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Reactions of NH Radicals. IV. Photolysis of HN_3 in the Presence of CH_4 at 313 nm

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The photolysis of HN_3 vapor in the presence of CH_4 was studied at 313 nm, 30 °C, and a low light intensity. The reaction products were N_2, H_2, NH_4N_3, $CH_3NH_2\cdot HN_3$, and CH_3N_3. CH_3 radicals were also detected as intermediates. The quantum yields of these products were measured as a function of the CH_4 and HN_3 pressures. The following mechanisms for the main reactions were proposed: $HN_3+h\nu(313\,\text{nm})\rightarrow N_2+NH(a^1\Delta)$; $NH(a^1\Delta)+HN_3\rightarrow 2N_2+2H$(2a); $NH(a^1\Delta)+HN_3\rightarrow N_3+NH_2$ (2b); $NH(a^1\Delta)+HN_3\rightarrow N_2+N_2H_2^*$ (2c); $NH(a^1\Delta)+CH_4\rightarrow CH_3NH_2^*$ (3); $NH(a^1\Delta)+CH_4\rightarrow NH(X^3\Sigma^-)+CH_4$ (4); $CH_3NH_2^*\rightarrow H+CH_2NH_2$ or CH_3NH (5); $CH_3NH_2^*\rightarrow CH_3+NH_2$ (6). The rate-constant ratios at 30°C were: $k_3/k_2=0.175$; $k_4/k_2=0.177$; $k_6/k_5=0.133$. The collisional deactivation of $CH_3NH_2^*$ was not found in the total pressure range, from 6.4 to 24.3 kPa.

The photolysis of HN_3 in the presence of Xe,[1] C_2H_6,[2] and C_2H_4[3] at 313 nm has been studied previously, and the following facts were found: HN_3 is a useful source for the first excited singlet, NH $(a^1\Delta)$; ethylamine is produced by the insertion of NH $(a^1\Delta)$ into a C–H bond of C_2H_6, and the reactions of NH $(a^1\Delta)$ with HN_3 and C_2H_4 having the π bond are much faster than that with C_2H_6 consisting of only the σ bond.

On the reactions of $NH(a^1\Delta)$ with C_2H_6, the collisional deactivation by C_2H_6 from $NH(a^1\Delta)$ to $NH(X^3\Sigma^-)$ was also found.[2] Therefore, it is of interest to compare these reactions between saturated hydrocarbons for the insertion and collisional deactivation reactions. In this work, methane, which is the simplest hydrocarbon, was chosen as the reactant.

On the reactions of NH with CH_4, Miller[4] has found N_2, H_2, and NH_4N_3 as the main products, with HCN and C_2H_6 as minor products, in the photolysis of HN_3 with CH_4. However, the formation of $CH_3NH_2\cdot HN_3$ could not be found in the mass-spectrometric analysis. Cornell *et al.*[5] have studied the flash and steady photolyses of $HN_3(DN_3)$ with hydrocarbons including methane. They have found that the principal nitrogen-containing products are HCN and alkanenitriles in the steady state photolysis. Richardson and Setser[6] have studied the thermal decomposition of HN_3 in the presence of CH_4 and other hydrocarbons over the temperature range of 285—470 °C. They have found N_2, NH_3, and a nonvolatile polymer as the products in the HN_3 and CH_4 system. However, the formations of H_2, CH_3NH_2, and N_2H_4 were negative in the mass-spectrometric and gas-liquid chromatographic analyses. Thus, they have concluded that the pyrolysis of HN_3 is not a good source of NH.

It appears to be significant to compare the insertion efficiencies of $NH(a^1\Delta)$ into C–H bonds of simple saturated hydrocarbons, the collisional spin-relaxation efficiencies of $NH(a^1\Delta)$ by such hydrocarbons, and the unimolecular decomposition rates of the alkylamines formed by the insertion reactions. From such a standpoint, the reaction mechanism and rates of the photolysis of HN_3 in the presence of CH_4 were investigated in this work to continue the study with C_2H_6.[2]

Experimental

The methane, obtained from the Takachiho Chemical Co., was 99.8% pure. It was purified each time before use by condensation and evacuation at −196 °C and the temperature of solid nitrogen (about −220 °C). The preparation and purification of HN_3, like the apparatus and procedure used for the reaction, were the same as those described previously.[1,2] All the runs in this work were carried out at 313 nm and 30 °C. The light intensity was reduced with a screen to suppress any radical–radical reactions. The irradiation time was 90 min, and the degree of conversion of HN_3 was less than 4% for all the runs.

The reaction products were N_2, H_2, NH_4N_3, $CH_3NH_2\cdot HN_3$, and CH_3N_3. The formation of CH_3N_3, passing through a Dry Ice–acetone trap, was found by gas-chromatographic analysis using a Silicone SE-30 column.[3] No HCN was detected by the pyridine-pyrazolone method.[7]

In order to inspect the radical intermediates, the products of the photolysis of HN_3 with CH_4 and NO were analysed by gas chromatography using an 1-m column of Silicone SE-30 at room temperature. Similarly, the products of the photolysis of $CH_3N_2CH_3$ with NO or NO_2 were also analysed gas-chromatographically where the same conditions. The retention times of the two peaks of the former products were in accord with those of the latter products. This suggests the formation of CH_3 radicals as intermediates.

For the identification of NH_4N_3 and $CH_3NH_2\cdot HN_3$, the volatile, white products trapped at the temperature of Dry Ice–acetone were analyzed by means of a mass spectrometer (Hitachi RMU6E); the spectrum is shown in Fig. 1. The peaks of m/z=17, 18, 30, 31, 42, 43, and 57 correspond to NH_3^+, NH_4^+, $CH_2NH_2^+$ or CH_3NH^+, $CH_3NH_2^+$, N_3^+, HN_3^+, and $CH_3N_3^+$ respectively. However, the parent peaks of NH_4N_3 (m/z=60) and $CH_3NH_2\cdot HN_3$ (m/z=74) were not found, although a low ionizing voltage of 15 V was applied. On the other hand, the volatile, white products were introduced into a solid-sodium-hydroxide column to remove the HN_3.[2] A mass spectrum of the HN_3-removed products at the ionizing voltage of 17 V is shown in Fig. 2. The peaks of m/z=17 and 31 indicate the molecular ions of NH_3 and CH_3NH_2 respectively. Thus, the formation of $CH_3NH_2\cdot HN_3$ and NH_4N_3 was verified.

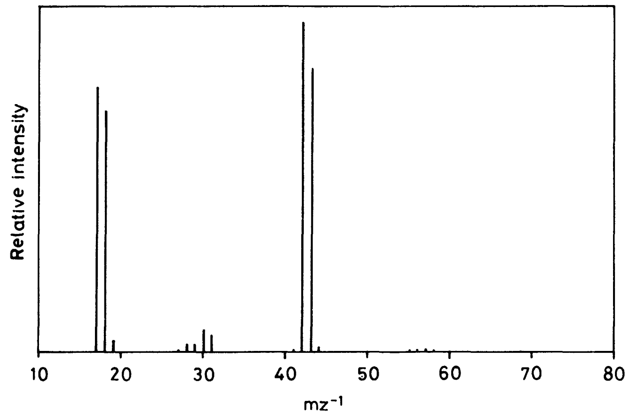


Fig. 1. Mass spectrum of the products trapped at the Dry Ice-acetone temperature. The ionizing voltage is 15 V.

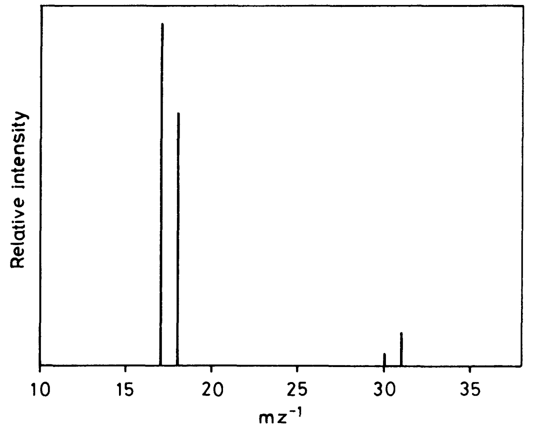


Fig. 2. Mass spectrum of the substances removed HN_3 from the products trapped at the Dry Ice-acetone temperature. The ionizing voltage is 17 V.

The HN_3-removed products were also subjected to gas-chromatographic analysis at 10 °C using a 2-m column of KOH(5%)-paraffin liquid(20%) coated on Chromosorb WAW. The formation of CH_3NH_2 was thus confirmed. However, little CH_3NH_2 was formed in the presence of a small amount of NO.

On the quantitative analyses of N_2, H_2, NH_4N_3, and $CH_3NH_2\cdot HN_3$, the reaction products were separated at the temperatures of solid nitrogen and Dry Ice-acetone. The gases passing through the trap at −220 °C are N_2, H_2, and a part of the CH_4 used as the reactant. The separation of H_2 from the mixture was carried out using a silica-gel column at −196 °C.[1] The separation of N_2 and CH_4 was achieved by gas chromatography using a 5A molecular-sieve column.[2]

NH_4N_3 and $CH_3NH_2\cdot HN_3$, condensed at the temperature of Dry Ice-acetone, were introduced into a CuO column at about 550 °C. The amounts of N_2, NO, N_2O, and CO_2 formed as combustion products were determined by the method described previously.[2] The amounts of $CH_3NH_2\cdot HN_3$ and NH_4N_3 can be calculated from those equations: $[CH_3NH_2\cdot HN_3]=[CO_2]$ and $[NH_4N_3]=([N_2]+[N_2O])/2+[NO]/4-[CO_2]$.

The quantum yields of the reaction products were determined using HN_3 as an actinometer.[1]

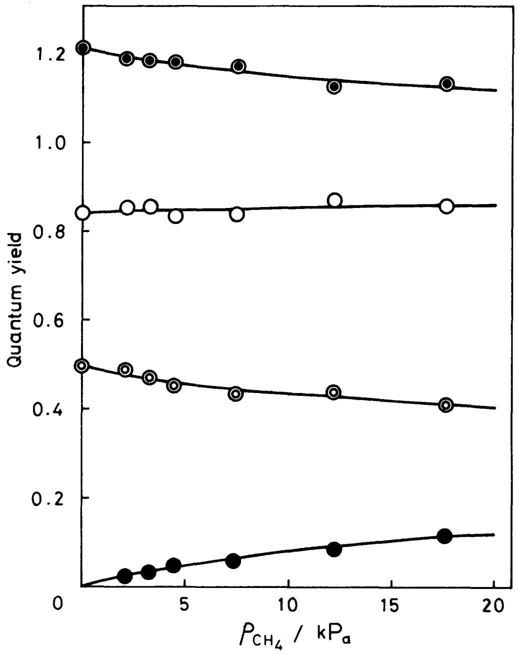


Fig. 3. Results of the photolysis of HN_3 of 6.67 kPa, measured as a function of CH_4 pressure at 313 nm, 30 °C, and the low absorbed light intensity of 4.45×10^{14} quanta s^{-1}. ⊙, $\phi_{N_2}/4$; ○, $\phi_{NH_4N_3}$; ◎, ϕ_{H_2}; ●, $\phi_{CH_3NH_2\cdot HN_3}$.

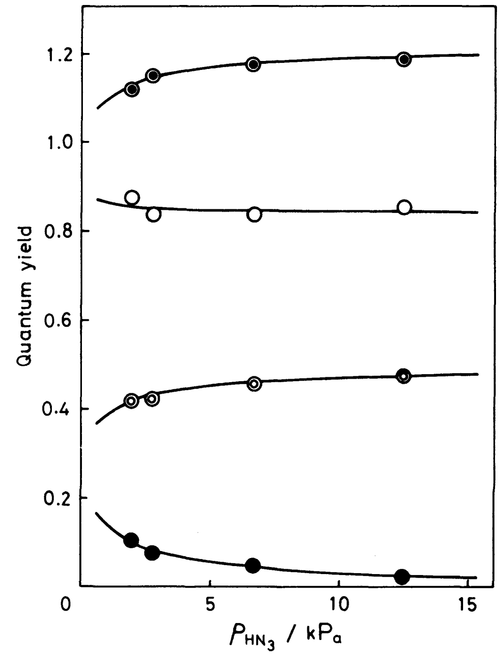


Fig. 4. Results of the photolysis measured as a function of HN_3 pressure at 4.44 kPa of CH_4, 30 °C, 313 nm, and the incident light intensity of 3.83×10^{15} quanta s^{-1}. ⊙, $\phi_{N_2}/4$; ○, $\phi_{NH_4N_3}$; ◎, ϕ_{H_2}; ●, $\phi_{CH_3NH_2\cdot HN_3}$.

Results

The results of the photolysis of HN_3 of 6.67 kPa, measured as a function of the CH_4 pressure at 313 nm and at 30 °C, and the absorbed-light intensity of 4.45×10^{14} quanta s^{-1} are shown in Fig. 3. It may be seen in Fig. 3 that ϕ_{N_2} and ϕ_{H_2} decrease, but $\phi_{CH_3NH_2\cdot HN_3}$ and $\phi_{NH_4N_3}$ increase, as the CH_4 pressure increases.

Figure 4 shows the results of the photolysis measured as a function of the HN_3 pressure at 4.44 kPa of CH_4, 30 °C, 313 nm, and at the incident-light intensity of 3.83×10^{15} quanta s^{-1}. In Fig. 4, it is found that ϕ_{N_2} and ϕ_{H_2} increase, but $\phi_{NH_4N_3}$ and $\phi_{CH_3NH_2\cdot HN_3}$ decrease, with an increase in the HN_3 pressure.

Discussion

Reaction Mechanism. On the basis of the experimental results in this work and in the light of the results achieved by previous investigators, the following reaction mechanism is postulated for the photolysis of HN_3 vapor in the presence of CH_4, where A and M denote HN_3 and CH_4 molecules respectively:

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

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

$$NH(a^1\Delta) + A \longrightarrow N_3 + NH_2 \tag{2b}$$

$$NH(a^1\Delta) + A \longrightarrow N_2 + N_2H_2^* \tag{2c}$$

$$NH(a^1\Delta) + M \longrightarrow CH_3NH_2^* \tag{3}$$

$$NH(a^1\Delta) + M \longrightarrow NH(X^3\Sigma^-) + M \tag{4}$$

$$CH_3NH_2^* \longrightarrow H + CNH_4 \tag{5}$$

$$CH_3NH_2^* \longrightarrow CH_3 + NH_2 \tag{6}$$

$$CNH_4 + A \longrightarrow CH_3NH_2 + N_3 \tag{7}$$

$$CNH_4 + A \longrightarrow CH_3N_3 + NH_2 \tag{8}$$

$$CH_3 + A \longrightarrow CH_4 + N_3 \tag{9}$$

$$CH_3NH_2 + A \longrightarrow CH_3NH_2\cdot HN_3. \tag{10}$$

The succeeding reactions for species consisting of only nitrogen and hydrogen atoms are as follows:[1] $NH(X^3\Sigma^-)+A\rightarrow H_2+2N_2$ (11); $NH(X^3\Sigma^-)+A\rightarrow NH_2+N_3$ (12); $H+A\rightarrow H_2+N_3$ (13); $H+A\rightarrow NH_2+N_2$ (14); $N_2H_2^*\rightarrow N_2H_2^{**}$ (15); $N_2H_2^*+A\rightarrow N_2+H_2+A$ (16); $N_2H_2^*+A\rightarrow NH_3+2N_2$ (17); $N_2H_2^{**}+A\rightarrow NH_3+2N_2$ (18); $NH_2+A\rightarrow NH_3+N_3$ (19); $NH_3+A\rightarrow NH_4N_3$ (20); $N_3+A\rightarrow N_3\cdot A$ (21); $2N_3\cdot A\rightarrow 3N_2+2A$ (22).

Since the formation of methylamine has been confirmed by the mass-spectrometric and gas-chromatographic measurements, it is clear that the first excited singlet, $NH(a^1\Delta)$, formed by the photolysis of HN_3 at 313 nm[1] reacts to give methylamine by insertion into a C–H bond of CH_4, just as in the case where the formation of $C_2H_5NH_2$ was found in the photolysis of HN_3 with C_2H_6.[2] Reaction 4 is a collisional spin-relaxation process by CH_4 from $NH(a^1\Delta)$ to $NH(X^3\Sigma^-)$, as was found for Xe[1] and C_2H_6.[2]

Since the enthalpy change of Reaction 3 is −459.8 kJ mol^{-1}, Reactions 5 and 6 are energetically possible. The unimolecular decompositions of $CH_3NH_2^*$ to give $2H_2+HCN$, CH_2+NH_3, and $H_2+CH_2{=}NH$ are also energetically possible. However, these reactions can probably be excluded for the following reasons: No HCN was detected; the formation of C_2H_6 by the insertion reaction, $CH_2+CH_4\rightarrow C_2H_6$, was not observed, and the detachment of H_2 from $CH_3NH_2^*$ by the molecular mechanism was not found in the reaction kinetics to be discussed later. Reactions other than those described above are not energetically possible for the unimolecular decompositions of $CH_3NH_2^*$, judging from the standard heats of formation listed in Table 1.

For the CNH_4 formed by Reaction 5, two structures of CH_2NH_2 and CH_3NH are possible. Hadley and Volman[8] have found, by means of the ESR method, that the major radical formed by the photolysis of methylamine in a solid matrix at 184.9 nm is CH_3NH. Hatano *et al.*[9] have also found, by a ESR study that CH_3NH is preferentially formed in the photolysis, by the use of low-pressure mercury lamp, of methylamine adsorbed on the surface of the porous Vycor glass at 77 K. On the photolyses of CD_3NH_2 vapor at 184.9, 147.0, and 123.6 nm, the formations of both CD_2NH_2 and CD_3NH are considerable, judging from the amounts of H_2, HD, and D_2 formed in the absence and the presence of C_2D_4[10] or NO and O_2.[11] Fukui *et al.*[12] have observed that the production of CH_2NH_2 from methylamine is less than that of CH_3NH upon the electron impact, while the peak of $CD_2NH_2^+$ was much higher than that of CD_3NH^+ in the mass spectrum of CD_3NH_2. On the other hand, according to simple estimations made by the RRK theory,[13] the greater part of the $CH_3NH_2^*$ can be expected to decompose to give CH_2NH_2, because the bond-dissociation energy of CH_3NH–H is 19.7 kJ mol^{-1}, higher than that of H–CH_2NH_2.[14] Judging from the results cited above, it seems that both CH_2NH_2 and CH_3NH radicals are formed in Reaction 5.

Reaction 6 is supported by the fact that CH_3 radicals were detected as intermediates. The collisional deactivation of $CH_3NH_2^*$ by a third body is negative, because $\phi_{CH_3NH_2\cdot HN_3}$ depends on the concentration ratio $[CH_4]/[HN_3]$, but is independent of the total pressure of CH_4 and HN_3, as will be discussed later. Reaction 7 means that CH_3NH_2 is formed by the hydrogen abstraction of CNH_4 (CH_2NH_2 and CH_3NH) from HN_3. The idea of the existence of CNH_4 radicals is supported by the fact that the formation of CH_3NH_2 is suppressed in the presence of NO. In the same way as has been discussed previously for the succeeding reactions of CH_2NH_2 radicals,[2] Reaction

TABLE 1. STANDARD HEATS OF FORMATION

Species	$\Delta H^\circ_{f,298}$ kJ mol^{-1}	Ref.	Species	$\Delta H^\circ_{f,298}$ kJ mol^{-1}	Ref.
H	218.0	a	CH_3	146.9	f
$N(^4S_{3/2})$	474.1	a	CH_4	−74.8	f
$N(^2D_{5/2})$	703.7	a	CN	418.4	f
$NH(X^3\Sigma^-)$	352.2	a	HCN	130.5	f
$NH(a^1\Delta)$	506.6	a	HNC	482.4	g
$NH_2(\tilde{X}^2B_1)$	171.5	a	CH=NH	312	h
NH_3	−46.0	a	CH_2=N	260	i
HN_3	299.8	a	CH_2=NH	94.6	f
$C(^3P_o)$	715.0	b	CH_2NH_2	154.8	j
$C(^1D_2)$	837.0	b,c	CH_3NH	174.5	k
CH	594.1	b	CH_3NH_2	−28.0	f
$CH_2(\tilde{X}^3\Sigma_g^-)$	384.5	d	CH_3N_3	280.3	f
$CH_2(\tilde{a}^1A_1)$	<481	d,e	CH_3-N=CH_2	72.4	f

a: Ref. 1. b: J.A. Kerr, *Chem. Rev.*, **66**, 465 (1966). c: C.E. Moore, "Atomic Energy Levels," Vol. I. National Bureau of Standards, Washington (1949); "Selected Tables of Atomic Spectra," NSRDS-NBS 3, National Bureau of Standards, Washington (1965~). d: W.A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968). e: G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, New York (1966). f: Ref. 2. g: Ref. 14a. h: Estimated by assuming that the enthalpy change of the CH_2=NH→H+CH=NH reaction is 435 kJ mol^{-1}. i: Estimated by assuming that the enthalpy change of the CH_3-N=CH_2→CH_3+N=CH_2 reaction is 335 kJ mol^{-1}. j: Ref. 14e. k: Ref. 14b.

8 was introduced for the following reasons: the reaction is energetically possible, and CH_3N_3 was found, but no products other than those described above could be detected.

The possibility of the formation of CH_3NH_2 by means of the cross-combination reaction $CH_3+NH_2 \rightarrow CH_3NH_2$ can be excluded, because no C_2H_6 or N_2H_4 (m/z=32) was found to be formed by the self-dimerization reactions of the CH_3 and NH_2 radicals. Miller[4] has found the formation of small amounts of C_2H_6 and HCN in the photolysis of HN_3 with CH_4. The formation of HCN was also observed in the photolysis of HN_3 with C_2H_6 at high light intensities.[2] It seems that these products are formed by these reactions: $2CH_3 \rightarrow C_2H_6$ and $CNH_4+N_3 \rightarrow HCN+N_2+NH_3$. However, these reactions are negative in the present work, because the photolysis was carried out at a low light intensity and no C_2H_6 and HCN could be detected.

Reaction 9 is a hydrogen-abstraction reaction by CH_3 radicals from HN_3. Konar and Darwent[15] have reported k_9 to be 1.48×10^{-16} cm^3 molecule^{-1} s^{-1} at 25 °C. Creak *et al.*[16] have reported that the specific rate of a hydrogen abstraction reaction by CH_3 radicals from CH_4 is $10^{-11.78}$ exp[−62.34(kJ mol^{-1})/RT] cm^3 molecule^{-1} s^{-1}. From both data, it is found that the hydrogen-abstraction reaction from HN_3 is 7.6×10^6 times faster than that from CH_4 at 25 °C. On the other hand, Bras and Combourieu[17] have found that the rate constant for the reactions of hydrogen atoms with HN_3 is $10^{-10.60}$ exp[−19.25(kJ mol^{-1})/RT] cm^3 molecule^{-1} s^{-1}. Kurylo and Timmons[18] have reported that the specific rate of a hydrogen-abstraction reaction by hydrogen atoms from CH_4 is $10^{-9.94}$ exp[−49.37(kJ mol^{-1})/RT] cm^3 molecule^{-1} s^{-1}. From both results, it is found that the reactions of hydrogen atoms with HN_3, Reactions 13 and 14, is 3.4×10^4 times faster than that with CH_4 at 30 °C.

Judging from these results, it seems that the reactions of CH_4 with the CH_3, $NH(X^3\Sigma^-)$, H, NH_2, and N_3 radicals are negligible, and that these radicals disappear upon such reactions with reactive HN_3 as Reactions 9, 11 to 14, 19, 21, and 22. Reactions 10, 15 to 18, and 20 have been discussed previously[1,2] and so are omitted here.

Reaction Kinetics. The following reaction kinetics were formulated to confirm the mechanism of Reactions 1 to 22 and to obtain the rate-constant ratios.

On the quantum yield of $CH_3NH_2 \cdot HN_3$, this equation:

$$\frac{1}{\phi_{CH_3NH_2\cdot HN_3}} = \frac{k_5+k_6}{k_5}\,\frac{k_7+k_8}{k_7}\left(\frac{k_3+k_4}{k_3}+\frac{k_2}{k_3}\,\frac{[HN_3]}{[CH_4]}\right) \tag{I}$$

can be derived, where:

$$k_2 = k_{2a} + k_{2b} + k_{2c}.$$

The plot of $1/\phi_{CH_3NH_2\cdot HN_3}$ *vs.* $[HN_3]/[CH_4]$ is shown in Fig. 5.

On the formations of H_2 and $CH_3NH_2 \cdot HN_3$, Eq. II can be derived:

$$\begin{aligned}\frac{\phi_{H_2}}{\phi_{CH_3NH_2\cdot HN_3}} &= \frac{k_7+k_8}{k_7}\left(\frac{k_4}{k_3}\,\frac{k_5+k_6}{k_5}\,\frac{k_{11}}{k_{11}+k_{12}}+\frac{k_{13}}{k_{13}+k_{14}}\right)\\ &\quad+\frac{k_5+k_6}{k_5}\,\frac{k_7+k_8}{k_7}\left(\frac{2k_{2a}}{k_3}\,\frac{k_{13}}{k_{13}+k_{14}}\right.\\ &\quad\left.+\frac{k_{2c}}{k_3}\,\frac{k_{16}}{k_{16}+k_{17}+k_{15}/[HN_3]}\right)\frac{[HN_3]}{[CH_4]}\end{aligned} \tag{II}$$

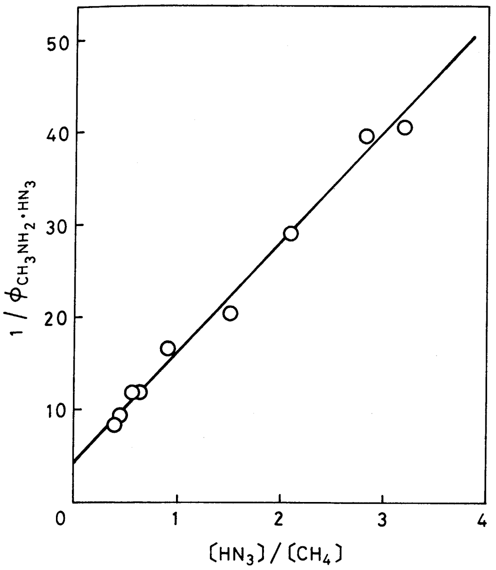


Fig. 5. Plot of $1/\phi_{CH_3NH_2\cdot HN_3}$ *vs.* $[HN_3]/[CH_4]$.

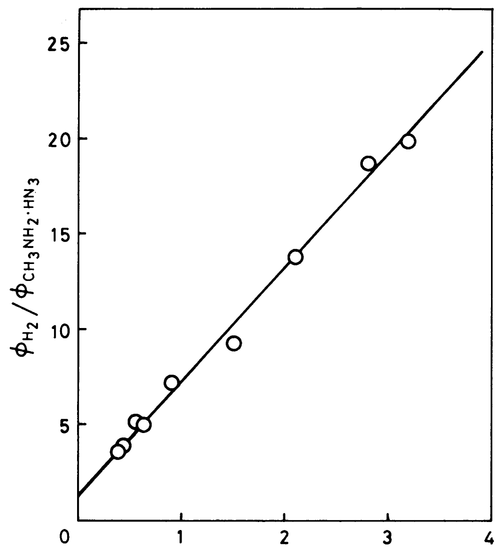


Fig. 6. Plot of $\phi_{H_2}/\phi_{CH_3NH_2\cdot HN_3}$ against $[HN_3]/[CH_4]$.

The plot of $\phi_{H_2}/\phi_{CH_3NH_2\cdot HN_3}$ *vs.* $[HN_3]/[CH_4]$ is shown in Fig. 6.

Equation III can be derived for the formations of N_2, H_2, and $CH_3NH_2\cdot HN_3$:

$$\frac{\phi_{N_2}+\phi_{H_2}}{\phi_{CH_3NH_2\cdot HN_3}} = \frac{k_7+k_8}{k_7}\left(1+4\frac{k_3+k_4}{k_3}\,\frac{k_5+k_6}{k_5}\right) + 4\frac{k_2+k_{2a}}{k_3}\,\frac{k_5+k_6}{k_5}\,\frac{k_7+k_8}{k_7}\,\frac{[HN_3]}{[CH_4]} \qquad \text{(III)}$$

The plot of $(\phi_{N_2}+\phi_{H_2})/\phi_{CH_3NH_2\cdot HN_3}$ *vs.* $[HN_3]/[CH_4]$ is shown in Fig. 7.

By using the values obtained previously[1] of $k_{2a}/k_2=0.336$, $k_{2c}/k_2=0.414$, $k_{12}/k_{11}=3.22$, $k_{14}/k_{13}=1.15$, $k_{15}/k_{16}=2.27\times10^{-7}$ mol cm^{-3}, and $k_{17}/k_{16}=1.19$, the values of $k_3/k_2=0.175$, $k_4/k_2=0.177$, $k_6/k_5=0.133$, and $k_8/k_7=0.85$ can be obtained from the intercepts and the slopes in Figs. 5, 6, and 7. As to the value of k_8/k_7, a value similar to that for CH_2NH_2 radicals[2] was obtained.

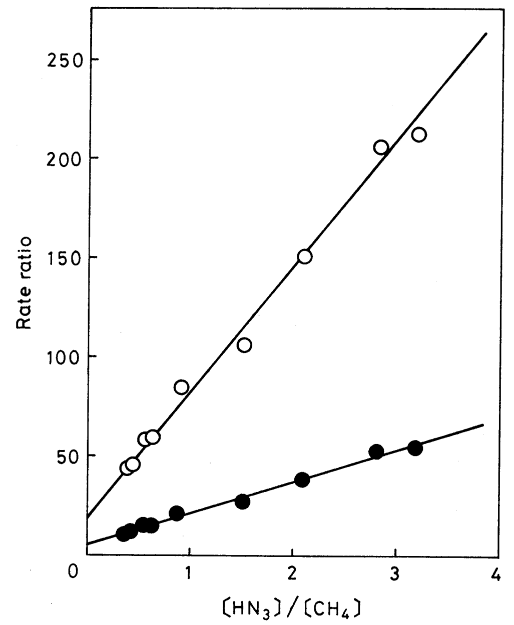


Fig. 7. Plots of $(\phi_{N_2}+\phi_{H_2})/\phi_{CH_3NH_2\cdot HN_3}$ (○) and $(\phi_{NH_4N_3}+\phi_{H_2})/\phi_{CH_3NH_2\cdot HN_3}$ (●) *vs.* $[HN_3]/[CH_4]$. The lower straight line was calculated from Eq. IV using the known rate constant ratios.

In order to verify the rate-constant ratios obtained above, Eq. IV was derived for the formations of NH_4N_3, H_2, and $CH_3NH_2\cdot HN_3$:

$$\frac{\phi_{NH_4N_3}+\phi_{H_2}}{\phi_{CH_3NH_2\cdot HN_3}} = \frac{k_3+k_4}{k_3}\,\frac{k_5+k_6}{k_5}\,\frac{k_7+k_8}{k_7} + \frac{k_8}{k_7} + \frac{k_2+k_{2a}}{k_3}\,\frac{k_5+k_6}{k_5}\,\frac{k_7+k_8}{k_7}\,\frac{[HN_3]}{[CH_4]} \qquad \text{(IV)}$$

The plot of $(\phi_{NH_4N_3}+\phi_{H_2})/\phi_{CH_3NH_2\cdot HN_3}$ *vs.* $[HN_3]/[CH_4]$ is also shown in Fig. 7. The values calculated from Eq. IV using the rate-constant ratios obtained above are shown by the lower straight line in Fig. 7. Fig. 7 shows that the straight line accords well with the experimental values.

Comparisons of Rate Constants. Chao *et al.*[19] have studied the decomposition rate of the chemically activated CH_3NH_2 which was formed by the reaction of NH_3 with the $^1CH_2$ produced by the photolysis of CH_2N_2. They have found that the specific rate of the unimolecular decomposition is 1.7×10^{10} s^{-1} for the photolysis at 435.8 nm and 2.3×10^{10} s^{-1} at 366 nm. The half-lifes for $C_2H_5NH_2^{*}$[2] and n-$C_3H_7NH_2^{*}$[20] were evaluated from these unimolecular decomposition rates. The half-life for $CH_3NH_2^{*}$ in this work was also calculated using the RRKM theory, as will be discussed below. These hallf-lifes are shown in Table 2. Here, the half-life (τ) was calculated from the

TABLE 2. HALF-LIFE AND DECOMPOSITION MODE OF CHEMICALLY ACTIVATED ALKYLAMINES

Alkylamine	Half life(τ) s	Fraction by radical mechanism (R_r)	Fraction of R-CH_2NH_2 bond fission ($R_{R\text{-}CH_2NH_2}$)
CH_3NH_2[a]	$\approx 7.7\times10^{-12}$[e]	1.00	0.88[j]
CH_3NH_2[b]	4.1×10^{-11}[f], 3.0×10^{-11}[g]		
$C_2H_5NH_2$[c]	6.8×10^{-11}	0.96[h]	1.00
n-$C_3H_7NH_2$[d]	1.78×10^{-10}	0.28[i]	0.96[k]

a) This work. b) Ref. 19. c) Ref. 2. d) Ref. 20. e) From the RRKM calculation by the Gorin model. f) CH_2N_2 was photodecomposed at 435.8 nm. g) CH_2N_2 was photolyzed at 366 nm. h) The residual fraction is due to the $C_2H_5NH_2^* \rightarrow CH_3CN+2H_2$ reaction. i) The residual is caused by these reactions; n-$C_3H_7NH_2^* \rightarrow CH_4+C_2H_5N$, $C_2H_4+CH_3NH_2$, $C_2H_6+CH_2NH$, $H_2+C_3H_7N$, and $C_3H_6+NH_3$. j) This is the maximum value, because the CH_3NH-H bond fission may also be possible. The residual is due to $CH_3NH_2^* \rightarrow CH_3+NH_2$. k) This value was estimated from these relations: the formation ratio of n-$C_3H_7NH_2$ to i-$C_3H_7NH_2$ is 1.55; the decomposition rate to give C_2H_5 radicals from both n- and i-$C_3H_7NH_2^*$ is 1.39 times faster than the rate to give CH_3 radicals, and the half-life of n-$C_3H_7NH_2^*$ is almost the same as that of i-$C_3H_7NH_2^*$. The residual fraction is due to n-$C_3H_7NH_2^* \rightarrow CH_3+CH_2CH_2NH_2$.

$\tau=\ln 2/\sum_i k_i$ relation, where k_i is the specific rate of i-th unimolecular decomposition. It can be seen in Table 2 that the half-life increases with an increase in the carbon number of alkylamines and with a decrease in the total internal energy in the $CH_3NH_2^*$ molecules, as will be discussed below.

The ratio of the sum of the rates of decomposition caused by the radical mechanism to the sum of all the decomposition rates, R_r, is also shown in Table 2. The ratio for decompositions by the molecular mechanism increases with an increase in the carbon number of alkylamines. This may be because the chance for the formation of three- and four-center transition states, resulting in decompositions by the molecular mechanism, increases with an increase in the molecular complexity.

The ratio of the R-CH_2NH_2 bond fission rate to the sum of all single-bond fission rates by the radical mechanism, $R_{R-CH_2NH_2}$, is also shown in Table 2, where R means H for CH_3NH_2, CH_3 for $C_2H_5NH_2$, and C_2H_5 for n-$C_3H_7NH_2$. It is found that the ratio for the R-CH_2NH_2 bond fission is very high on these amines. Meanwhile, no C–N bond fission was observed on the unimolecular decomposition of $C_2H_5NH_2^*$,[2] although the C–N bond dissociation energy is 20.2 kJ mol^{-1} lower than that of the C–C bond. Similarly, hardly no C–N bond fission was found on the unimolecular decomposition of n-$C_3H_7NH_2^*$,[20] and the probability of the CH_3–$CH_2CH_2NH_2$ bond fission was also found to be very small. Such a high R-CH_2NH_2 bond fission efficiency may be because the CH_2NH_2 group of the activated complex which produces the R-CH_2NH_2 bond rupture is stabilized by the interaction of an unpaired electron of the C atom with nonbonding electrons of the N atom in the next position.[21]

Although the R-CH_2NH_2 bond fission proceeds with a high efficiency, the $k_5>k_6$ relation can not be explained in terms of the enthalpy, for the $CH_3NH_2 \rightarrow H+CH_2NH_2$ reaction is 54.4 kJ mol^{-1} more endothermic than the $CH_3NH_2 \rightarrow CH_3+NH_2(\tilde{X}\,^2B_1)$ reaction.

On the other hand, Kassab *et al.*[22] have computed the potential surface on the decomposition of CH_3NH_2 using *ab initio* methods; they have suggested this reaction:

$$CH_3NH_2 \longrightarrow CH_3 + NH_2(\tilde{A}\,^2A_1) \qquad (6)$$

for the decomposition of $CH_3NH_2(A')$ in the ground state, as well as where the $NH_3 \rightarrow H+NH_2(\tilde{A}\,^2A_1)$ reaction can be anticipated for the decomposition of ammonia in the ground state[23] from the correlation by symmetry.[24] Provided that the electronic state of NH_2 formed by Reaction 6 is $\tilde{A}\,^2A_1$, Reaction 6 becomes 68.2 kJ mol^{-1} more endothermic than Reaction 5. In this case, the $k_5>k_6$ relation is explainable.

As for the $HN_3+NH(a^1\Delta) \rightarrow N_3+NH_2(\tilde{A}\,^2A_1)$ reaction, of the same kind as Reaction 6, the formation of $NH_2(\tilde{A}\,^2A_1)$ has been observed by McDonald *et al.*[25] and Piper *et al.*[26] Kajimoto *et al.*[27] have also observed the emission of $NH_2(\tilde{A}\,^2A_1)$ formed by a similar reaction, $HN_3+H \rightarrow N_2+NH_2(\tilde{A}\,^2A_1)$. The formation of $NH_2(\tilde{A}\,^2A_1)$ by Reaction 6 is also supported by the fact that hardly no C–N bond rupture was found in the unimolecular decompositions of $C_2H_5NH_2^*$[2] and $C_3H_7NH_2^*$.[20]

In order to examine the adequacy of Reaction 6 bring about $NH_2(\tilde{A}\,^2A_1)$ and to obtain the absolute value of k_6, calculation by means of the RRKM theory was carried out. The specific rate calculated by means of the RRKM theory for the unimolecular decompositions of chemically activated molecules, k_E, is given by this equation:[28]

$$k_E = \frac{q_r^{\ddagger} q_{ir}^{\ddagger}}{q_r} \frac{\Gamma(s)}{\Gamma(s^{\ddagger}+r^{\ddagger}/2+1)} \frac{\prod_{i=1}^{s} h\nu_i}{h\prod_{i=1}^{s^{\ddagger}} h\nu_i^{\ddagger}(kT)^{r^{\ddagger}/2}} \times \frac{[E^{\ddagger}+a^{\ddagger}E_z^{\ddagger}]^{s^{\ddagger}+r^{\ddagger}/2}}{[E^{\ddagger}+E_0+aE_z]^{s-1}} \qquad \text{(V)}$$

Here, s, $s^{\ddagger}$, and $r^{\ddagger}$ indicate the numbers of degrees of freedom for the vibrations of the molecule, and for the vibrations and internal free rotations of the activated complex, respectively.

In the case of a single-bond fission, the activated complex should be very loose because of the critical state, and it must have the same structure as that for the radical recombination which is a reverse reaction. Thus, the Gorin model[29] was used in this case, assuming that the activated complex is an associated form of the CH_3 radical (planar, D_{3h}) and the $NH_2(\tilde{A}\,^2A_1(\Pi))$ radical (linear, $D_{\infty h}$). According to this "loosest" model, s, $s^{\ne}$, and $r^{\ne}$ become 15, 10, and 5 respectively.

q_r and $q_{ir}^{\ne}$ are the partition functions for the rotation of the molecule and the internal free rotation of the complex. By the Gorin model, the partition function for the rotation of the complex, $q_r^{\ne}$, can be expressed by this equation:[30]

$$q_r^{\ne} = \frac{8\pi^2\Gamma(2/3)\mu kT}{\sigma h^2}\left(\frac{2A}{kT}\right)^{1/3} \qquad \text{(VI)}$$

Since both CH_3 and NH_2 groups are nonpolar, the attractive potential constant in the Lennard-Jones 12-6 intermolecular potential, A, can be calculated from the Slater and Kirkwood equation[3,31] for the dispersion term. The polarizabilities of the CH_3 and NH_2 groups were estimated to be 2.24 and 1.78×10^{-30} m^3 from the atomic polarizabilities of 1.039(C), 0.905(N), and $0.401(H)\times10^{-30}\,m^3$. The number of outer-shell electrons is 7 for both CH_3 and NH_2 groups. The σ in Eq. VI is unity in this case.

The internal energy change of Reaction 6 at 0 K, E_o, was estimated to be 460.8 kJ mol^{-1} from the standard enthalpy change of 469.0 kJ mol^{-1}. The vibrational wave numbers ($\bar{\nu}_i$)[32] and the moments of inertia[19] for the CH_3NH_2 molecule and the vibrational wave numbers ($\bar{\nu}_i^{\ne}$)[33–35] and the moments of inertia for the complex are shown in Table 3. The last term in Eq. V was calculated from the relations derived by Rabinovitch *et al.*[36] The values of k_6 at 303 K, measured as a function of the excess energy ($E^{\ne}$) in the activated complex, are shown in Fig. 8.

On the photolysis of HN_3 at 313 nm, an excess energy of 177.9 kJ mol^{-1} is released and then distributed to N_2 and NH($a^1\Delta$) as fragments. Since the distribution fraction of the energy to NH($a^1\Delta$) is unclear, it was assumed that slightly less than one half of the excess energy is divided to NH($a^1\Delta$). Then, the total internal energy in CH_3NH_2* formed by Reaction 3 becomes about 540 kJ mol^{-1}. Since E_o is 460.8 kJ mol^{-1}, $E^{\ne}$ becomes about 79 kJ mol^{-1}. The value of k_6 corresponding to this energy is $1.05\times10^{10}\,s^{-1}$ as may be seen in Fig. 8. From $k_6/k_5=0.133$, $k_5=7.9\times10^{10}\,s^{-1}$ is obtained. Thus, the half-life of CH_3NH_2* obtained from $\tau=\ln 2/(k_5+k_6)$ becomes 7.7×10^{-12} s.

RRKM calculations by the methods described above were also carried out for the decomposition rates of the CH_3NH_2* formed under the reaction conditions performed by Chao *et al.*;[19] the calculated values were found to be consistent with their experimental values. The low $E^{\ne}$ was the reason that the decomposition rates observed by them are slow as compared with that in this work.

On the other hand, the specific rate for the collisional deactivation of CH_3NH_2* by a third body(Q), k_z, can be calculated from the Lennard-Jones collision frequency as described previously.[2] The values of σ and ε/k used in the calculation are 4.30 and 500 for CH_3NH_2,[37] 3.82 and 137 for CH_4,[38] and 3.98 Å and 240 K for HN_3[2] respectively. The highest total pressure in the present work is 24.27 kPa (P_{HN_3}=6.67 and P_{CH_4}=17.60 kPa). In this case, the rate ratio of the collisional deactivation to the unimolecular decompositions of CH_3NH_2*, $k_z[Q]/(k_5+k_6)$, becomes 0.038. This result is consistent with the experimental finding that the collisional

Table 3. Models for the unimolecular decomposition of CH_3NH_2

	Molecule		Complex	
Wavenumber cm^{-1}	3424	1430	3162(2)[a]	
	3360	1424	3044(1)[a]	
	2985	1195	1396(2)[a]	
	2962	1130	607(1)[b]	
	2820	1044	3440(1)[c]	
	1623	780	3325(1)[d]	
	1485	264	633(2)[d]	
	1474			
Moment of inertia 10^{-47} kg m^2	38.4		5.85[e]	3.34[f]
	36.5		2.92[e]	3.34[f]
	7.8		2.92[e]	

a) Ref. 33. b) Ref. 34. c) Estimated value for the antisymmetric stretching vibration of $NH_2(\tilde{A}\,^2A_1(\Pi))$. d) Ref. 35. e) Ref. 24, p. 609. Calculated from r_o(C–H)= 1.079 Å for $CH_3(\tilde{X}\,^2A_2'', D_{3h})$. f) Ref. 35. Calculated from r_o(N–H)=1.004 Å for $NH_2(\tilde{A}\,^2A_1(\Pi))$.

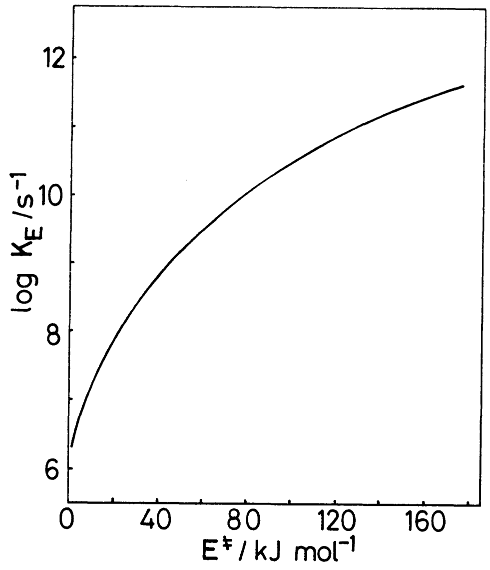


Fig. 8. Specific rate of Reaction 6 by the RRKM calculation, measured as a function of the excess energy.

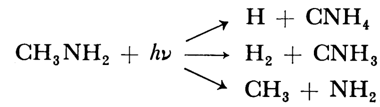
TABLE 4. RELATIVE FRACTIONS FOR THE UNIMOLECULAR DECOMPOSITIONS OF THE CHEMICALLY AND PHOTOCHEMICALLY ACTIVATED METHYLAMINE

Wavelength	Excitation energy	Relative fraction/%		
nm	kJ mol^{-1}	H+CNH_4	H_2+CNH_3	CH_3+NH_2
Chemically activated$^{a)}$	≈540$^{e)}$	88.3	0	11.7
244—194$^{b)}$	490—617	91.3	0$^{f)}$	8.7
184.9$^{c)}$	647	89.1	7.4	3.5
147$^{d)}$	814	68	19	13
147$^{c)}$	814	56.4	38.7	4.9
123.6$^{c)}$	968	55.6	37.9	6.5

a) This work. b) Ref. 39. c) Ref. 11. d) Ref. 10. e) Estimated from the enthalpy change. f) The formation amount of H_2 converges to zero with an increase in the pressure of O_2 as a scavenger.

deactivation of CH_3NH_2* could not be found within the limits of experimental accuracy. It thus appears that the calculated values of k_5, k_6, and τ obtained above are reasonable.

On the photolysis of CH_3NH_2 vapor, the primary processes are, in general, given by this mechanis:[10,11,39]



$$CH_3NH_2 + h\nu \longrightarrow \begin{cases} H + CNH_4 \\ H_2 + CNH_3 \\ CH_3 + NH_2, \end{cases}$$

except for the decompositions of CH_3NH_2+$h\nu$(123.6 nm)→CH_4+NH($c^1\Pi$) and others in very-short-wavelength systems.[40] Provided that the succeeding reactions for H atoms and CH_3 radicals are H+RH→H_2+R, CH_3+RH→CH_4+R, and 2CH_3→C_2H_6, the relative fractions for three photodissociation processes can be calculated by means of the following simplified relations: [H_2−H_2(scav)]/[H_2+CH_4+2C_2H_6] for H+CNH_4; [H_2(scav)]/[H_2+CH_4+2C_2H_6] for H_2+CNH_3; [CH_4+2C_2H_6]/[H_2+CH_4+2C_2H_6] for CH_3+NH_2. Here, [H_2(scav)] indicates the amount of H_2 formed in the presence of a scavenger such as O_2 and NO. The relative fractions are shown in Table 4, together with the fractions for the umimolecular decompositions of CH_3NH_2* formed by Reaction 3.

Table 4 shows that the relative fractions for the chemically activated CH_3NH_2* are very similar to those for the photochemically activated CH_3NH_2* at 244 to 194 nm, and that the fraction for the formation of H_2 by the molecular mechanism increases with an increase in the excitation energy. It is also found that the fraction for H+CNH_4 is always larger than the fraction for CH_3+NH_2. Regarding this trend, Kassab *et al.*[22] have found, from theoretical considerations, that the potential barrier resulting in the CH_3-NH_2 bond rupture is higher than that for the CH_3NH-H bond rupture on the photodissociation of the lowest excited singlet, CH_3NH_2.

On the efficiencies of the reactions of NH($a^1\Delta$) with saturated hydrocarbons, the rate-constant ratio of the insertion reaction of NH($a^1\Delta$) into a C-H bond to the reactions of NH($a^1\Delta$) with HN_3 is 0.175 (k_3/k_2) for CH_4 and 0.334 for C_2H_6.[2] The low efficiency for CH_4 may be due to the facts that the number of C-H bonds of CH_4 is less than that of C_2H_6 and that the C-H bond-dissociation energy of CH_4 is higher than that of C_2H_6. The rate-constant ratio of the collisional spin relaxation of NH($a^1\Delta$) to Reaction 2 is 0.177 (k_4/k_2) for CH_4, and 0.217 for C_2H_6.[2] The difference may be because the collisional spin-relaxation efficiency depends on the molecular complexity, that is, the number of atoms constituting a saturated hydrocarbon molecule. More details will be presented in a later work.[20]

Summary. The reaction efficiencies of NH($a^1\Delta$) with CH_4 and the unimolecular decomposition rates of the CH_3NH_2* formed by the insertion were investigated. The insertion efficiency of NH($a^1\Delta$) into a C-H bond of CH_4 was 0.52 as compared with that of C_2H_6. This difference appears to be caused by the higher C-H bond dissociation energy and the lower C-H bond number than those for C_2H_6. The collisional deactivation efficiency of NH($a^1\Delta$) to NH($X^3\Sigma^-$) by CH_4 was 0.82 of that by C_2H_6. The unimolecular decomposition, CH_3NH_2*→H+CNH_4 (5), was 7.5 times faster than the CH_3NH_2*→CH_3+NH_2 (6) decomposition, although the C-H or N-H bond dissociation energy is higher than that of the C-N bond. However, this is explainable provided that the electronic state of NH_2 formed by Reaction 6 is $\tilde{A}^2A_1$. From the RRKM calculation by the Gorin model, $k_5 \approx 7.9 \times 10^{10}\,s^{-1}$, $k_6 \approx 1.05 \times 10^{10}\,s^{-1}$, and τ (half-life of CH_3NH_2*)$\approx 7.7 \times 10^{-12}$ s were estimated. These results are in accord with the experimental result that the collisional deactivation of CH_3NH_2* was not observed in the total pressure range lower than 24.3 kPa.

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