August, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *2363—2370 (1983)* 2363

Reactions of NH Radicals. III. Photolysis of HN_3 in the Presence of C_2H_4 at 313 nm

Sukeya Kodama

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

(Received September 13, 1982)

Photolysis of HN_3 vapor in the presence of C_2H_4 was studied at 313 nm and 30 °C. The main products were N_2, H_2, CH_4, C_2H_6, NH_4N_3, $C_2H_5N\cdot HN_3$ (salt of C_2H_5N (azomethines) with HN_3), HCN, CH_3CN, CH_3N_3, and $C_2H_5N_3$. The quantum yields of these products were measured as a function of the light intensity and pressures of HN_3 and C_2H_4. The following mechanism for the main reactions was infered: $HN_3+h\nu(313\text{ nm})\rightarrow NH(a^1\Delta)+N_2$; $NH(a^1\Delta)+HN_3\rightarrow 2N_2+2H$ (2a); $NH(a^1\Delta)+HN_3\rightarrow NH_2+N_3$(2b); $NH(a^1\Delta)+HN_3\rightarrow N_2+N_2H_2^*$ (2c); $NH(a^1\Delta)+C_2H_4\rightarrow C_2H_5N^*$ (aziridine and vinylamine) (3); $C_2H_5N^*\rightarrow CH_3+CH_2N$ (4); $C_2H_5N^*\rightarrow H_2+CH_3CN$ (5); $C_2H_5N^*\rightarrow H+C_2H_4N$ (6); $C_2H_5N^*\rightarrow C_2H_3+NH_2$ (7). The rate constant ratios at 30 °C are: $k_3/k_2=1.64$; $k_5/k_4=0.102$; $k_6/k_4=0.564$; $k_7/k_4=0.734$. The collisional deactivation from $NH(a^1\Delta)$ to $NH(X^3\Sigma^-)$ by C_2H_4 was not found. The lifetime of $C_2H_5N^*$ is much shorter than 6.8×10^{-11} s for $C_2H_5NH_2^*(\leftarrow NH(a^1\Delta)+C_2H_6)$. The relative and absolute rates for the reactions of $NH(a^1\Delta)$ with HN_3, Xe, C_2H_6, and C_2H_4 are discussed.

The photolysis of HN_3 in the presence of Xe[1] and C_2H_6[2] at 313 nm has been studied previously, and it was found that HN_3 is a useful source for the first excited singlet $NH(a^1\Delta)$; ethylamine is produced by insertion of $NH(a^1\Delta)$ into a C–H bond of C_2H_6.

On the other hand, an addition reaction to a π bond as well as the insertion reaction is to be expected in the reactions of $NH(a^1\Delta)$ with unsaturated hydrocarbons, as were found in the reactions of unsaturated hydrocarbons with the isoelectronic species such as $O(^1D)$,[3] $S(^1D)$,[4] and $CH_2(^1A_1)$.[5] Therefore, it is of interest that the reactions of $NH(a^1\Delta)$ with C_2H_4 having π bond are compared with those for C_2H_6 having σ bond only.

On the photolysis of HN_3 with C_2H_4 in the vapor phase, Miller[6] has found that the reaction products are N_2, H_2, CH_4, C_2H_6, HCN, CH_3CN, NH_4N_3, and a yellowish film of polymeric material. Cornell, Berry, and Lwowski[7] have found the products of H_2, CH_4, HCN, CH_3CN, and an amorphous solid in the flash and steady photolyses. Back and his co-workers[8] have studied the reactions of C_2H_4 with NH formed by the photolysis of HNCO, and reported that no aziridine, vinylamine, nor other nitrogen-bearing products could be detected. Tidemann and Schiendler[9] have obtained $\phi_{C_2H_6}=0.56$ and $\phi_{n\text{-}C_4H_{10}}=0.03$ in the photolysis of HN_3 vapor with C_2H_4.

Jacox and Milligan[10] have observed the formation of aziridine in the photolysis of HN_3 with C_2H_4 in an argon matrix at 4 K. Recently, Kitamura, Tsunashima, and Sato[11] have found N_2, NH_3, and aziridine in the photolysis of HN_3 in liquid ethylene at the Dry Ice–methanol temperature, and obtained the relative yields of $NH_3/N_2=0.16$ and aziridine/$N_2=0.18$, independently of $[HN_3]/[C_2H_4]$.

Many results have been obtained for the reactions of NH with C_2H_4, however, they are insufficient to explain in detail the reaction mechanism and the reaction rates. Therefore, the photolysis of HN_3 vapor with C_2H_4 was reinvestigated in the present work.

Experimental

Ethylene obtained from Takachiho Chemical Co. was 99.9% in purity, and was purified each time before use by condensation and evacuation at −160 and −196 °C. Preparation and purification of HN_3, and the apparatus and procedure for reaction were the same as described previously.[1,2] All runs in this work were carried out at 313 nm at 30 °C. The light intensity was controlled with screens, and the irradiation time was varied from 10 to 120 min. The degree of conversion of HN_3 was below a few per cent for all runs.

The main reaction products were N_2, H_2, CH_4, C_2H_6, NH_4N_3, $C_2H_5N\cdot HN_3$ (salt by HN_3 with C_2H_5N(azomethines)), HCN, CH_3CN, CH_3N_3, $C_2H_5N_3$, and polymers. C_2H_2, C_3H_8, C_4H_8, and n-C_4H_{10} are also found as small amount.

For the identification of azides, CH_3N_3,[12] $C_2H_5N_3$,[13] n-$C_3H_7N_3$,[14] n-$C_4H_9N_3$,[15] and $N_3CH_2CH_2N_3$[16] were prepared as reference samples, $N_3(CH_2)_4N_3$ was prepared by heating for about 12 hours in a water bath a mixture of NaN_3 (35 g), $Br(CH_2)_4Br$ (46 g), C_2H_5OH (40 cm^3), and water (100 cm^3). The retention times of these azides were measured by gas chromatography using a silicone oil column (1 m) at 35 °C. The relative retention times, zero for CH_4 and unity for benzene, are shown in Table 1 together with $N_3CH_2CH_2Cl$ and $N_3(CH_2)_4Br$ formed as monosubstituted azides of $ClCH_2$-CH_2Cl and $Br(CH_2)_4Br$. The formations of CH_3N_3 and $C_2H_5N_3$ were ascertained using the data in Table 1. While, n-$C_3H_7N_3$, n-$C_4H_9N_3$, $N_3CH_2CH_2N_3$, and $N_3(CH_2)_4N_3$ could not be detected as a product.

The formation of HCN was verified by the pyridine–pyrazolone method.[17] The formation of CH_3CN was confirmed by gas chromatography using a squalene column (2 m) at 40 °C and a silicone oil column (1 m) at 35 °C.

The basic products(B) such as NH_3 and amines react with acidic HN_3 to give salts ($B\cdot HN_3$) as white volatile powders.[2] Therefore, the white volatile products trapped at the Dry Ice–acetone temperature were introduced into a solid sodium

Table 1. Relative retention times of azides by a silicone oil column (1 m) at 35 °C[a]

Azide	Relative retention time	Azide	Relative retention time
HN_3	0.187	$N_3(CH_2)_2Cl$	2.25
CH_3N_3	0.194	$N_3(CH_2)_2N_3$	5.08
$C_2H_5N_3$	0.382	$N_3(CH_2)_4Br$	22.9
n-$C_3H_7N_3$	0.846	$N_3(CH_2)_4N_3$	27.2
n-$C_4H_9N_3$	2.03		

a) The relative retention time was measured on the basis of zero for methane and unity for benzene.

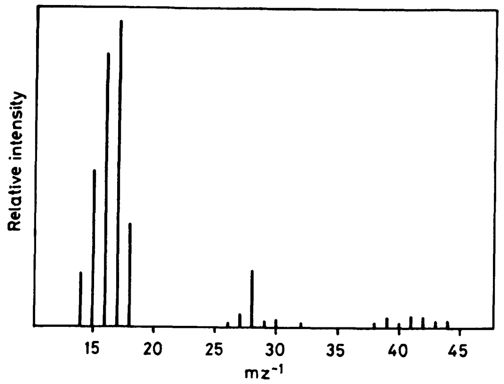


Fig. 1. Mass spectrum of a substance removed HN_3 from the white volatile products trapped at the Dry Ice–acetone temperature. The ionizing voltage is 15 eV.

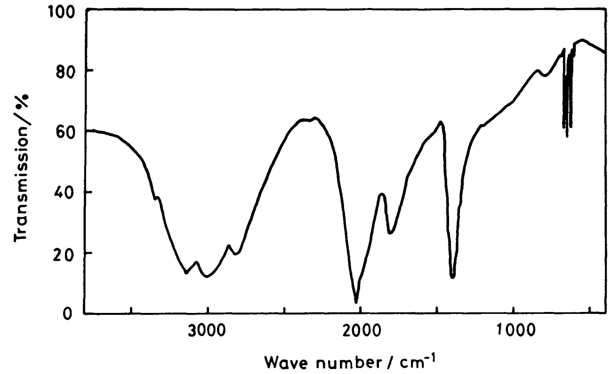


Fig. 2. Infrared spectrum of the white volatile products.

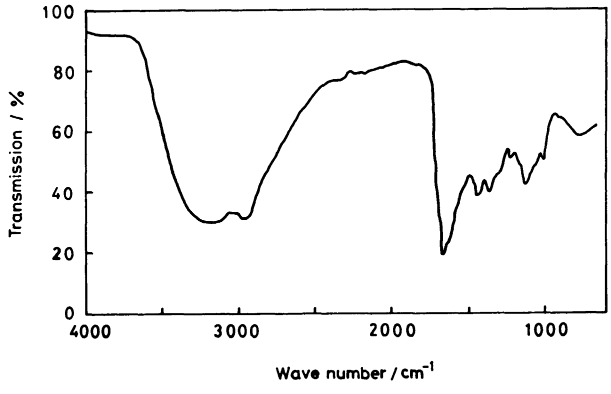


Fig. 3. Infrared spectrum of a substance prepared by removing ethanol from an ethanol solution of the yellowish polymeric material formed on the inside of the reaction cell.

hydroxide column to remove HN_3 from $B{\cdot}HN_3$ by the reaction $B{\cdot}HN_3+NaOH\longrightarrow B+NaN_3+H_2O$. A mass spectrum of the HN_3-free products at the ionizing voltage of 15 eV is shown in Fig. 1.

The spectrum is more complicated than the spectrum of the mixture of NH_3, CH_3NH_2, and $C_2H_5NH_2$ formed in the photolysis of HN_3 with C_2H_6.[2] It seems that $m/z=16$. 17, and 18 correspond to NH_2^+, NH_3^+, NH_4^+,[2] and the other peaks are due to $C_2H_5N^+$ ($m/z=43$) and its fragments. The large fragment peaks of $m/z=15$ and 28 may be due to the cracking reactions of $C_2H_5N\xrightarrow{e^-}CH_3^+ + CH_2{=}N$ (or $CH{=}NH$), $CH_3+CH_2{=}N^+$ (or $CH{=}NH^+$), $C_2H_4^+ + NH$, and $C_2H_4+NH^+$. However, the later two may be minor, because both need fission of two single bonds for aziridine and vinylamine and a double bond for CH_3–$CH{=}NH$. A mass spectrum of the HN_3-free products at the ionizing voltage of 75 V is inconsistent with that of aziridine measured at 70 V.[18] Vinylamine is not stable in the normal state. Judging from these reasons, the C_2H_5N may be CH_3–$N{=}CH_2$ or CH_3–$CH{=}NH$.

An infrared spectrum of the white volatile products trapped at Dry Ice–acetone temperature was observed by the KBr disk method, and is shown in Fig. 2. Since the spectrum is almost the same as the spectrum of solid NH_4N_3 at 90 K,[19] it was not possible to identify the structure of C_2H_5N from the spectrum in Fig. 2.

A yellowish film of polymeric material was formed on the inside of the reaction cell. The yellowish material is nonvolatile, very highly viscous, and soluble in ethanol. An infrared spectrum by the KBr disk method of a substance prepared by removing ethanol from an ethanol solution of the yellowish material is shown in Fig. 3. It is found from the spectrum that the substance includes the functional groups of NH (3200 and 1620), CH_3 (2960, 2870, 1450, 1380, and 1125), CH_2 (2950, 2850, 1450, and 1300), C=N (1670), and C–N (1230, 1175, and 1040 cm^{-1}).

A yellowish oily liquid[6] is formed by mixing aziridine and HN_3 at room temperature and the vapor phase. However, an infrared spectrum of the oily liquid is different from the spectrum in Fig. 3. Accordingly, it seems that the yellowish film of polymeric material does not result from aziridine.

N_2, H_2, CH_4, C_2H_6, NH_4N_3, and $C_2H_5N{\cdot}HN_3$ of the reaction products were determined quantitatively. First, these products were separated at solid nitrogen temperature (−210 °C), −160 °C, and Dry Ice–acetone temperature. Quantitative analyses of N_2, H_2, and CH_4, noncondensable gases at −210 °C, were carried out by the procedures described previously.[2] The total amount of C_2H_6 and unconverted C_2H_4, passing through a trap at −160 °C, was determined by a Toepler gauge. C_2H_6 and C_2H_4 were separated by the gas chromatography using a silica gel column (2 m) at 80 °C.

NH_4N_3 and $C_2H_5N{\cdot}HN_3$ condensed at Dry Ice–acetone temperature were introduced into a CuO column at about 550 °C. The amounts of N_2, NO, N_2O, and CO_2 as combustion products were determined by the method described previously.[2] The amounts of $C_2H_5N{\cdot}HN_3$ and NH_4N_3 can be calculated from the equations of $[C_2H_5N{\cdot}HN_3]=[CO_2]/2$ and $[NH_4N_3]=([N_2]+[N_2O]-[CO_2])/2+[NO]/4$.

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

Results

Results for the photolysis of HN_3 of 6.7 kPa, measured as a function of C_2H_4 pressure at 313 nm, 30 °C, and the absorbed light intensity of 2.2×10^{15} quanta s^{-1} are shown in Fig. 4. It is seen in Fig. 4 that ϕ_{H_2} and $\phi_{NH_4N_3}$ decrease drastically by adding C_2H_4 in small amount.

Figure 5 shows the results of the photolysis measured as a function of HN_3 pressure at 4.0 kPa of C_2H_4, 30 °C, 313 nm, and the incident light intensity of 1.9×10^{16} quanta s^{-1}. In Fig. 5, it is found that ϕ_{N_2} and $\phi_{C_2H_6}$ increase, but ϕ_{CH_4} decreases with an increase of HN_3 pressure. It is also found that the formation rate of N_2, R_{N_2}, increases rectilinearly as the HN_3 pressure increases.

Figure 6 shows the results of the photolysis measured as a function of the absorbed light intensity at 6.7 kPa of

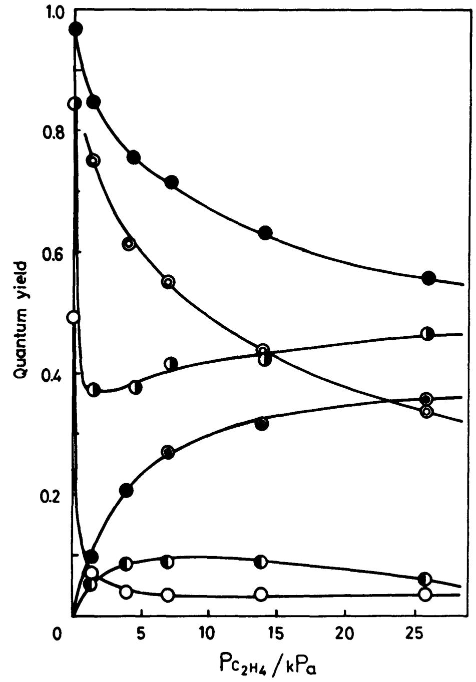


Fig. 4. Results of the photolysis of HN_3 of 6.7 kPa, measured as a function of C_2H_4 pressure at 313 nm, 30 °C, and the absorbed light intensity of 2.2×10^{15} quanta s^{-1}. ●, $\phi_{N_2}/5$; ◎, $\phi_{C_2H_6}$; ◑, $\phi_{NH_4N_3}$; ⊙, ϕ_{CH_4}; ◐, $\phi_{C_2H_5N\cdot HN_3}$; ○, ϕ_{H_2}.

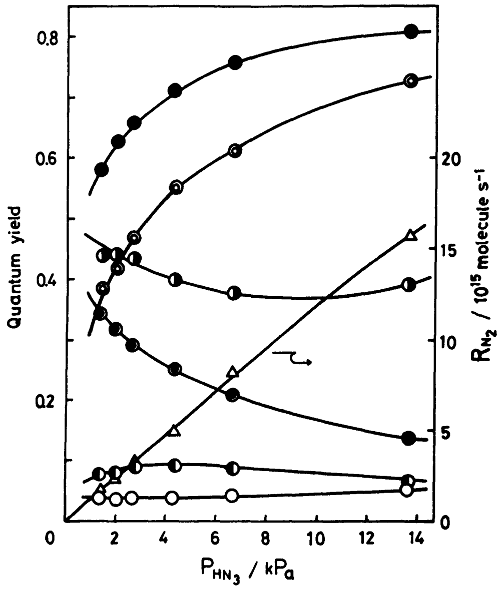


Fig. 5. Results of the photolysis measured as a function of HN_3 pressure at 4.0 kPa of C_2H_4, 30 °C, 313 nm, and the incident light intensity of 1.9×10^{16} quanta s^{-1}. △, R_{N_2}. The other marks are the same as those in Fig. 4.

HN_3, 4.0 kPa of C_2H_4, 30 °C, and 313 nm. It is shown in Fig. 6 that all quantum yields are independent of the light intensity.

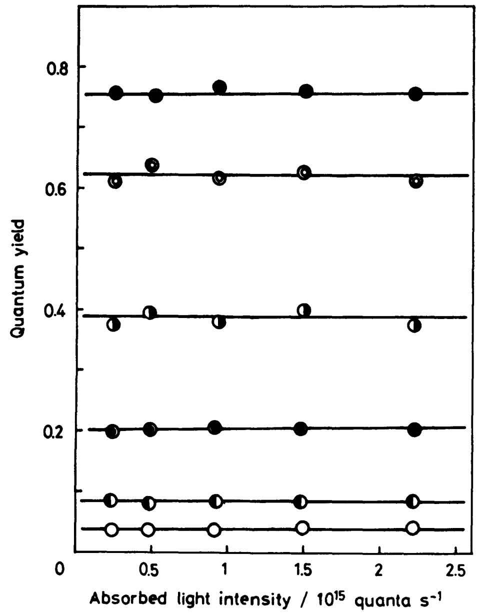


Fig. 6. Results of the photolysis measured as a function of the absorbed light intensity at 6.7 kPa of HN_3, 4.0 kPa of C_2H_4, 30 °C, and 313 nm. The marks are the same as those in Fig. 4.

Discussion

Reaction Mechanism. On the basis of the experimental results in this work and in the light of the results achieved by previous investigators, we have postulated the following mechanism for the photolysis of HN_3 vapor in the presence of C_2H_4, where A and E mean HN_3 and C_2H_4 molecules, respectively:

$$A + h\nu(313\,\text{nm}) \longrightarrow N_2 + NH(a^1\Delta) \tag{1}$$
$$NH(a^1\Delta) + A \longrightarrow 2N_2 + 2H \tag{2a}$$
$$NH(a^1\Delta) + A \longrightarrow NH_2 + N_3 \tag{2b}$$
$$NH(a^1\Delta) + A \longrightarrow N_2 + N_2H_2{}^* \tag{2c}$$
$$NH(a^1\Delta) + E \longrightarrow C_2H_5N^* \tag{3}$$
$$C_2H_5N^* \longrightarrow CH_3 + CH_2N \tag{4}$$
$$C_2H_5N^* \longrightarrow H_2 + CH_3CN \tag{5}$$
$$C_2H_5N^* \longrightarrow H + C_2H_4N \tag{6}$$
$$C_2H_5N^* \longrightarrow C_2H_3 + NH_2 \tag{7}$$
$$C_2H_4N + A \longrightarrow C_2H_5N + N_3 \tag{8}$$
$$C_2H_4N + E \longrightarrow C_4H_8N \tag{9}$$
$$H + A \longrightarrow H_2 + N_3 \tag{10}$$
$$H + A \longrightarrow NH_2 + N_2 \tag{11}$$
$$H + E \longrightarrow C_2H_5 \tag{12}$$
$$CH_2N + A \longrightarrow N_2 + HCN + NH_2 \tag{13}$$
$$N_2H_2{}^* + E \longrightarrow N_2 + C_2H_6 \tag{14}$$
$$R(CH_3,C_2H_3,C_2H_5,\text{ and }NH_2)+A \longrightarrow RH+N_3 \tag{15}$$
$$NH_3 + A \longrightarrow NH_4N_3 \tag{16}$$
$$C_2H_5N + A \longrightarrow C_2H_5N\cdot HN_3 \tag{17}$$
$$C_4H_8N + E \longrightarrow \text{Polymers} \tag{18}$$
$$N_3 + A \longrightarrow A\cdot N_3 \tag{19}$$
$$N_3 + E \longrightarrow E\cdot N_3 \tag{20}$$
$$A\cdot N_3 + A\cdot N_3 \longrightarrow 2A + 3N_2 \tag{21}$$
$$A\cdot N_3 + E\cdot N_3 \longrightarrow A + CH_3N_3 + HCN + N_2 \tag{22}$$
$$E\cdot N_3 + E\cdot N_3 \longrightarrow C_2H_5N_3 + CH_3CN + N_2 \tag{23}$$

Thermochemical considerations were taken into account by using the standard heats of formation listed previously.1,2)

Of the reactions of the first excited singlet $NH(a^1\Delta)$ with C_2H_4, the insertion reaction into the C–H bond and the addition reaction to the π bond are to be expected. Therefore, the $C_2H_5N^*$ formed by Reaction 3 are vibrationally excited vinylamine and aziridine molecules.

If the collisional spin relaxation process

$$NH(a^1\Delta) + E \longrightarrow NH(X^3\Sigma^-) + E$$

takes place, the formations of aziridine and $C_2H_5NH_2$ are expected according to the reactions

$$\begin{tikzcd}
 & & \text{aziridine} \\
NH(X^3\Sigma^-) \arrow[r, "E"] & C_2H_5N(\text{Triplet}) \arrow[ur] \arrow[dr, "A"'] & \\
 & & C_2H_6N(\text{doublet}) \arrow[dl, "A"] \\
 & C_2H_5NH_2. &
\end{tikzcd}$$

However, the possibility of the relaxation process seems to be negligible because neither of the products were found.

Reactions 4 to 7 are unimolecular decomposition processes of vibrationally excited $C_2H_5N^*$, and these are possible energetically. An other energetically possible reaction is

$$NH(a^1\Delta) + C_2H_4 \longrightarrow C_2H_2 + NH_3,$$

which is exothermic with 378 kJ mol^{-1}. The trace formation of C_2H_2 is probably due to this reaction. The reaction

$$NH(a^1\Delta) + C_2H_4 \longrightarrow CH_4 + HCN$$

is also exothermic with 503 kJ mol^{-1}, but the reaction to give CH_4 and HCN by this molecular mechanism could not be formulated in the reaction kinetics discussed later. Since the weakest bond in the $C_2H_3NH_2$ molecule is C–N bond,20) the precursor for C_2H_3 and NH_2 radicals in Reaction 7 seems to be vibrationally excited vinylamine. The C_2H_4N radicals formed by Reaction 6 will be removed by hydrogen abstraction from HN_3 and addition to the π bond of C_2H_4 by such reactions as 8 and 9.

Reaction 12 is well known and very efficient.21) Reaction 13 may proceed *via* an intramolecular hydrogen abstraction in the addition intermediate $H-\dot{N}-N=N-N=CH_2$. Reaction 14 is the hydrogenation reaction of C_2H_4 by $N_2H_2^*$ which is an effective hydrogenation reagent.22) The previously discussed reactions,1,2) $N_2H_2^* \rightarrow N_2H_2^{**}$, $N_2H_2^* + HN_3 \rightarrow N_2 + H_2 + HN_3$, and $N_2H_2^* + HN_3 \rightarrow 2N_2 + NH_3$, were omitted by assuming that Reaction 14 is very fast. Reaction 15 is the hydrogen abstraction reaction by CH_3, C_2H_3, C_2H_5, or NH_2 radicals from HN_3 as a good hydrogen donor.23) The reactions, $NH_2 + C_2H_4 \rightarrow C_2H_4NH_2$ and $C_2H_4NH_2 + HN_3 \rightarrow C_2H_5NH_2 + N_3$, are excluded because the $m/z=45$ peak $(C_2H_5NH_2^+)$ was not found in the mass spectrum.

The trace formations of C_3H_8, 1-C_4H_8, and n-C_4H_{10}9) are probably due to the reactions

$$R(CH_3,C_2H_3,C_2H_5) + C_2H_4 \longrightarrow R\text{-}C_2H_4$$
$$R\text{-}C_2H_4 + HN_3 \longrightarrow R\text{-}C_2H_5 + N_3.$$

The rate constant at 25 °C is 8.9×10^7 cm^3 mol^{-1} s^{-1} for the hydrogen abstraction from HN_3 by CH_3 radicals23) and is about 1.2×10^6 cm^3 mol^{-1} s^{-1} for the addition of CH_3 radicals to C_2H_4.24) The trace formation of C_3H_8 is explainable by comparing both rate constants. The same reason can also be applied for the trace formations of 1-C_4H_8 and n-C_4H_{10}. Reactions 4, 7, and 12 are supported by the existences of CH_3, C_2H_3, and C_2H_5 radicals.

The basic C_2H_5N (azomethines) formed by Reaction 8 may react to form the azide salt $(C_2H_5N \cdot HN_3)$ of the white volatile powder by reaction with acidic HN_3 as Reaction 17 as well as the case of amines.2) The C_4H_8N formed by Reaction 9 may react to produce the yellowish polymers *via* addition to C_2H_4 as Reaction 18.

Reactions 19 to 23 were introduced to explain the disappearance of N_3 radicals and the formations of HCN, CH_3CN, CH_3N_3, and $C_2H_5N_3$. It has been found in the flash photolysis of HN_3 that N_3 radicals disappear very rapidly in the presence of HN_3.25,26) This seems due to the formation of an addition intermediate $(A \cdot N_3)$, Similarly intermediate $(E \cdot N_3)$ can be expected, because the addition of N_3 radicals to π bond of C_2H_4 is possible. Reactions 22 and 23 are supported by the facts that CH_3N_3 was found as a product, and $C_2H_5N_3$ of almost the same amount as CH_3CN is formed. The reactions

$$N_3 \cdot A + E \cdot N_3 \longrightarrow N_3(CH_2)_2N_3 + A$$
$$2E \cdot N_3 \longrightarrow N_3(CH_2)_4N_3$$

are excluded because $N_3(CH_2)_2N_3$ and $N_3(CH_2)_4N_3$ were not found as a product.

Reactions other than those mentioned above have been discussed previously,1,2) and are omitted here.

Reaction Kinetics. The reaction kinetics were carried out to confirm the mechanism of Reactions 1 to 23 and to obtain the rate constant ratios.

On the quantum yield of CH_4, the equation

$$\phi_{CH_4}^{-1} = \frac{k_4+k_5+k_6+k_7}{k_4}\left(1+\frac{k_2}{k_3}\frac{[HN_3]}{[C_2H_4]}\right) \qquad \text{(I)}$$

can be derived, where

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

The plot of $1/\phi_{CH_4}$ *versus* $[HN_3]/[C_2H_4]$ is shown in Fig. 7.

On the formations of CH_4 and $C_2H_5N \cdot HN_3$, the equation

$$\frac{\phi_{CH_4}}{\phi_{C_2H_5N \cdot HN_3}} = \frac{k_4}{k_6}\left(1+\frac{k_9}{k_8}\frac{[C_2H_4]}{[HN_3]}\right) \qquad \text{(II)}$$

is obtained, and the linear relation is shown in Fig. 8.

Equation III was derived for the formations of CH_4, C_2H_6, H_2, and NH_4N_3, and its relation is plotted in Fig. 9.

$$\frac{\phi_{C_2H_6}+\phi_{H_2}+\phi_{NH_4N_3}}{\phi_{CH_4}} = \frac{k_4+k_5+k_7}{k_4} + \frac{k_2+k_{2a}}{k_3}\,\frac{k_4+k_5+k_6+k_7}{k_4}\,\frac{[HN_3]}{[C_2H_4]} \qquad \text{(III)}$$

As to the formations of H_2, CH_4, and C_2H_6, the equation

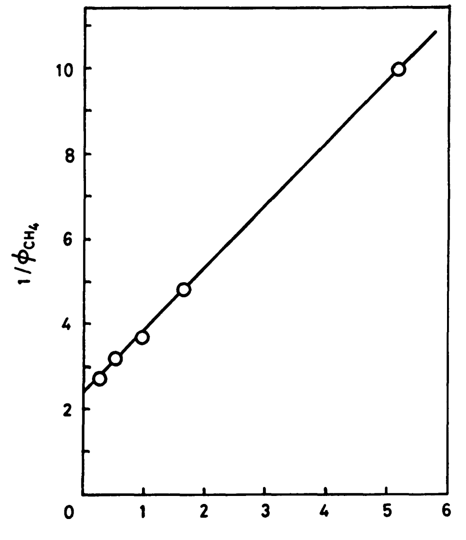


Fig. 7. Plot of $1/\phi_{CH_4}$ *versus* $[HN_3]/[C_2H_4]$.

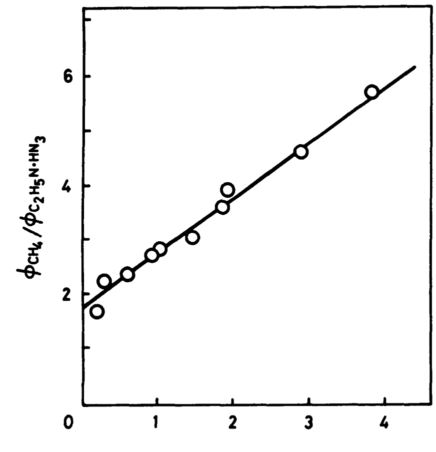


Fig. 8. Plot of $\phi_{CH_4}/\phi_{C_2H_5N\cdot HN_3}$ *versus* $[C_2H_4]/[HN_3]$.

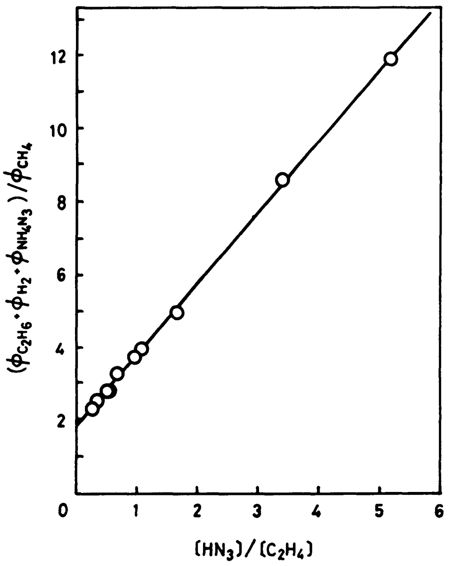


Fig. 9. Plot of $(\phi_{C_2H_6}+\phi_{H_2}+\phi_{NH_4N_3})/\phi_{CH_4}$ against $[HN_3]/[C_2H_4]$.

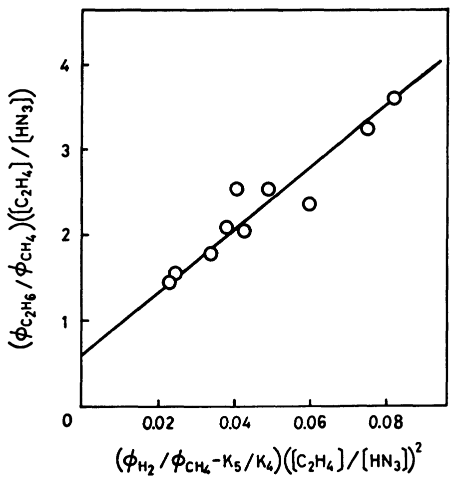


Fig. 10. Plot for Eq. IV.

$$\frac{\phi_{C_2H_6}}{\phi_{CH_4}}\frac{[C_2H_4]}{[HN_3]}=\frac{k_{2a}}{k_3}\frac{k_4+k_5+k_6+k_7}{k_4}+\frac{k_{12}}{k_{10}}\left(\frac{\phi_{H_2}}{\phi_{CH_4}}-\frac{k_5}{k_4}\right)\frac{[C_2H_4]^2}{[HN_3]^2} \qquad \text{(IV)}$$

can be deerivd. Plot of $\phi_{C_2H_6}[C_2H_4]/\phi_{CH_4}[HN_3]$ *versus* $(\phi_{H_2}/\phi_{CH_4}-k_5/k_4)([C_2H_4]/[HN_3])^2$ is shown in Fig. 10, where the value of 0.102 for k_5/k_4 was selected to obtain the best straight line.

From the intercepts and the slopes in Figs. 7 to 10, and by using $k_{2b}/k_{2a}=0.746$ and $k_{11}/k_{10}=1.15$ obtained previously,1) we obtain $k_3/k_2=1.64$, $k_5/k_4=0.102$, $k_6/k_4=0.564$, $k_7/k_4=0.734$, $k_9/k_8=0.560$, $k_{2c}/k_{2a}=1.23$, and $k_{12}/k_{10}=36.4$.

On the formations of N_2 and CH_4, the equation

$$\frac{\phi_{N_2}}{\phi_{CH_4}}=\frac{2k_4+k_5+k_6+k_7}{k_4}+\frac{(k_4+k_6+k_7)\alpha}{k_4}+\frac{k_4+k_5+k_6+k_7}{k_4}\left(\frac{k_2}{k_3}+\frac{2(k_{2a}+k_{2c})+(k_{2a}+k_{2b})\alpha}{k_3}\right)\times\frac{[HN_3]}{[C_2H_4]}+\left(\frac{k_6}{k_4}+\frac{2k_{2a}}{k_3}\frac{k_4+k_5+k_6+k_7}{k_4}\frac{[HN_3]}{[C_2H_4]}\right)\Big/\left(1+\frac{k_{10}}{k_{11}}+\frac{k_{12}}{k_{11}}\frac{[C_2H_4]}{[HN_3]}\right) \qquad \text{(V)}$$

can be derived, where

$$\alpha=1+2\left(1+\frac{k_{20}}{k_{19}}\frac{[C_2H_4]}{[HN_3]}\right)^{-2}.$$

Here, α was derived by assuming $k_{21}=k_{23}$ and $k_{22}=2k_{21}$, because Reactions 21 to 23 are radical-radical reactions. If $A\cdot N_3$ is non-existent ($k_{19}=0$), the stoichiometry of N_2 forming from two moles of N_3 becomes 1 by Reactions 22 and 23. The stoichiometry in the absence of $E\cdot N_3$ ($k_{20}=0$) becomes 3 by Reaction 21. Thus, α depends on the ratios of k_{20}/k_{19} and $[C_2H_4]/[HN_3]$.

The experimental values of ϕ_N/ϕ_{CH_4} *versus* $[HN_3]/[C_2H_4]$ were plotted in Fig. 11 together with the values calculated from Eq. V for two cases of $\alpha=1$ and $\alpha=3$ using the rate constant ratios obtained above. It is clear that the appropriate value for α is between 1 and 3. The values of ϕ_{N_2}/ϕ_{CH_4} calculated using $k_{19}/k_{20}=2.70$ are shown by the doted line in Fig. 11, and are in good accord with the experimental values.

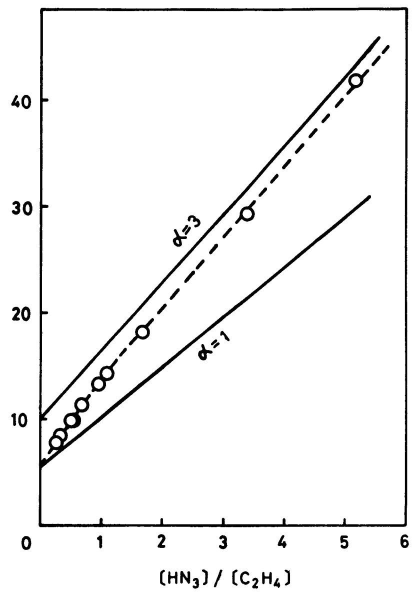
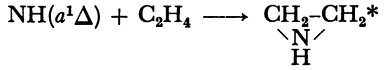


Fig. 11. Plots of ϕ_{N_2}/ϕ_{CH_4} *versus* $[HN_3]/[C_2H_4]$. ○, experimental value of ϕ_{N_2}/ϕ_{CH_4}; ---, calculated value of ϕ_{N_2}/ϕ_{CH_4} by Eq. V with $k_{19}/k_{20}=2.70$. The upper and under solid lines denote the calculated values of ϕ_{N_2}/ϕ_{CH_4} by Eq. V with $a=3$ and $a=1$, respectively.

Comparisons of the Rate Constants. Bras *et al.*[27] have reported that the rate constant for the reactions of hydrogen atoms with HN_3 is $2.54\times10^{-11}\exp(-4600/RT)$ cm^3 $molecule^{-1}$ s^{-1} in the temperature range from 293 to 462 K. On the other hand, Sugawara *et al.*[21] have found that the specific rate for the addition of hydrogen atoms to C_2H_4 is $4.70\times10^{-11}\exp(-2178/RT)$ cm^3 $molecule^{-1}$ s^{-1} in the temperature range from 206 to 461 K. From both results, it is found that the addition to C_2H_4 is 103 times faster than the reactions with HN_3 at 30 °C. In the present system, the rate constant ratio $k_{12}/(k_{10}+k_{11})$, is 17.0. The discrepancy seems to be due to "hot" hydrogen atoms because Reaction 2a is highly exothermic with 370 kJ mol^{-1}, and the hot atom effect is rather effective for reaction with high activation energy. If the value of k_{12} obtained by Sugawara *et al.*[21] is used as a basis, the absolute values of $k_{10}=2.09\times10^{10}$ and $k_{11}=2.40\times10^{10}$ cm^3 mol^{-1} s^{-1} in the present reaction conditions can be obtained from the rate constant ratios of k_{11}/k_{10} evaluated previously[1] and k_{12}/k_{10} obtained above.

Since the $C_2H_5N^*$ ($C_2H_3NH_2^*$ and aziridine*) decomposes before it is stabilized by collision with a third body M, the lifetime of $C_2H_5N^*$ is much shorter than the lifetime ($\tau=6.8\times10^{-11}$ s) of $C_2H_5NH_2^*$ formed by the insertion of $NH(a^1\Delta)$ into C–H bond of C_2H_6.[2] On the thermodynamic considerations of the reactions,



$$NH(a^1\Delta) + C_2H_4 \longrightarrow \underset{\underset{H}{\diagdown N \diagup}}{CH_2\text{–}CH_2^*} \qquad (3a)$$

$$NH(a^1\Delta) + C_2H_4 \longrightarrow C_2H_3NH_2^* \qquad (3b)$$

$$NH(a^1\Delta) + C_2H_6 \longrightarrow C_2H_5NH_2^* \qquad (3e)$$

ΔH_{3a} is almost the same as ΔH_{3e}, although Reaction 3b is 40 kJ mol^{-1} more exothermic than Reaction 3e. Therefore, the main reason for the short lifetime may be because the internal degrees of freedom of $C_2H_5N^*$ are six less than those of $C_2H_5NH_2^*$.

If we assume that all $C_2H_3NH_2^*$ molecules decompose to give C_2H_3 and NH_2 radicals as Reaction 7, and all molecules of aziridine formed by Reaction 3a decompose by Reactions 4 to 6, the reaction yield ratio of the addition to the π bond to the insertion into the C–H bond, k_{3a}/k_{3b}, is given by

$$k_{3a}/k_{3b} = (k_4+k_5+k_6)/k_7 = 2.27.$$

This ratio is similar to the result that the ratio of the addition to the insertion is 2.75 for the reactions of $NH(a^1\Delta)$ with C_3H_6 in the liquid phase.[11]

If all $C_2H_3NH_2^*$ molecules decompose to give C_2H_3 and NH_2 as assumed above, the reactivity ratio of the insertion of $NH(a^1\Delta)$ into a C–H bond of C_2H_4 to that of C_2H_6, k_{3b}/k_{3e}, is given by

$$\frac{k_{3b}}{k_{3e}} = \left(\frac{k_3}{k_2}\,\frac{k_7}{k_4+k_5+k_6+k_7}\right)\bigg/\left(\frac{k_{3e}}{k_2}\right).$$

By using $k_{3e}/k_2=0.334$ obtained previously,[2] $k_{3b}/k_{3e}=1.50$ is obtained. The ratio per C–H bond is given by $6k_{3b}/4k_{3e}=2.25$. This means that the insertion of $NH(a^1\Delta)$ into a C–H bond which consists of a sp^2 hybrid orbital is more efficient than for the sp^3 hybrid orbital. For the photolysis of COS in the presence of both C_2H_4 and C_2H_6,[28] it has been found that the insertion rate of $S(3^1D_2)$ per C–H bond of C_2H_4 is 1.15 times faster than that of C_2H_6. This result has the same tendency as for $NH(a^1\Delta)$.

Kitamura *et al.*[11] have studied the photolysis of HN_3 in a binary solution of C_2H_6 and C_2H_4 at Dry Ice–methanol temperature, and found that the formation ratio of $C_2H_5NH_2/N_2$ decreases with an increase of the mole fraction of C_2H_4. Provided that in their experimental conditions N_2 is formed only by Reaction 1 except the high mole fraction range of C_2H_6, and that all the molecules of $C_2H_5NH_2^*$ formed by Reaction 3e are stabilized by collisions with solvent molecules, then $k_3/k_{3e}=4.4$ is obtained from the plot of $N_2/C_2H_5NH_2$ *versus* $[C_2H_4]/[C_2H_6]$. Our value for k_3/k_{3e} is $4.9((k_3/k_2)/(k_{3e}/k_2))$. The slight discrepancy seems to be due to the differences of the experimental conditions of wavelength, temperature, phase, *etc.*

When the reactions of $NH(a^1\Delta)$ with reactant (X) are presented by the general expressions,

$$NH(a^1\Delta) + X \longrightarrow \text{Products} \qquad k_r$$

$$NH(a^1\Delta) + X \longrightarrow NH(X^3\Sigma^-) + X \qquad k_d$$

the values of k_r/k_2 and k_d/k_2 for HN_3,[1] Xe,[1] C_2H_6,[2] and C_2H_4 are shown in Table 2. The following tendencies are shown in Table 2: k_r/k_2 for C_2H_6 consisting of σ bonds only is very low as compared with those for HN_3 and C_2H_4 having π bond; Xe and C_2H_6 have some

Table 2. Relative reactivity of $NH(a^1\Delta)$ with X

X	k_r/k_2	k_d/k_2
HN_3[a]	1.000	≈0
Xe[a]	0	0.187
C_2H_6[b]	0.334	0.217
C_2H_4[c]	1.637	≈0

a) Ref. 1. b) Ref. 2. c) This work.

Table 3. Comparisons of k_q (X) with k_b at about 300 K

X	$\frac{k_q(X)}{10^{14}\ cm^3\ mol^{-1}\ s^{-1}}$	$\frac{\alpha}{10^{-24}\ cm^3}$	N_e	$\frac{k_b}{10^{14}\ cm^3\ mol^{-1}\ s^{-1}}$	$\frac{k_q(X)}{k_b}$
HN_3	1.084	3.50[a]	16	3.89	0.279
Xe	0.202	4.04[b]	8	3.23	0.063
C_2H_6	0.597	4.48[c]	14	4.03	0.148
C_2H_4	1.775	4.22[d]	12	3.97	0.447

a) Estimated from the polarizability of hydrogen atom (0.401×10^{-24} cm³) and the polarizabilities of NO, N_2, N_2O, and NH_3 molecules. b) M. Lallemand and D. Vidal, *J. Chem. Phys.*, **66**, 4776 (1977). c) P. Sliwinski, *Z. Phys. Chem. (Frankfurt am Main)*, **63**, 263 (1969). d) N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. London, Ser. A*, **295**, 334 (1966).

ability to induce collisional spin relaxation; the relaxation efficiencies by HN_3 and C_2H_4 having π bond are negligible. The relaxation efficiency by Xe, which is a monatomic molecule, is comparable to that of C_2H_6 consisting of eight atoms. It is probably due to a heavy atom effect.[29]

The absolute rate constant for the disappearance of $NH(a^1\Delta)$ by HN_3 was reported to be 5.6×10^{13} cm³ mol⁻¹ s⁻¹ by Paur and Bair,[26] and 10.84×10^{13} cm³ mol⁻¹ s⁻¹ by Piper, Krech, and Taylor.[30] If the rate constant obtained by Piper *et al.*, k_2(PKT), is used as a basis, the absolute rate constant for the quenching of $NH(a^1\Delta)$ by X, $k_q(X)$, can be calculated by the equation

$$k_q(X) = \frac{(k_r+k_d)_X}{k_2} k_2(PKT).$$

The calculated values of $k_q(X)$ are shown in Table 3.

On the other hand, the maximum rate constant of the bimolecular reaction in the gas phase, k_b, can be calculated by the equation[31]

$$k_b = \frac{2\Gamma(1-2/s)N_A}{\sigma}\left(\frac{2\pi kT}{\mu}\right)^{1/2}\left[\frac{(s-2)A}{2kT}\right]^{2/s},$$

when the intermolecular attractive potential, u, is expressed by $u=-A/r^s$. Here, A, r, Γ, N_A, σ, k, and μ mean the attractive potential constant, the intermolecular distance, the gamma function, Avogadro's number, the symmetry number, Boltzmann's constant, and the reduced mass, respectively. The attractive potential is given by

$$A = A_{dis} + \alpha_{NH}\mu_D(X)^2 + \alpha_x\mu_D(NH)^2 + 2\mu_D(NH)^2\mu_D(X)^2/3kT,$$

where α is the polarizability, and μ_D the dipole moment. The dispersion effect term of A, A_{dis}, is given by Slater and Kirkwood[32] as

$$A_{dis} = \frac{3\,h\,e\,\alpha_{NH}\alpha_X}{4\,\pi m_e^{1/2}[(\alpha/N_e)_{NH}^{1/2} + (\alpha/N_e)_X^{1/2}]}.$$

Here, h, N_e, and e and m_e are Planck's constant, the number of outer-shell electrons, and the charge and mass of an electron, respectively.

The values of k_b calculated using $s=6$ and $\sigma=1$ are shown in Table 3 together with α and N_e for X. The values of $\alpha=1.38\times10^{-24}$ cm³,[33] $N_e=6$, and $\mu_D=1.627$ debye[34] for NH, and $\mu_D=0.847$ debye[35] for HN_3 were used for the calculation. It is shown in Table 3 that the reactivity of the first excited singlet $NH(a^1\Delta)$ is, in general, very high, especially $k_q(C_2H_4)$ which is close to one-half of its maximum rate constant.

Table 4. Comparisons of the over-all quenching rate constants at about 300 K

Quencher	Quenching rate constant 10^{-11} cm³ molecule⁻¹ s⁻¹			
	$C(2^1D_2)$	$O(2^1D_2)$	$S(3^1D_2)$	$NH(a^1\Delta)$
HN_3				18[h]
Xe	11[a]	7.2[c]	4.0[f]	3.4[i]
C_2H_6		26.0[d]	4.3[g]	9.9[j]
C_2H_4	≈37[b]	35.6[e]	25[g]	29.5[k]

a) Ref. 36. b) Ref. 37. c) Ref. 41. d) Estimated from $k_q^{O(^1D)}(CO_2)=10\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Ref. 40) and $k_q^{O(^1D)}(C_2H_6)/k_q^{O(^1D)}(CO_2)=2.6$ (Ref. 39). e) Estimated from $k_q^{O(^1D)}(C_2H_6)=26.0\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (d)) and $k_q^{O(^1D)}(C_2H_4)/k_q^{O(^1D)}(C_2H_6)=1.37$ (Ref. 38). f) Estimated from $k_q^{S(^1D)}(C_2H_4)=25\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ (g)) and $k_q^{S(^1D)}(Xe)/k_q^{S(^1D)}(C_2H_4)=0.16$ (Ref. 43). g) From Refs. 4 and 42. h) Ref. 30. i) From Refs. 1 and 30. j) From Refs. 2 and 30. k) From Ref. 30 and the present work.

The absolute and relative quenching rates of $C(2^1D_2)$,[36,37] $O(2^1D_2)$,[38–41] and $S(3^1D_2)$[42,43] by Xe, C_2H_6, C_2H_4, and others have been observed widely. These over-all quenching rate constants are shown in Table 4 together with those for $NH(a^1\Delta)$. It is found in Table 4 that the trend on the collisional quenching of $NH(a^1\Delta)$ is very similar to those of the first excited singlet atoms.

The author is gratefully indebted to Emeritus Professor Osamu Toyama of University of Osaka Prefecture for his helpful discussion. I would also like to thank Dr. Hideo Tabata, Mr. Akio Tomiyasu, and Katsuichi Ohta for their asistances.

References

1) S. Kodama, *Bull. Chem. Soc. Jpn.*, **56**, 2348 (1983).

2) S. Kodama, *Bull. Chem. Soc. Jpn.*, **56**, 2355 (1983).

3) R. J. Cvetanović, *Adv. Photochem.*, **1**, 115 (1963); R. E. Huie and J. T. Herron, *Prog. React. Kinet.*, **8**, 1 (1975).

4) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **4**, 143 (1966).

5) W. B. DeMore and S. W. Benson, *Adv. Photochem.*, **2**, 219 (1964); H. M. Frey, *Prog. React. Kinet.*, **2**, 131 (1964); "Carbene Chemistry," ed by W. Kirmse, Academic Press, New York (1971); "Carbenes," ed by M. Jones, Jr., and R. A. Moss, John Wiley and Sons, New York (1973), I.

6) E. D. Miller, Ph. D. Dissertation, Catholic University of America, Washington, D. C., 1961.

7) D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am.*

Chem. Soc., **88**, 544 (1966).

8) J. L. Brash and R. A. Back, *Can. J. Chem.*, **43**, 1778 (1965); W. D. Woolley and R. A. Back, *ibid.*, **46**, 295 (1968).

9) P. Tiedemann and R. N. Schindler, Technical Report, JUL-505-PC (1968).

10) M. E. Jacox and D. E. Milligan, *J. Am. Chem. Soc.*, **85**, 278 (1963).

11) T. Kitamura, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **54**, 55 (1981).

12) F. O. Rice and C. J. Grelecki, *J. Phys. Chem.*, **61**, 830 (1957); M. S. O'Dell and B. deB. Darwent, *Can. J. Chem.*, **48**, 1140 (1970).

13) O. Dimroth and W. Wislicenus, *Ber.*, **38**, 1573 (1905).

14) E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, **22**, 238 (1957).

15) J. H. Boyer and J. Hamer, *J. Am. Chem. Soc.*, **77**, 951 (1955).

16) M. O. Forster and H. F. Fierz, *J. Chem. Soc.*, **93**, 1071 (1908).

17) J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).

18) G. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961).

19) D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1475 (1955).

20) The bond dissociation energies of C–N, N–H, and C–H in $C_2H_3NH_2$ molecule are about 390, 406, and 434 kJ mol^{-1}, respectively.

21) K. Sugawara, K. Okazaki, and S. Sato, *Bull. Chem. Soc. Jpn.*, **54**, 2872 (1981).

22) S. K. Vidyarthi, C. Willis, R. A. Back, and R. M. McKitrick, *J. Am. Chem. Soc.*, **96**, 7647 (1974); C. Willis, R. A. Back, J. M. Parsons, and J. G. Purdon, *ibid.*, **99**, 4451 (1977); D. J. Pasto and D. M. Chipman, *ibid.*, **101**, 2290 (1979).

23) R. S. Konar and B. deB. Darwent, *Can. J. Chem.*, **48**, 2280 (1970).

24) R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, **46**, 1694 (1967).

25) R. J. Paur and E. J. Bair, *J. Photochem.*, **1**, 255 (1973).

26) R. J. Paur and E. J. Bair, *Int. J. Chem. Kinet.*, **8**, 139 (1976).

27) G. Le Bras and J. Combourieu, *Int. J. Chem. Kinet.*, **5**, 559 (1973).

28) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 1443 (1965).

29) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings Publishing Co., Menlo Park, California (1978), p. 38.

30) L. G. Piper, R. H. Krech, and R. L. Taylor, *J. Chem. Phys.*, **73**, 791 (1980).

31) K. Yang and T. Ree, *J. Chem. Phys.*, **35**, 588 (1961).

32) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931); J. G. Kirkwood, *Physik. Z.*, **33**, 57 (1932).

33) Estimated by assuming the atomic polarizabilities of 0.401×10^{-24} cm^3 for H and 0.975×10^{-24} cm^3 for N.

34) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **45**, 1063 (1966).

35) E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950).

36) D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, **67**, 2886 (1971).

37) D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, **67**, 3166 (1971).

38) W. B. DeMore, *J. Phys. Chem.*, **73**. 391 (1969).

39) R. J. Cvetanović, *Can. J. Chem.*, **52**, 1452 (1974).

40) G. E. Stein, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, *J. Chem. Phys.*, **65**, 4761 (1976).

41) J. A. Davidson, H. I. Schiff, T. J. Brown, G. E. Streit, and C. J. Howard, *J. Chem. Phys.*, **69**, 1213 (1978).

42) P. Fowles, M. deSorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 1352 (1967).

43) D. L. Little, A. Dalgleish, and R. J. Donovan, *Discuss. Faraday Soc.*, **53**, 211 (1972).