J. Phys. Chem. **1988**, *92*, 5019-5024 **5019**

Acknowledgment. The NMR data were partly obtained at the Southern California Regional NMR Facility, supported by NSF Grant CHE84-40137. The materials preparation and characterization was supported by U.S. Department of Energy University Coal Programs Grant No. DE-FG22-84PC70775. We are grateful to Larry Henling for performing the elemental analysis of the materials.

Registry No. PFA, 25212-86-6; PEG, 25322-68-3; H_2O, 7732-18-5; C, 7440-44-0; Triton X100, 9002-93-1; glycerol, 56-81-5.

Reactions of NH Radicals. 6. Reactions of $NH(a^1\Delta)$ with C_2H_2 and Unimolecular Decompositions of $C_2H_3N^*$

Sukeya Kodama

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan *(Received: July 14, 1987)*

Photolysis of HN_3 vapor in the presence of C_2H_2 was studied at 313 nm and 303 K. The products were N_2, H_2, CH_4, C_2H_4, C_2H_6, NH_4N_3, $C_4H_5N{\cdot}HN_3$ (salt of C_4H_5N with HN_3), HCN, CH_3CN, and polymers. From the quantum yields of these products, measured as a function of the pressure of C_2H_2 or HN_3, the following mechanism for the main reactions was inferred: $HN_3 + h\nu(313\text{ nm}) \rightarrow NH(a^1\Delta) + N_2$; $NH(a^1\Delta) + HN_3 \rightarrow 2N_2 + 2H$ (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); $NH(a^1\Delta) + C_2H_2 \rightarrow C_2H_3N^*$ ($\underline{CH{=}CH{-}NH}$ and $CH{\equiv}C{-}NH_2$) (3); $C_2H_3N^* \rightarrow CH_3 + CN$ (4); $C_2H_3N^* \rightarrow H + C_2H_2N$ (5); $C_2H_3N^* \rightarrow C_2H + NH_2$ (6). The rate constant ratios at 303 K are $k_3/k_2 = 1.2_0$, $k_5/k_4 = 15_7$, and $k_6/k_4 = 0.82$. The efficiency of the insertion to give $CH{\equiv}C{-}NH_2$ in reaction 3 was about 0.05 of that of the addition to form $\underline{CH{=}CH{-}NH}$. The spin relaxation of $NH(a^1\Delta)$ to $NH(X^3\Sigma^-)$ by C_2H_2 and the collisional deactivation of $C_2H_3N^*$ were not found. The rearrangement from $\underline{CH{=}CH{-}NH}$ to CH_3NC or CH_3CN and the unimolecular decomposition rates by the RRKM theory for reactions 4 and 6 were discussed. The relative and absolute rate constants were compared for the reactions of $NH(a^1\Delta)$ with various reactants.

Introduction

In previous works,[1-5] it was found that the first excited singlet $NH(a^1\Delta)$ radicals insert into the C–H bonds of CH_4,[4] C_2H_6,[2] and C_3H_8[5] to give amines and that the addition of $NH(a^1\Delta)$ to the π bond of C_2H_4[3] takes place with a high efficiency. The reactions of NH with alkenes have also been investigated by several workers.[6,7]

On the reactions of NH with alkynes, Jacox and Milligan[7] have suggested the production of $CH_2{=}C{=}NH$ in the photolysis of HN_3 with C_2H_2 in an Ar matrix at 4 K. However, the details of such a reaction in the vapor phase are not obvious so far. Thus, the photolysis of HN_3 vapor in the presence of C_2H_2 was carried out in this work, to examine quantitatively the reactions of $NH(a^1\Delta)$ with C_2H_2 as the simplest alkyne and to compare with those with C_2H_4.[3]

Experimental Section

Acetylene obtained from Takachiho Chemical Co. was 99.8% pure. It was purified each time before use by condensation and evacuation at 143 and 93 K. The preparation and purification methods of HN_3 and the apparatus and procedure for the reaction were the same as have been described previously.[1,2] All the runs in this work were carried out at 313 nm and 303 K. The irradiation time was usually 30 min, and the degree of conversion of HN_3 was less than several percent for all the runs.

The detectable reaction products were N_2, H_2, CH_4, C_2H_4, C_2H_6, NH_4N_3, HCN, CH_3CN, amine, and polymers. The formation of HCN was verified by the pyridine–pyrazolone method.[8] The formation of CH_3CN was confirmed by gas chromatography with silicone oil or a poly(ethylene glycol) column.

An infrared spectrum by the KBr disk method of the products that were trapped at 195 K is shown in Figure 1. The formation of NH_4N_3 can be identified by the main three peaks at 3120, 2010, and 1390 cm^{-1}.[1] The residual small peaks seem to arise from an amine having functional groups such as $\equiv$C–H (3350), CH_2 (3000, 2850), NH (1540), C–N (1210), and –C$\equiv$C–H (650 cm^{-1}).

The yellowish polymers deposited on the wall of the reaction cell were extracted with ethanol, and the ethanol solvent was eliminated by vacuum distillation. An infrared spectrum of the polymers by the KBr disk method is shown in Figure 1. The polymers seem to be composed of functional groups such as NH ($\sim$3400, 1610, and 1525), CH_3 (2960, 1450, and 1380), CH_2 (2925, 2850, 1450, and 1260), N_3 (2100), C=N (1680), and C–N (1190 cm^{-1}).

As to the quantitative analyses of N_2, H_2, CH_4, C_2H_4, C_2H_6, NH_4N_3, and the amine, the reaction mixture was separated by trapping at solid nitrogen temperature ($\sim$55 K) for C_2H_4, C_2H_6, and a part of C_2H_2, at 93 K for HN_3 and large part of C_2H_2, and at 195 K for NH_4N_3 and the amine, respectively. Analyses of N_2, H_2, and CH_4, noncondensable gases at 55 K, were carried out by the procedures described previously.[2] The separations of

---

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

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

(3) Kodama, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2363.

(4) Kodama, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2891.

(5) Kodama, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2900.

(6) Miller, E. D. Ph.D. Dissertation, Catholic University of America, Washington, DC, 1961. Back, R. A. *J. Chem. Phys.* **1964**, *40*, 3493. Brash, J. L.; Back, R. A. *Can. J. Chem.* **1965**, *43*, 1778. Cornell, D. W.; Berry, R. S.; Lwowski, W. *J. Am. Chem. Soc.* **1966**, *88*, 544. Tiedemann, P.; Schindler, R. N. *Ber. Kernforschungsanlage Juelich* **1968**, JUEL-550-PC. (*Chem. Abstr.* **1969**, *71*, 55501k.) Woolley, W. D.; Back, R. A. *Can. J. Chem.* **1968**, *46*, 295. Kitamura, T.; Tsunashima, S.; Sato, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 55. Hamada, J.; Tsunashima, S.; Sato, S. *Ibid.* **1983**, *56*, 662.

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

(8) Kruse, J. M.; Mellon, M. G. *Anal. Chem.* **1953**, *25*, 446.

0022-3654/88/2092-5019$01.50/0

TABLE I: Results of the Photolysis of HN_3 in the Presence of C_2H_2[a]

P, kPa		reaction time, min	quantum yield[b]							$10^6 N_{C_2H_4}$, mol
HN_3	C_2H_2		N_2	CH_4	C_2H_4	C_2H_6	H_2	NH_4N_3	$C_4H_5N \cdot HN_3$	
2.89	4.23	40	3.61	0.0380	0.909	0.0213	0.057	0.187	0.0796	3.21
6.67	4.23	30	4.00	0.0259	0.722	0.0327	0.074	0.262	0.0322	5.67
15.68	4.23	30	4.21	0.0141	0.709	0.0672	0.121	0.361	0.0089	12.05
20.17	4.23	45	4.22	0.0117	0.663	0.0769	0.117	0.351	0.0083	13.93
6.67	1.68	15	4.12	0.0128	0.567	0.0558	0.151	0.392	0.0082	4.46
6.67	2.37	30	4.12	0.0167	0.601	0.0452	0.122	0.349	0.0166	4.72
6.67	8.41	30	3.73	0.0345	0.816	0.0212	0.065	0.179	0.0654	6.41
6.67	11.52	30	3.54	0.0407	0.894	0.0164	0.053	0.137	0.0830	7.02
6.67	15.64	30	3.28	0.0403	0.779	0.0104	0.073	0.155	0.0969	6.12

[a] The photolysis was carried out at 313 nm and 303 K. The absorbed light intensity was about 2.6×10^{15} quanta s^{-1} at 6.67 kPa of HN_3. [b] The quantum yield values are good only to two significant figures.

TABLE II: Selected Heats of Formation

species	$\Delta H°_{f,298}$, kJ mol^{-1}	ref	species	$\Delta H°_{f,298}$, kJ mol^{-1}	ref
H	218.0	*a*	CN	418.4	*c*
$NH(a^1\Delta)$	506.6	*a*	HCN	130.5	*c*
HN_3	299.8	*a*	CH_2CN	243	*e*
NH_2	171.5	*a*	CH_2NC	309	*f*
trans-N_2H_2	238.1	*b*	CH_3CN	79.9	*c*
cis-N_2H_2	257.7	*b*	CH_3NC	150.2	*c*
$H_2N{=}N$	361.1	*b*	$HC{\equiv}C{-}NH_2$	222	*c*
CH_3	146.9	*c*	$H_2C{=}C{=}NH$	238	*c*
C_2H	543.9	*d*	$H_2C{-}CH{=}N$	287	*g*
C_2H_2	226.7	*c*	$HC{=}C{-}NH$	358	*g*

[a] Reference 1. [b] Casewit, C. J.; Goddard, W. A., III, *J. Am. Chem. Soc.* **1980**, *102*, 4057. [c] Reference 2. [d] Sharma, D. K. S.; Franklin, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 6562. [e] Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2755. [f] Estimated from the standard heats of formation of H and CH_3NC, and $D(H{-}CH_2NC) = 377$ kJ mol^{-1} (Hicks, K. W.; Lesiecki, M. L.; Riseman, S. M.; Guillory, W. A. *J. Phys. Chem.* **1979**, *83*, 1936). [g] Bock, H.; Dammel, R.; Aygen, S. *J. Am. Chem. Soc.* **1983**, *105*, 7681.

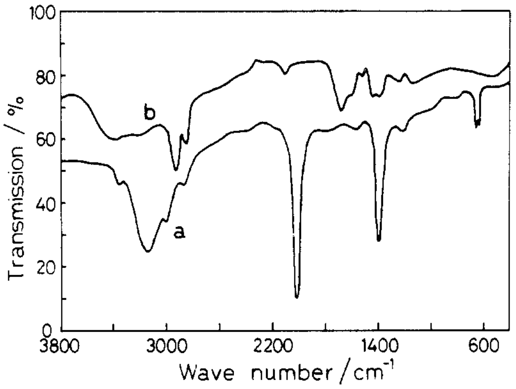


Figure 1. Infrared spectra by the KBr disk method: (a) products trapped at 195 K; (b) polymers deposited on the wall of the reaction cell.

C_2H_6, C_2H_4, and C_2H_2 were performed by gas chromatography with a silica gel column (2 m) at 353 K.

The while volatile products condensed at 195 K were introduced into a CuO column at about 820 K.[1,2] The combustion products were N_2, NO, N_2O, CO_2, and H_2O. The amount of the amine is equal to $[CO_2]/4$, if it is assumed that the chemical formula of the amine is $C_4H_5N \cdot HN_3$ as is discussed below. Then, the amount of NH_4N_3 can be estimated from the equation $[NH_4N_3] = (2[N_2] + [NO] + 2[N_2O] - [CO_2])/4$.

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

Results

Results of the photolysis of HN_3 in the presence of C_2H_2 at 313 nm and 303 K are shown in Table I. It is found in Table I that the quantum yields of N_2, H_2, C_2H_6, and NH_4N_3 increase but the quantum yields of CH_4, C_2H_4, and $C_4H_5N \cdot HN_3$ decrease with an increase of the pressure of HN_3 at the constant C_2H_2 pressure of 4.23 kPa.

It is also found in Table I that the quantum yields of CH_4, C_2H_4, and $C_4H_5N \cdot HN_3$ increase but the quantum yields of N_2, H_2, C_2H_6, and NH_4N_3 decrease by increasing of the pressure of C_2H_2 at the constant HN_3 pressure of 6.67 kPa and the constant absorption light intensity of 2.6×10^{15} quanta s^{-1}.

The effect for the suppression of the incident light intensity by screens was also examined at the constant pressures of 6.67 kPa for HN_3 and 4.23 kPa for C_2H_2. However, all the quantum yields were almost the same as the original yields, except C_2H_6 decreased with a decrease of the light intensity.

Discussion

Reaction Mechanism. On the basis of the present experimental results and in light of the results achieved by previous investigations,[1-5] the following reaction mechanism was postulated for the photolysis of HN_3 in the presence of C_2H_2:

$$HN_3 + h\nu\ (313\ \text{nm}) \rightarrow N_2 + NH(a^1\Delta) \tag{1}$$

$$NH(a^1\Delta) + HN_3 \rightarrow 2N_2 + 2H \tag{2a}$$

$$NH(a^1\Delta) + HN_3 \rightarrow NH_2 + N_3 \tag{2b}$$

$$NH(a^1\Delta) + HN_3 \rightarrow N_2 + N_2H_2^* \tag{2c}$$

$$NH(a^1\Delta) + C_2H_2 \rightarrow C_2H_3N^* \tag{3}$$

$$C_2H_3N^* \rightarrow CH_3 + CN \tag{4}$$

$$C_2H_3N^* \rightarrow H + C_2H_2N \tag{5}$$

$$C_2H_3N^* \rightarrow NH_2 + C_2H \tag{6}$$

$$H + HN_3 \rightarrow H_2 + N_3 \tag{7}$$

$$H + HN_3 \rightarrow NH_2 + N_2 \tag{8}$$

$$H + C_2H_2 \rightarrow C_2H_3 \tag{9}$$

$$H + C_2H_4 \rightarrow C_2H_5 \tag{10}$$

$$N_2H_2^* + C_2H_2 \rightarrow N_2 + C_2H_4 \tag{11}$$

$$N_2H_2^* + C_2H_4 \rightarrow N_2 + C_2H_6 \tag{12}$$

$$C_2H_2N + HN_3 \rightarrow CH_3CN + N_3 \tag{13}$$

$$C_2H_2N + HN_3 \dashrightarrow \text{polymers} \tag{14}$$

$$C_2H_2N + C_2H_2 \rightarrow C_4H_4N \tag{15}$$

$$C_2H_2N + C_2H_2 \dashrightarrow \text{polymers} \tag{16}$$

$$R(CH_3, C_2H, C_2H_3, C_2H_5, NH_2, CN, \text{and } C_4H_4N) + HN_3 \rightarrow RH + N_3 \tag{17}$$

$$N_3 + HN_3 \rightarrow HN_3 \cdot N_3 \tag{18}$$

$$N_3 + C_2H_2 \rightarrow C_2H_2 \cdot N_3 \tag{19}$$

$$HN_3 \cdot N_3 + HN_3 \cdot N_3 \rightarrow 2HN_3 + 3N_2 \tag{20}$$

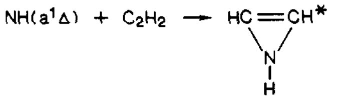
$$HN_3 \cdot N_3 + C_2H_2 \cdot N_3 \rightarrow HN_3 + 2HCN + 2N_2 \tag{21}$$

$$C_2H_2{\cdot}N_3 + C_2H_2{\cdot}N_3 \rightarrow 4HCN + N_2 \qquad (22)$$

$$NH_3 + HN_3 \rightarrow NH_4N_3 \qquad (23)$$

$$C_4H_5N + HN_3 \rightarrow C_4H_5N{\cdot}HN_3 \qquad (24)$$

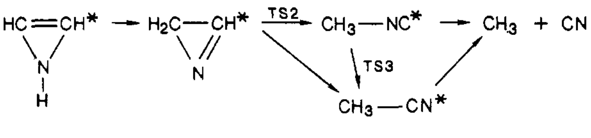
Reaction 3 includes both the addition of $NH(a^1\Delta)$ to the π bond of C_2H_2 and the insertion of $NH(a^1\Delta)$ into the C–H bond of C_2H_2,[7] as were found in the reactions with C_2H_4:[3]


(3a)

$$NH(a^1\Delta) + C_2H_2 \rightarrow HC{\equiv}C{-}NH_2^* \qquad (3b)$$

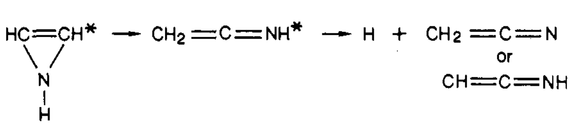
The collisional spin relaxation of $NH(a^1\Delta)$ to $NH(X^3\Sigma^-)$ by C_2H_2, $NH(a^1\Delta) + C_2H_2 \rightarrow NH(X^3\Sigma^-) + C_2H_2$, was not found as in HN_3[1] and C_2H_4,[3] which has a π bond.

Reactions 4–6 are unimolecular decomposition reactions of chemically activated $C_2H_3N^*$. These reactions are possible energetically, judging from the heats of formation listed in Table II. Reaction 4 seems to proceed with the following process:


(4′)

The route of 2*H*-azirine → $CH_3NC \rightarrow CH_3CN$ is based on an ab initio molecular orbital study by Lohr et al.,[9] where TS2 and TS3 mean the transition states in the route. The intermediates CH_3NC and CH_3CN in reaction 4′ are found by Jacox et al.,[7] but no 2*H*-azirine was observed in the photolysis of HN_3 with C_2H_2 in an Ar matrix at 4 K. The formation of CH_3 radicals by the reactions of $C_2H_3N^* \rightarrow CH_2 + HCN$ and $CH_2 + HN_3 \rightarrow CH_3 + N_3$ can be excluded, because $CH_3C{\equiv}CH$ and $CH_2{=}C{=}CH_2$ from reaction of $CH_2 + C_2H_2 \rightarrow C_3H_4$ were not found.

Jacox et al.[7] have also suggested $CH_2{=}C{=}NH$ as a major product in the photolysis. Therefore, a part of the reactions to release H atom from $C_2H_3N^*$ may proceed via $CH_2{=}C{=}NH^*$:


(5′)

However, it is difficult to specify which of six $C_2H_3N^*$ isomers is the precursor to release the H atom. The formations of C_2H and NH_2 by reaction 6 may be caused by $CH{\equiv}C{-}NH_2^*$:

$$CH{\equiv}C{-}NH_2^* \rightarrow C_2H + NH_2 \qquad (6')$$

because only $CH{\equiv}C{-}NH_2$ of six C_2H_3N isomers has the NH_2 functional group.

The H_2 from the $C_2H_3N^*$ was not found within experimental error. The collisional deactivation of $C_2H_3N^*$ by a third body was also not found as was that[3,4] of $C_2H_5N^*$ and $CH_3NH_2^*$.

Reactions 9 and 10 are well-known and very efficient reactions.[10] Reactions 11 and 12 are the hydrogenation reactions of C_2H_2 and C_2H_4 by a diimide, which is an effective hydrogenation reagent for alkenes and alkynes.[11] Therefore, reactions 9 and 11 for the formation of C_2H_4 are conceivable in analogy with reactions 10 and 12 to form C_2H_6 in the photolysis of HN_3 with C_2H_4.[3] Thus, the formation of C_2H_6 seems to proceed successively by the reactions of H and $N_2H_2^*$ with C_2H_4 formed by reactions 9, 17, and 11.

For the chemical structure of C_2H_2N radicals formed by reaction 5, the following six species are conceivable:

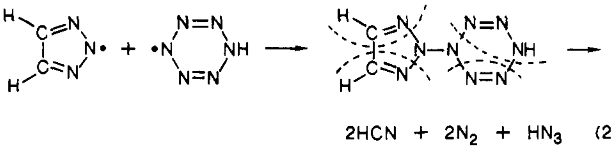
$$\underset{a}{{\cdot}CH_2{-}C{\equiv}N} \rightleftharpoons \underset{b}{CH_2{=}C{=}N{\cdot}}$$

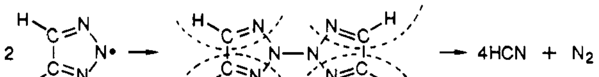
$$\underset{c}{CH{\equiv}C{-}\dot{N}H} \rightleftharpoons \underset{d}{{\cdot}CH{=}C{=}NH}$$

$$\underset{e}{{\cdot}C{\equiv}C{-}NH_2} \qquad \underset{f}{{\cdot}CH_2{-}NC}$$

Species a may be appropriate to specify as the radical that gives CH_3CN by hydrogen abstraction from HN_3 as in reaction 13. Species c may be the most suitable structure as the C_2H_2N radical to give C_4H_4N in reaction 15, judging from the findings that $C_4H_5N{\cdot}HN_3$ produced from C_4H_4N have the functional groups of $-C{\equiv}C{-}H$, $=C{-}H$, C–N, and NH. Then, the chemical structure of $CH{\equiv}C{-}NH{-}CH{=}CH_2$ may represent amine (C_4H_5N). The other species seem to disappear to give polymers via the reactions with HN_3 and C_2H_2 as reactions 14 and 16.

Reaction 17 is the hydrogen abstraction reaction by various radicals from HN_3, which is a good hydrogen donor.[12] Reactions 18–22 were introduced to explain the results that the amount of N_2 from N_3 radicals is less than the amount that is expected from the reaction $2N_3 \rightarrow 2N_2$, which is found in C_2H_4,[3] and that a considerable amount of HCN is formed. $C_2H_2{\cdot}N_3$ radicals formed by the addition of N_3 to the π bond of C_2H_2 may be stabilized by forming a five-membered ring, such as triazoles formed by the reactions of alkynes with HN_3.[13] For reactions 21 and 22, the (21′) and (22′) are possible.


(21′)


(22′)

The basic amine (C_4H_5N) formed by reactions 15 and 17 may be stabilized by forming the azide salt ($C_4H_5N{\cdot}HN_3$) with acidic HN_3 as reaction 24.[2–5] Reactions 1, 2, 7, 8, and 23 have been discussed previously[1] and are omitted here.

Rate Constant Ratios. The quantum yields were measured as a function of $[HN_3]/[C_2H_2]$ to support the mechanism of reactions 1–24 and to obtain the rate constant ratios.

On the formations of CH_4, C_2H_4, C_2H_6, H_2, and NH_4N_3, eq I–III can be derived.

$$\frac{1}{\phi_{CH_4}} \doteq \frac{k_4 + k_5 + k_6}{k_4}\left(1 + \frac{k_2}{k_3}\frac{[HN_3]}{[C_2H_2]}\right) \qquad (I)$$

$$\frac{\phi_{H_2} + \{k_7/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})}{\phi_{CH_4}} = \frac{k_7}{k_7 + k_8}\left(\frac{k_5}{k_4} + \frac{2k_{2a} + k_{2c}}{k_3}\frac{k_4 + k_5 + k_6}{k_4}\frac{[HN_3]}{[C_2H_2]}\right) \qquad (II)$$

$$\frac{\phi_{NH_4N_3} + \{k_8/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})}{\phi_{CH_4}} = \frac{k_6 + k_5k_8/(k_7 + k_8)}{k_4} + \frac{k_4 + k_5 + k_6}{k_4}\left(\frac{k_{2b}}{k_3} + \frac{2k_{2a} + k_{2c}}{k_3}\frac{k_8}{k_7 + k_8}\right)\frac{[HN_3]}{[C_2H_2]} \qquad (III)$$

Plots of $1/\phi_{CH_4}$, $[\phi_{H_2} + \{k_7/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})]/\phi_{CH_4}$, and $[\phi_{NH_4N_3} + \{k_8/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})]/\phi_{CH_4}$ versus $[HN_3]/[C_2H_2]$ are shown in Figure 2. Here, the values of $k_7/(k_7$

---

[9] Lohr, L. L.; Hanamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1983**, *105*, 5541.

[10] Sugawara, K.; Okazaki, K.; Sato, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2872.

[11] Abramovitch, R. A.; Davis, B. A. *Chem. Rev.* **1964**, *64*, 149. Miller, C. E. *J. Chem. Educ.* **1965**, *42*, 254. Wills, C.; Back, R. A.; Parsons, J. M.; Purdon, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 4451. Pasto, D. J. *Ibid.* **1979**, *101*, 6852. Back, R. A. *Rev. Chem. Intermed.* **1984**, *5*, 293.

[12] Konar, R. S.; Darwent, B. deB. *Can. J. Chem.* **1970**, *48*, 2280.

[13] Hartzel, L. W.; Benson, F. R. *J. Am. Chem. Soc.* **1954**, *76*, 667.

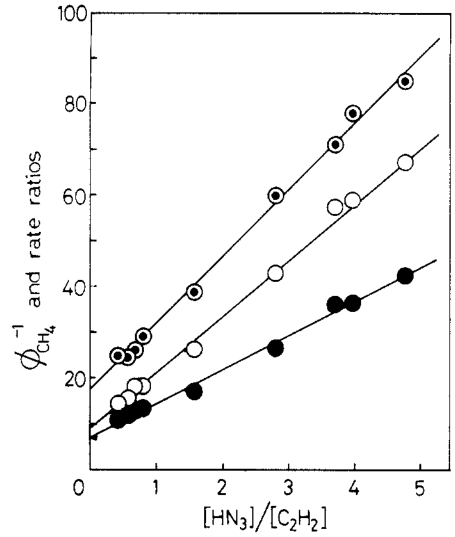


Figure 2. Plots for eq I–III: (⊙) $1/\phi_{CH_4}$; (○) $[\phi_{NH_4N_3} + \{k_8/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})]/\phi_{CH_4}$; (●) $[\phi_{H_2} + \{k_7/(k_7 + k_8)\}(\phi_{C_2H_4} + 2\phi_{C_2H_6})]/\phi_{CH_4}$.

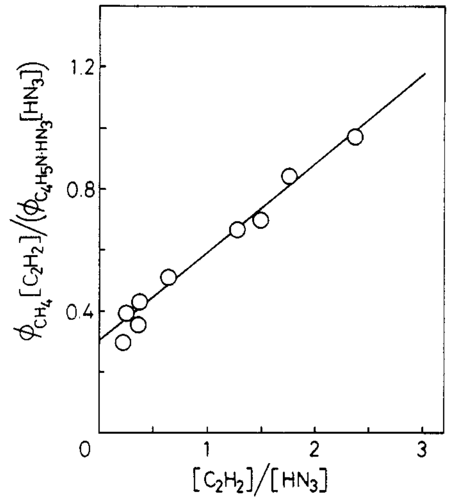


Figure 3. Plot for eq IV.

$+ k_8) = 0.46_5$ and $k_8/(k_7 + k_8) = 0.53_5$ were used from $k_8/k_7 = 1.1_5$ obtained previously.[1] From the intercepts and the slopes of the straight lines, the values of $(k_4 + k_5 + k_6)/k_4 = 17._5$, $k_2(k_4 + k_5 + k_6)/(k_3k_4) = 14._6$, $k_5k_7/\{k_4(k_7 + k_8)\} = 7.3_0$, $(2k_{2a} + k_{2c})(k_4 + k_5 + k_6)k_7/\{k_3k_4(k_7 + k_8)\} = 7.3_6$, $(k_6/k_4) + k_5k_8/\{k_4(k_7 + k_8)\} = 9.2_1$, and $[(k_{2b}/k_3) + (2k_{2a} + k_{2c})k_8/\{k_3(k_7 + k_8)\}]\{(k_4 + k_5 + k_6)/k_4\} = 12._1$ were obtained. From these values, the values of $k_3/k_2 = 1.2_0$, $k_5/k_4 = 15._7$, $k_6/k_4 = 0.82$, $k_{2b}/k_2 = 0.25_1$, and $(2k_{2a} + k_{2c})/k_2 = 1.0_9$ were obtained. The values of k_{2b}/k_2 and $(2k_{2a} + k_{2c})/k_2$ are well in accord with those obtained previously,[1] where $k_2 = k_{2a} + k_{2b} + k_{2c}$.

On the formations of CH_4 and amine, eq IV can be derived.

$$\frac{\phi_{CH_4}}{\phi_{C_4H_5N\cdot HN_3}}\frac{[C_2H_2]}{[HN_3]} = \frac{k_4}{k_5}\left(\frac{k_{13} + k_{14}}{k_{15}} + \frac{k_{15} + k_{16}}{k_{15}}\frac{[C_2H_2]}{[HN_3]}\right) \tag{IV}$$

A plot of the relation is shown in Figure 3. From the intercept and the slope in Figure 3, the values of $(k_{13} + k_{14})/k_{15} = 4.7_8$ and $k_{16}/k_{15} = 3.5_8$ are obtained by using $k_5/k_4 = 15._7$. From these values, it is suggested that only 10.7% of C_2H_2N formed by reaction 5 reacts to give amine.

Comparisons of Rate Constants. The enthalpies of the reactants and the products and the paths for reactions 1–6 are shown in Figure 4 with the heats of formation listed in Table II. It is found that the route of

$$2H\text{-azirine}^* \xrightarrow{\text{TS2}} CH_3NC^* \xrightarrow{\text{TS3}} CH_3CN^*$$

in reaction 4′ seems to be possible, because the enthalpies of the transition states of TS2 and TS3[9] are lower than that of $NH(a^1\Delta) + C_2H_2$.

TABLE III: Model for the Unimolecular Decomposition of HC≡C–NH$_2$

	HC≡C–NH$_2$ molecule		activated complex	
wavenumber, cm^{-1}	3346	1104	3440 (1)[a]	
	3344	661	3360 (1)[a]	
	3258	603	1497 (1)[b]	
	2152	513	3325 (1)[c]	
	1597	450	1848 (1)[c]	
	1264	371	630 (2)[c]	
moment of inertia, 10^{-47} kg m^2	85.06		3.43 (1)[b]	18.22 (2)[d]
	82.84		2.16 (1)[b]	
	2.70		1.18 (1)[b]	

[a] Estimated from the wavenumbers of the symmetric and asymmetric stretching vibrations of the NH_2 group in NH_3, CH_3NH_2, NH_2CN, and NH_2CHO molecules. [b] Reference 20. [c] Reference 19. [d] Reference 21.

TABLE IV: Fractional Yields on the Unimolecular Decompositions of $C_2H_3N^*$ and $C_2H_5N^*$

decomp from $C_2H_3N^*$		decomp from $C_2H_5N^*$[a]	
products	yield, %	products	yield, %
$CH_3 + CN$	5.7	$CH_3 + CH_2N$	41.7
$H_2 + C_2HN$	0	$H_2 + CH_3CN$	4.2
$H + C_2H_2N$	89.6	$H + C_2H_4N$	23.5
$NH_2 + C_2H$	4.7	$NH_2 + C_2H_3$	30.6

[a] Reference 3.

Moreover, it appears that the rates of the unimolecular decompositions by reactions 4 and 5 are very fast, because the enthalpy difference between $NH(a^1\Delta) + C_2H_2$ and $CH_3 + CN$, $H + CH_2NC$, or $H + CH_2CN$ is large. However, the enthalpy difference between $NH(a^1\Delta) + C_2H_2$ and $C_2H + NH_2$ is small. Therefore, the specific rate for the unimolecular decomposition of reaction 6 was examined.

The specific rate for the unimolecular decomposition of chemically activated species, k_E, can be calculated by the RRKM theory[14] with the equation[4]

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

In the case of a single-bond fission, the activated complex should be very loose, because it must have the same structure as that for the radical–radical recombination, which is a reverse reaction. Thus, the Gorin model[15] was adopted for the activated complex. Then, the partition function for rotation of the complex, $q_r^{\ddagger}$, can be expressed by the equation[4,16]

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

The attractive potential constant for the intermolecular force between X and Y, A, can be given by the equation[3]

$$A = \frac{3he\alpha_X\alpha_Y}{4\pi m_e^{1/2}[(\alpha/N_e)_X^{1/2} + (\alpha/N_e)_Y^{1/2}]} + \alpha_X\mu_D(Y)^2 + \alpha_Y\mu_D(X)^2 + 2\mu_D(X)^2\mu_D(Y)^2/3kT \tag{VII}$$

---

(14) Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 355, 359. Whitten, G. Z.; Rabinovitch, B. S. *Ibid.* **1964**, *41*, 1883.

(15) Gorin, E. *Acta Physicochim. URSS* **1938**, *9*, 681. Gorin, E.; Kauzmann, W.; Walter, J.; Eyring, H. *J. Chem. Phys.* **1939**, *7*, 633.

(16) Waage, E. V., rabinovitch, B. S. *Chem. Rev.* **1970**, *70*, 377.

TABLE V: Comparisons of the Relative and Absolute Rate Constants on the Reactions of NH Radicals with Various Reactions[a]

X	$\frac{k_r}{k_2}$	$\frac{k_d}{k_2}$	$\frac{k_r + k_d}{k_2}$	$10^{-14}k_q(a^1\Delta)_X$, $cm^3\ mol^{-1}\ s^{-1}$	$10^{-14}k_q(c^1\Pi)$,[b] $cm^3\ mol^{-1}\ s^{-1}$	$10^{-14}k_q(A^3\Pi)$,[b] $cm^3\ mol^{-1}\ s^{-1}$
HN_3	1.00	0	1.00	1.0_8		
Xe	0	0.18_7	0.18_7	0.20		
CH_4	0.17_5	0.17_7	0.35_2	0.38	0.35	0.45
C_2H_6	0.33_4	0.21_7	0.55_1	0.60	0.86	1.13
C_3H_8	1.2_8	0.26_2	1.5_4	1.6_7	1.67	1.50
C_2H_4	1.6_4	0	1.6_4	1.7_8	2.88	1.19
C_2H_2	1.2_0	0	1.2_0	1.3_0		

[a] k_r/k_2, k_d/k_2, and $(k_r + k_d)/k_2$ are the experimental values obtained in previous[1-5] and present work. $k_q(a^1\Delta)_X$ was calculated by using eq IX. [b] Reference 32.

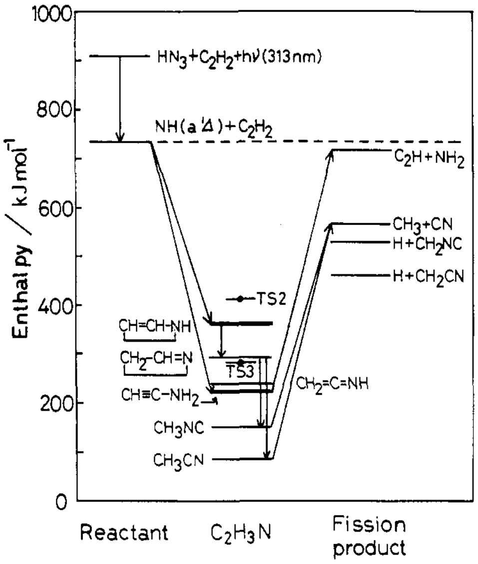


Figure 4. Enthalpies of the reactants, the transition states (●), and the primary C_2H_3N (boldface solid lines), secondary C_2H_3N, and fission products.

with use of the approximation by Slater and Kirkwood[17] for the dispersion term.

The values used in the calculation of the decomposition rate of $HC{\equiv}C{-}NH_2{}^*$ are shown in Table III for the wavenumbers of the vibrations of $HC{\equiv}C{-}NH_2$,[18] C_2H,[19] and NH_2,[20] and for the moments of inertia of the rotations of $HC{\equiv}C{-}NH_2$,[18] C_2H,[21] and NH_2.[20] The values of $\alpha(C_2H) = 3.09 \times 10^{-30}\ m^3$,[20] $\alpha(NH_2) = 1.82 \times 10^{-30}\ m^3$,[22] $\mu_D(C_2H) = 0.704$ D,[23] $\mu_D(NH_2) = 2.10$ D,[24] $N_e(C_2H) = 9$, $N_e(NH_2) = 7$, $s = 12$, $s^\ddagger = 7$, $r^\ddagger = 5$, $E_0(HC_2{-}NH_2) = 486.9\ kJ\ mol^{-1}$,[25] and $T = 303$ K were also used in the calculation. The values of k_E calculated as a function of $E^\ddagger$ for reaction 6′ were 1.3×10^{10}, 1.9×10^{11}, and $1.0 \times 10^{12}\ s^{-1}$ at 50, 100, and 150 kJ of $E^\ddagger$, respectively.

Since the enthalpy change of reaction 3b is −511.3 kJ, the excess energy participating in the decomposition of reaction 6′, $E^\ddagger$, becomes 24.4 kJ at the standard state of $NH(a^1\Delta)$. However, $NH(a^1\Delta)$ and N_2 formed by reaction 1 contain an excess energy of 175.4 kJ, which is the difference between the enthalpies of $HN_3 + C_2H_2 + h\nu(313\ nm)$ and $NH(a^1\Delta) + C_2H_2$ as seen in Figure 4. Therefore, it is assumed that when one-half of the excess energy in the photolysis is possessed by $NH(a^1\Delta)$, $E^\ddagger$ becomes 112.1 kJ. When one-third of the excess energy is retained by $NH(a^1\Delta)$, $E^\ddagger$ becomes 82.9 kJ. The specific rates of reaction 6′ at 82.9 and 112.1 kJ of $E^\ddagger$ are 8.7×10^{10} and $3.0 \times 10^{11}\ s^{-1}$, respectively.

On the other hand, the sum of the collision numbers of $C_2H_3N^*$ with C_2H_2 and HN_3, calculated by using the Lennard-Jones collision frequency,[2,26] was about $2.7 \times 10^9\ s^{-1}$ at the highest total pressure systems of 20.17 kPa of HN_3 and 4.23 kPa of C_2H_2, and 6.67 kPa of HN_3 and 15.64 kPa of C_2H_2. Judging from these situations, it seems that almost all of $C_2HNH_2{}^*$ decomposes to give C_2H and NH_2 without deactivating by collision.

The rates of the unimolecular decompositions of CH_3CN^* and CH_3NC^* in reaction 4′ were also calculated by the same procedure as that used in the calculation of the decomposition rate of $C_2HNH_2{}^*$, and it was found that the decomposition rates of CH_3CN^* and CH_3NC^* are much faster than the rate for $C_2HNH_2{}^*$. Therefore, it is clear that CH_3CN as a final product is not caused by the collisional deactivation of CH_3CN^* in reaction 4′. Thus, CH_3CN seems to arise from another process, that is, reaction 13.

The yield of reaction 4 is fairly low as compared with that of reaction 5, although the decompositions of CH_3CN^* and CH_3NC^* are very fast. It may be because the reactions releasing H atom from 1*H*-azirine* and the succeeding $C_2H_3N^*$ intermediates are predominant. Reaction 5′ seems also to proceed with a very fast rate, because $CH_2{=}C{=}NH^*$ is a simple molecule with large excess energy, as is the case of reactions 4′ and 6′.

The fractional yields on the unimolecular decompositions of $C_2H_3N^*$ are shown in Table IV together with those for $C_2H_5N^*$.[3] The decomposition pattern of $C_2H_3N^*$ to give CH_3, H, and NH_2 is in common with that of $C_2H_5N^*$, except for a small formation of H_2 from $C_2H_5N^*$. The formation of H_2 from $C_2H_3N^*$ seems to be difficult because the resultant C_2HN species are in high enthalpy states possessing two unpaired electrons. On the other hand, the fractional yield for the detachment of H atom from $C_2H_3N^*$ is fairly high as compared with that from $C_2H_5N^*$. The high yield may be because the fissions of the C–H and N–H bonds are easier than those of the highly unsaturated C–C and C–N bonds in $C_2H_3N^*$.

If we assume that all of $CH{\equiv}C{-}NH_2{}^*$ decomposes to give C_2H and NH_2 and that CH_3 and H arise from 1*H*-azirine* only, the value of $k_{3b}/k_2 = 0.056$ can be estimated from the relation

$$\frac{k_{3b}}{k_2} = \frac{k_3}{k_2}\,\frac{k_6}{k_4 + k_5 + k_6} \qquad \text{(VIII)}$$

The ratio of the efficiency per C–H bond for the insertion of $NH(a^1\Delta)$ into a C–H bond of C_2H_2 to that of CH_4 can be derived to be 0.64 from the ratio $(k_{3b}/2k_2)/\{k_{3(CH_4)}/4k_2\}$ by using $k_{3(CH_4)}/k_2 = 0.17_5$.[4] The insertion efficiency, in general, decreases with an increase of the C–H bond dissociation energy (D).[5] Thus, the ratio of 0.64 seems to be appropriate, judging from the values of $D(C{-}H)_{CH_4} = 438$[5] and $D(C{-}H)_{C_2H_2} = 535\ kJ\ mol^{-1}$.[27]

---

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

(18) Saebo, S.; Farnell, L.; Riggs, N. V.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5047.

(19) Milligan, D. E.; Jacox, M. E.; Abouaf-Marguin, L. *J. Chem. Phys.* **1967**, *46*, 4562.

(20) Herzberg, G. *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966; p 584.

(21) So, S. P.; Richards, W. G. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 660.

(22) Estimated from $\alpha(C_2H_2) = 3.49$, $\alpha(NH_3) = 2.22$, and $\alpha(H) = 0.401 \times 10^{-30}\ m^3$.

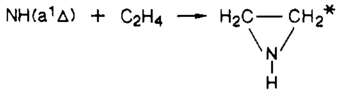
(23) Estimated from the charge distributions in C_2H radicals, presented in ref 21.

(24) Bell, S.; Shaefer, H. F. *J. Chem. Phys.* **1977**, *67*, 5173.

(25) The bond dissociation energy at 0 K, E_0, was calculated by using the heats of formation in Table II, the wavenumbers of vibrations in Table III, the principle of the equipartition of energy for the translational and rotational energies, and $\Delta E = \Delta H - \Delta nRT$.

(26) Troe, J. *J. Phys. Chem.* **1979**, *83*, 114.

The value of $k_{3a}/k_2 = 1.1_4$ can be estimated from the ratio $(k_3/k_2)\{(k_4 + k_5)/(k_4 + k_5 + k_6)\}$. Meanwhile, for the reactions of $NH(a^1\Delta)$ with C_2H_4:[3]


(3a')

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

it is expected that $k_{3b'}/k_2$ is nearly equal to $k_{3(CH_4)}/k_2 = 0.17_5$,[4] because $D(C-H)_{C_2H_4} = 434$ kJ mol^{-1} (ref 27) is almost the same as $D(C-H)_{CH_4}$. Then, the value of $k_{3a'}/k_2 \simeq 1.4_7$ can be estimated from $(k_{3a'} + k_{3b'})/k_2 = 1.6_4$.[3] From these results, it is suggested that the addition of $NH(a^1\Delta)$ to the π bond of C_2H_2 is less effective than that to the π bond of C_2H_4.

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

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

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

the values of k_r/k_2, k_d/k_2, and $(k_r + k_d)/k_2$ for C_2H_2 become 1.2_0, 0, and 1.2_0, respectively, because $k_3/k_2 = 1.2_0$ and the deactivation of $NH(a^1\Delta)$ by C_2H_2 to $NH(X^3\Sigma^-)$ is negligibly small. These values are shown in Table V together with those obtained previously.[1-5] It is found in Table V that k_r/k_2 of C_2H_2, C_2H_4, and HN_3, having a π bond, are, in general, higher than those for saturated hydrocarbons having a σ bond only, but k_d/k_2 for C_2H_2, C_2H_4, and HN_3 are negligible.

The absolute rate constant for the overall quenching of $NH(a^1\Delta)$ by X, $k_q(a^1\Delta)_X$, can be calculated by the equation

$$k_q(a^1\Delta)_X = \frac{(k_r + k_d)_X}{k_2} k_2(\text{PKT}) \qquad (\text{IX})$$

where k_2(PKT) means the absolute value of k_2 that was observed by Piper, Krech, and Taylor.[28] The value of $k_q(a^1\Delta)_X$ for C_2H_2 was estimated to be $1.3_0 \times 10^{14}$ cm^3 mol^{-1} s^{-1} by using k_2(PKT) = $1.0_8 \times 10^{14}$ cm^3 mol^{-1} s^{-1}.

The value of $k_q(a^1\Delta)_{C_2H_2}$ is shown in Table V together with those obtained previously.[3,5] It is found that $k_q(a^1\Delta)_{C_2H_2}$ is less than $k_q(a^1\Delta)_{C_2H_4}$ and similar to $O(2^1S_0)$.[29] It was also found that the values of $k_q(a^1\Delta)_X$ in Table V resemble closely the rate constants of the overall quenching of $C(2^1D_2)$, $O(2^1D_2)$, $S(3^1D_2)$, and $CH_2(^1A_1)$,[5] although the values of $k_q(a^1\Delta)_X$ based on k_2(PKT) are higher than the quenching rate constants of $NH(a^1\Delta)$ by CH_4, C_2H_4, and C_3H_8 that were observed by McDonald et al.[30] and Bower et al.[31]

Recently, the quenching rates of $NH(c^1\Pi)$ and $NH(A^3\Pi)$ by various hydrocarbons have been observed by Sasaki et al.[32] using a phase-shift method. These results, $k_q(c^1\Pi)$ and $k_q(A^3\Pi)$, are also listed in Table V. It is found that the quenching rate constants of $NH(a^1\Delta)$ are quite similar to those of $NH(c^1\Pi)$ and $NH(A^3\Pi)$. Judging from the quenching rates of $NH(a^1\Delta)$, $C(2^1D_2)$, $O(2^1D_2)$, $S(3^1D_2)$, $CH_2(^1A_1)$, $NH(c^1\Pi)$, and $NH(A^3\Pi)$, it is suggested that the electronically excited species show similar reactivity.

Acknowledgment. I am grateful to Jun Fukuchi for his cooperation.

Registry No. HN_3, 7782-79-8; C_2H_2, 74-86-2; NH, 13774-92-0; $CH{\equiv}CNH_2$, 52324-04-6; $\underline{CH{=}CHN}H_2$, 157-17-5; $C_4H_5N{\cdot}NH_3$, 115436-81-2.

---

(27) Calculated from the standard heats of formation listed in Table I of ref 2 and Table II.

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

(29) Donovan, R. J.; Husain, D. *Chem. Rev.* **1970**, *70*, 489.

(30) McDonald, J. R.; Miller, R. G.; Barnovski, A. *Chem. Phys.* **1978**, *30*, 133. Cox, J. W.; Nelson, H. H.; McDonald, J. R. *Ibid.* **1985**, *96*, 175.

(31) Bower, R. D.; Jacoby, M. T.; Blauer, J. A. *J. Chem. Phys.* **1987**, *86*, 1954.

(32) Sasaki, S.; Kano, A.; Tsunashima, S.; Sato, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1675.

Correlation between Gas-Phase and Solution-Phase Reactivities of Hydroxyl Radicals toward Saturated Organic Compounds

Timothy J. Wallington, Philippe Dagaut, and Michael J. Kurylo*

Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received: November 9, 1987)

The gas-phase and aqueous-solution-phase reactivities of hydroxyl radicals with a wide variety of organic compounds are compared. When kinetic data are available for the same reaction occurring in both phases, this comparison provides useful information about the reaction mechanism. Through this comparison we can demonstrate a linear correlation between the gas/solution-phase OH reactivities for numerous saturated organic compounds. This empirical relationship can be used together with mechanistic information to estimate the OH reactivity in one phase from the measured rate constant in the other. In order to develop and extend the correlation, we have used the flash photolysis resonance fluorescence technique to measure rate constants for the gas-phase reactions of OH radicals with methanol-d_4, ethanol-d_6, 2-chloroethanol, 2,2,2-trichloroethanol, 2,2,2-trifluoroethanol, acetone-d_6, 1,1,1-trifluoroacetone, and 1,2-butylene oxide at 298 K. These results are reported herein.

Introduction

One of the principal objectives of atmospheric chemical research is the elucidation of the fates of chemical species emitted into the atmosphere both naturally and as a result of human activities. Hydroxyl radical reactions are recognized as the major loss process for many organic compounds following such emission.[1,2] Thus, the calculation of atmospheric species lifetimes from accurate OH rate data has fostered a considerable scientific effort over the past two decades to accurately define the kinetics and mechanisms of OH reactions with a wide variety of organic compounds.

The significant kinetic data base for such reactions in both gas and solution phases[3,4] now allows for a comparative analysis to

---

(1) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry*; Wiley: New York, 1986.

(2) Wayne, R. P. *Chemistry of Atmospheres*; Oxford University: Oxford, 1986.