex. Therefore, appropriate corrections are needed in evaluating the yield from the rates of the N_2O production and the complex consumption.

Let the yields of N_2O arising from the photolyses of the 1 : 1 and 1 : 2 complexes be denoted as ϕ_1 and ϕ_2, respectively. Since N_2O is assumed to be formed from both complexes, we may write

$$d[N_2O] = -\phi_1\, d[HN_3\text{-}NO] - \phi_2\, d[HN_3\text{-}(NO)_2]. \tag{I}$$

The apparent overall yield of N_2O, defined as $\Phi \equiv -d[N_2O]/d[HN_3\text{-}NO]$ is then expressed as

$$\Phi = \phi_1 + \phi_2\, d[HN_3\text{-}(NO)_2]/d[HN_3\text{-}NO]. \tag{II}$$

The second term $d[HN_3\text{-}(NO)_2]/d[HN_3\text{-}NO]$ is expected to be proportional to χ_{NO}, which will be confirmed later. Thus, plots of Φ vs. χ_{NO} should provide the ϕ_1 value as the intercept at $\chi_{NO} \rightarrow 0$.

In order to evaluate the Φ value, the initial rate of the consumption of the 1 : 1 complex is needed. The complex peak at 1882 cm^{-1} which is the only peak distinguishable at the present resolution contains both the 1 : 1 and 2 : 1 complexes:

$$-dC/dt = -d[HN_3\text{-}NO]/dt - d[(HN_3)_2\text{-}NO]/dt, \tag{III}$$

where C is the amount of the complexes absorbing at 1882 cm^{-1}. Dividing both sides by $d[N_2O]/dt$, we can write

$$-dC/d[N_2O] = \Phi^{-1} - d[(HN_3)_2\text{-}NO]/d[N_2O], \tag{IV}$$

where the second term $d[(HN_3)_2\text{-}NO]/d[N_2O]$ should be proportional to χ_{HN_3} in view of the results illustrated in Fig. 6. Hence, by plotting $-dC/d[N_2O]$ against χ_{HN_3}, we obtain the reciprocal Φ from the intercept.

In practice, the values of dC/dt have been evaluated from the absorbance changes at 1882 cm^{-1} in the initial 4 min period. The initial decreasing rates of C have been divided by the initial production rates of N_2O (2224 cm^{-1}). Plots of the quotients against χ_{HN_3} at a fixed χ_{NO} value of 1.0%, for instance, have indeed proved to be linear, as is shown in Fig. 7. The intercept 0.48 leads to Φ=2.08 at χ_{NO}=1.0%.

The values of Φ at various χ_{NO} values have been measured in a similar way. Figure 8 shows the plots of Φ vs. χ_{NO}. As has been anticipated in the form of Eq. II, the plots are linear. The intercept gives $\phi_1=0.7\pm0.1$.

For the absorption peaks of HN_3, N_2O, and $(HN_3)_{1,2}$–NO, proportionalities between the concentrations and the absorbances have been assumed. Relative absorption coefficients are measured to be 1 : 1.15 : 0.225 for HN_3 (2136 cm^{-1}): N_2O (2224 cm^{-1}): $(HN_3)_{1,2}$–NO (1882 cm^{-1}). These values have been obtained from the IR spectra of the matrices made of the sample gases of known compositions. The absorption coefficient of the complex peak (1882 cm^{-1}) has been assumed to be equal to that of isolated NO monomer, because the IR absorption intensity of the N–O stretching would not be perturbed largely by the complexation.

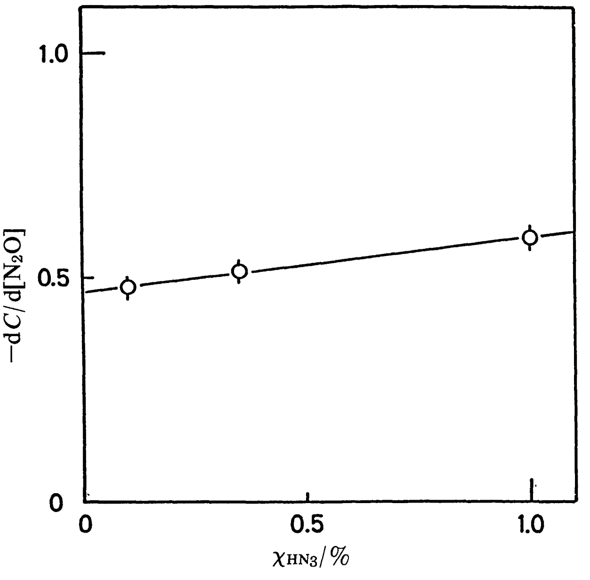

Fig. 7. χ_{HN_3} dependence of reciprocal yield, $-dC/d[N_2O]$, at a fixed χ_{NO} value of 1.0%. The intercept corresponds to the value of Φ^{-1}.

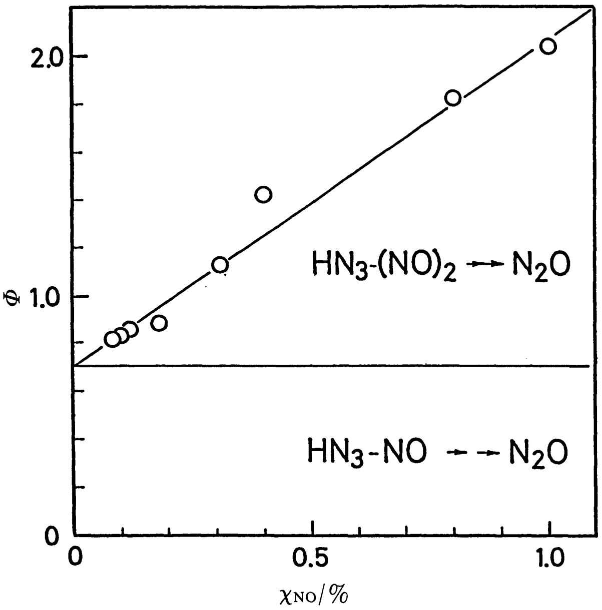

Fig. 8. [NO] dependence of the yield of N_2O from the photolysis of the 1 : 1 and 1 : 2 complexes HN_3-NO and HN_3-$(NO)_2$. The intercept corresponds to the absolute yield ϕ_1 of N_2O in reaction (1).

Discussion

Since NH($a^1\Delta$) formed by the photolysis of HN_3 is metastable, there may exist a physical quenching to NH($X^3\Sigma^-$):

$$NH(^1\Delta)+Ar \longrightarrow NH(^3\Sigma^-)+Ar. \tag{7}$$

Ramsthaler-Sommer et al. measured the lifetime of NH($a^1\Delta$) in argon matrix.[5] Their reported value of ca. 0.7 s at 12 K is long enough to allow the barrierless reaction (1) to complete without an influence of the quenching process (7).

The photoinduced reaction of the 1 : 1 complex can be regarded as reaction (1) in argon matrix cages. The value 0.7±0.1 obtained for ϕ_1 indicates that N_2O arises dominantly from reaction (1a) via the HNNO intermediacy. The result is perfectly compatible with the observation of HNO, whose production is a quite likely event as a fate of the H atom formed in reaction (1).

We have already noted the failure in detecting NH_2. For the purpose of more quantitative discussion, the infrared intensity of the NH_2 ν_2 band 1499 cm^{-1} is needed. Thus, we conducted separate photolysis experiments of NH_3/Ar and NH_3/CO in order to isolate the radical.

$$NH_3 \xrightarrow{h\nu} NH_2+H. \tag{8}$$

A low-pressure mercury discharge lamp with suprasil window provides 1849 Å UV light which should efficiently photodecompose NH_3. In the case of NH_3/Ar, the NH_2 ν_2 band at 1499 cm^{-1} showed only a slight absorption after an irradiation over a period of five hours, probably because of the recombination between the dissociated NH_2 and the H atom. In the NH_3/CO photolysis, on the other hand, effective productions of NH_2, HCO, and $HCONH_2$ have been observed.[6] Assuming that the amount of NH_2 produced is equal to that of NH_3 consumed, we have estimated a lower limit of the relative intensity of the NH_2 ν_2 band to the N_2O ν_3 band to be $I_{NH_2}/I_{N_2O}>0.1$. Obviously, this value is underestimated owing to the production of a significant amount of $HCONH_2$. By appling this value to a spectrum for HN_3/NO/Ar, in which an absorbance ratio A_{NH_2}/A_{N_2O} is found to be less than 0.01, we estimate an upper limit of the production ratio $d[NH_2]/d[N_2O]$ to be less than 0.1. Therefore, only less than 10% of N_2O might be formed via the succession of reaction (3) and

(4), if any.

We have also been cautious of the possibility that N_2O may be formed directly from NO. Although isolated NO monomer cannot be decomposed by irradiation with a low-pressure mercury discharge lamp, the dimer is susceptible to the photodissociation:[7]

$$\text{ONNO} \xrightarrow{h\nu} N_2O + O \qquad \lambda < 2400\,\text{Å} \qquad (9)$$

However, in the present experiments, reaction (9) will not participate significantly, since the intense Hg resonance line at 1849 Å has been attenuated to a large extent through the window used in this study. In fact, the initial production rate $d[N_2O]/dt$ (t=0) in the photolysis of NO/Ar (1/100) was found to be less than 2% that in the photolysis of HN_3/NO/Ar (1/1/100). Thus, N_2O formed in the photolysis of HN_3/NO/Ar has no doubt originated nearly exclusively from the photodecomposition of HN_3.

Our original aim of the present work was to detect the HNNO intermediate. This was unsuccessful, however. It is supposed that the nascent vibrationally excited HNNO has an extremely short lifetime compared to a period of time required for stabilization by collisions with Ar. Thus, fragmentation will take place prior to stabilization. Also, the photodecomposition might be so fast that the amount of HNNO could not reach the detection limit.

We have assigned a peak at 3554 cm^{-1} to the OH radical in the spectrum of an HN_3/NO/Ar matrix photolyzed. The infrared absorption of OH in argon matrix has not been established yet. There are some discrepancies among the reported values.[8–10] Acquista et al.[8] and Suzar et al.[9] conducted the photolysis of H_2O at 1218 Å and decomposition of H_2O by means of electron impact in argon matrix, respectively. Both of them assigned two absorptions near 3452 and 3428 cm^{-1} to the OH vibration. On the other hand, Cheng et al.[10] found a new peak at 3548.2 cm^{-1}, which was concluded to be due to the OH radical prepared in solid argon by means of the reactions of atomic H with NO_2, O_3, and atomic O. The shift of 21.4 cm^{-1} from 3569.6 cm^{-1} as the gas-phase fundamental band is within the common range of matrix shifts.[11] They pointed out the possibility that the absorptions at 3452 and 3428 cm^{-1} previously assigned to OH may be due to the hydroxyl radical in complex with either H_2O or one Ar atom. Our observation 3554 cm^{-1} supports the conclusion by Cheng et al. The difference of 6 cm^{-1} between their wavenumber and ours may have been caused by an interaction of OH with N_2, which has been formed simultaneously with OH via reaction (1b). N_2 matrix experiments to isolate OH will be interesting.

The formation of HONO observed in a considerable amount probably stems from the 1:2 complex HN_3–$(NO)_2$. By virtue of weakness of the N–N bonding in $(NO)_2$, its photolysis will be apt to form the same intermediate HNNO as does reaction (1).

$$NH(^1\Delta) + \text{ONNO} \longrightarrow [\text{HNNO}]^* + \text{NO} \qquad (11)$$

If HNNO formed in this reaction has still enough excess energy, reaction (1b) will follow to give OH, which may in turn recombine with the other NO molecule to form HONO.

$$\text{OH} + \text{NO} + \text{Ar} \longrightarrow \text{HONO} + \text{Ar} \qquad (12)$$

Finally, in addition to the chemical channels (1a) and (1b), a quenching process must be considered.

$$NH(^1\Delta) + \text{NO} \longrightarrow NH(^3\Sigma^-) + \text{NO} \qquad (1c)$$

Hack et al. measured the rate constant of reaction (1c) in the gas phase, to claim that its branching ratio was as large as 0.4.[2] If so, the reaction of $NH(^1\Delta)$ with NO will inevitably be accompanied by the reaction of $NH(^3\Sigma^-)$ with NO under the present conditions as well. Since N_2O may arise from $NH(^3\Sigma^-)$ as well as $NH(^1\Delta)$, our value of ϕ_1 (=0.7) may not directly correspond to the branching ratio of the singlet reaction (1a) alone. This final point is still open to inquiry. Nevertheless, the conclusion that reaction (1a) is the most dominant channel of the reacion between $NH(^1\Delta)$ and NO will be basically correct.

Conclusions

Product analyses of the photochemical reactions in HN_3/NO/Ar matrices at 12 K were conducted to investigate the microscopic mechanism of the reaction of $NH(^1\Delta)$ with NO. NH, N_2O, OH, HONO, and HNO were identified by the IR spectra. The absolute yield of N_2O from the phtolysis of the 1:1 complex HN_3–NO was found to be $\phi_1 = 0.7 \pm 0.1$. Also, a considerable amount of N_2O was confirmed to arise from the 1:2 complex HN_3–$(NO)_2$. The photolysis of the 2:1 or 2:2 complex $(HN_3)_2$–$(NO)_{1,2}$ was found not to contribute to the production of N_2O, indicating that $NH(^1\Delta)$ fragmented from one of two HN_3 would react with the other HN_3 preferentially.

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References

1) T. Fueno, M. Fukuda, and K. Yokoyama, *Chem. Phys.*, **124**, 265 (1988).

2) W. Hack and K. Rathmann, private communication.

3) G. C. Pimentel, S. W. Charles, and K. Rosengren, *J. Chem. Phys.*, **44**, 3029 (1966).

4) G. P. Kevopoulos and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **91**, 7572 (1969).

5) A. Ramsthaler-Sommer, K. E. Eberhardt, and U. Schurath, *J. Chem. Phys.*, **85**, 3760 (1986).

6) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **43**, 4487 (1965).

7) J. R. Sodeau and R. Withnall, *J. Phys. Chem.*, **89**, 4484 (1985).

8) N. Acquista, L. J. Schoen, and D. R. Lide, Jr., *J. Chem.*

Phys., **48**, 1534 (1968).

9) S. Suzer and L. Andrews, *J. Chem. Phys.*, **88**, 916 (1987).

10) B. M. Cheng, Y. P. Lee, and J. F. Ogilvie, *Chem. Phys. Lett.*, **151**, 109 (1988).

11) M. E. Jacox, *J. Mol. Spectrosc.*, **113**, 286 (1985).

12) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **41**, 2838 (1964).

13) M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **48**, 536 (1973).

14) L. Andrews and G. L. Johnson, *J. Chem. Phys.*, **76**, 2875 (1982).

15) W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **54**, 598 (1971).