

## Radiolysis of Mixtures of Hydrocarbons and Ammonia. I. Formation of Ethylamine from a Mixture of Ethylene and Ammonia

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The  $\gamma$ -radiolysis of a gaseous mixture of ethylene and ammonia has been investigated over the whole range of composition. The products of decomposition were primarily hydrogen, ethane, *n*-butane, ethylamine, and acetylene. It was observed that the yields of ethane, *n*-butane, and ethylamine increased with the increasing concentration of ammonia, and that the *G*-values of these products at 98 mol% ammonia were 0.52, 2.12, and 0.89, respectively. Addition of oxygen or nitric oxide as radical scavengers tended to reduce the yields remarkably. The *G*-value of ethyl radical was calculated from the *G*-values of ethane, *n*-butane, and ethylamine, and the limiting value of  $G(\text{C}_2\text{H}_5\cdot)$  was determined by extrapolation to 100 mol% ammonia. The value thus obtained agrees with the initial *G*-value of hydrogen radical, *i.e.*,  $G_{\text{H}}=7.0\pm 0.6$ , which was obtained by Eyre and Smithies in the study of the  $\gamma$ -radiolysis of ammonia gas<sup>1)</sup>. From these results, it was concluded that thermal hydrogen radicals produced by the  $\gamma$ -radiolysis react quickly with ethylene, giving ethane, *n*-butane, and ethylamine from ethyl radicals.

The radiolysis of olefins has been studied by many investigators. The primary process of hydrogen formation was investigated in detail by Hatano *et al.* on the simple olefins (ethylene, propylene, butene-1 and butene-2) under the action of  $\gamma$ -ray radiation.<sup>2-7)</sup> They concluded that almost all the hydrogens produced were non-scavengable and that they were produced by the decomposition of the so-called "super-excited state" which had been proposed by Platzman.<sup>8-10)</sup>

It is well-known that thermal hydrogen radicals react quickly with olefins to form alkyl radicals *viz.*, the olefins are good radical scavengers.

It is obvious that hydrogen radical formed in the radiolysis of ammonia finally leads to hydrogen molecule or ammonia molecule. Eyre and Smithies reported that the initial *G*-value of hydrogen radical in the radiolysis of ammonia was as large as  $7.0\pm 0.6$ .<sup>1)</sup>

It is expected, therefore, that the concentration of ethyl radical may increase in the radiolysis of a mixture of ammonia and ethylene in which ammonia gives a large *G*-value of hydrogen radical and ethylene is good radical acceptor. Thus the yields of the products produced by the reaction of ethyl radical might increase.

We have studied the  $\gamma$ -radiolysis of a gaseous mixture of ethylene and ammonia and will report on the mechanism of formation of ethane, *n*-butane, and ethylamine.

### Experimental

**Materials.** Ethylene gas of high purity (over 99.8%) from the Takachiho Trading Co. was purified more than

five times by bulb-to-bulb distillation, and only the middle fraction of the purified ethylene was used as the reactant. Purity was determined to be over 99.96% by gas chromatography. Ammonia of high purity (over 99.99%) from the Matheson Co. was dehydrated by metallic sodium and distilled by the bulb-to-bulb distillation method as in the case of ethylene, only the middle fraction of the purified ammonia being used as reactant. Purity of the ammonia was determined to be over 99.9% by gas chromatography. Oxygen and nitric oxide from the Takachiho Trading Co. were used without further purification.

**Irradiation.** A mixture of ethylene and ammonia was led into a 30 ml Pyrex glass ampoule fitted with a break-off seal at constant pressure (2 atm,  $2.4\times 10^{-3}$  mol). Irradiation was carried out at room temperature by Co-60  $\gamma$ -rays at the exposure-dose rate of  $1.9\times 10^5$  r/hr. In the run of hydrogen analysis, the experiment was carried out at 4 atm using a 3.1 ml Pyrex glass ampoule ( $5.0\times 10^{-4}$  mol of the mixture).

**Analysis.** **Ethylamine:** The irradiated sample was frozen at  $-196^\circ\text{C}$  and dissolved in 1.0 ml benzene. 0.1 ml of the solution was then injected into a gas chromatograph (Yanagimoto, 3DH) equipped with a flame ionization detector by means of a micro-syringe. A column (2 m  $\times$  3 mm) with 10% KOH and 10% tetraethylene pentamine on 80/100 mesh Porapak Q was connected directly to a column with 10% KOH and 10% Lubrol MO on 80/100 mesh Porapak Q and used at  $70^\circ\text{C}$ . The carrier gas was nitrogen. Ethylamine was identified by the following. The retention time of the peak was consistent with that of a standard ethylamine and the peak disappeared when the sample was passed through sulfuric acid.

**Hydrocarbons:** The analysis was carried out with a gas chromatograph (Yanagimoto, G8) equipped with a flame ionization detector. A column (2 m  $\times$  4 mm) filled with silica gel was used, with nitrogen as a carrier gas. Measurement was carried out by the temperature promotion method in the range  $50$ – $150^\circ\text{C}$  at a rate of  $4^\circ\text{C}/\text{min}$ .

**Hydrogen:** Non-condensable gases at  $-196^\circ\text{C}$  were collected by a Toepler-pump and analyzed by a gas chromatograph (Yanagimoto, GC220) equipped with a thermal conductivity detector. A column (5 m  $\times$  5 mm) with Molecular Sieve 5A was used at room temperature with argon as a carrier gas.

**Hydrazine:** The irradiated sample was frozen at  $-196^\circ\text{C}$  and dissolved in 2 ml water. The dissolved sample was analyzed by the method reported by Watt and Chrisp.<sup>11)</sup>

1) J. A. Eyre and D. Smithies, *Trans. Faraday Soc.*, **66**, 2199 (1970).

2) Y. Hatano, S. Shida, and S. Sato, *This Bulletin* **37**, 1854 (1964).

3) Y. Hatano and S. Shida, *ibid.*, **39**, 456 (1966).

4) Y. Hatano and S. Shida, *J. Chem. Phys.*, **46**, 4784 (1967).

5) Y. Hatano, S. Shida, and M. Inokuti, *ibid.*, **48**, 940 (1968).

6) Y. Hatano, S. Shida, and S. Sato, *This Bulletin* **41**, 1120 (1968).

7) Y. Hatano, *ibid.*, **41**, 1126 (1968).

8) R. L. Platzman, *Radiat. Res.*, **17**, 419 (1962).

9) R. L. Platzman and W. P. Jesse, *Nature*, **195**, 790 (1962).

10) R. L. Platzman, *J. Chem. Phys.*, **38**, 2775 (1963).

### Results

The products in the  $\gamma$ -radiolysis of ammonia were hydrogen, nitrogen, and hydrazine. Hydrogen and hydrazine were determined. In the case of ethylene radiolysis, hydrogen, methane, ethane, acetylene, propane, *n*-butane, *n*-pentane, and *n*-hexane were identified. These products were analyzed quantitatively except for *n*-pentane and *n*-hexane. In the  $\gamma$ -radiolysis of a mixture of ammonia and ethylene, formation of ethylamine was confirmed in addition to the above products.

In the radiolysis of pure ammonia, the  $G$ -value of hydrazine was very small, *i.e.*,  $G(\text{N}_2\text{H}_4)=0.01$ . In the case of the mixture of ammonia and ethylene,  $G(\text{N}_2\text{H}_4)$  was not more than 0.01.

Dependence of the  $G$ -value of hydrogen  $G(\text{H}_2)$  on the composition of the mixture is shown in Fig. 1. In the case of pure ethylene,  $G(\text{H}_2)$  is  $1.26 \pm 0.03$  both at 2 atm and 4 atm. This is consistent with the values reported.<sup>6,12</sup> Thus, there is no pressure effect in our experimental condition.

The dependence of the yield of ethylamine on dose at 90 mol% ammonia is shown in Fig. 2. The yield of ethylamine increases linearly with the increasing dose. From the slope of the straight line, the  $G(\text{C}_2\text{H}_5\text{NH}_2)$  is calculated to be 0.73.

The dependence of the yield of ethylamine on the composition of the mixture is shown in Fig. 3. The

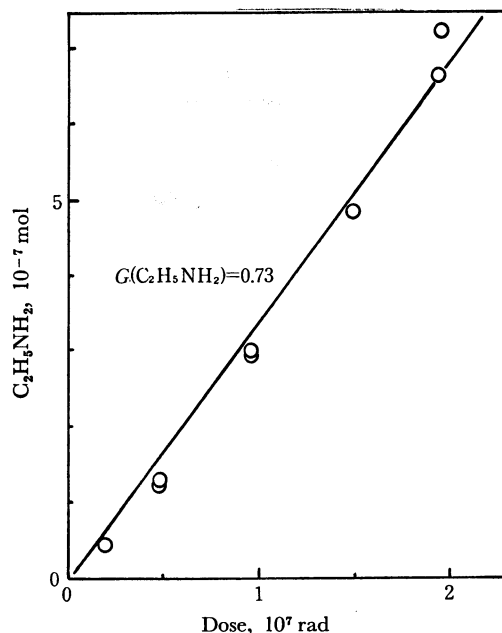


Fig. 2. Dose dependence of the yield of ethylamine.  $\text{C}_2\text{H}_4 + \text{NH}_3 = 2.4 \times 10^{-3}$  mol,  $(\text{C}_2\text{H}_4/\text{NH}_3 = 1/9)$

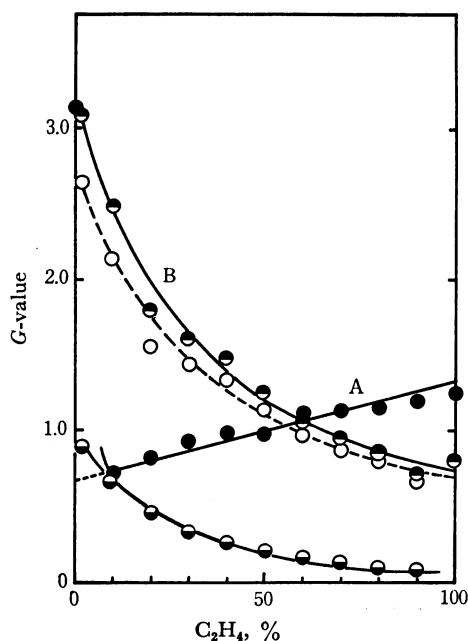


Fig. 1. Composition dependence of  $G$ -values. dose;  $1 \times 10^7$  rad,  $\text{C}_2\text{H}_4 + \text{NH}_3 = 2.4 \times 10^{-3}$  mol

- (A):  $G(\text{H}_2)$
- :  $G(\text{C}_2\text{H}_5\text{NH}_2)$
- :  $G(\text{C}_2\text{H}_4) + G(n\text{-C}_4\text{H}_{10})$
- (B):  $G(\text{C}_2\text{H}_4) + G(n\text{-C}_4\text{H}_{10}) + \frac{1}{2} \cdot G(\text{C}_2\text{H}_5\text{NH}_2)$

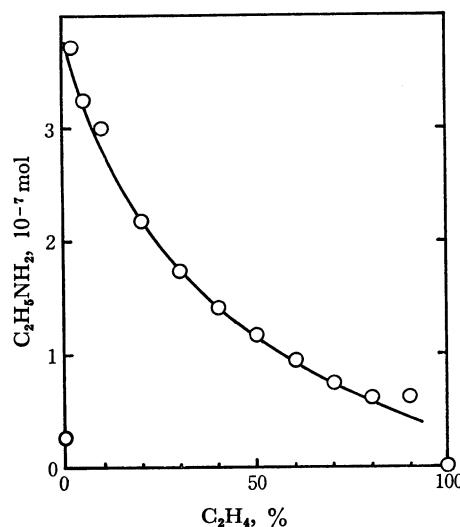


Fig. 3. Composition dependence of the yield of ethylamine. dose;  $1 \times 10^7$  rad,  $\text{C}_2\text{H}_4 + \text{NH}_3 = 2.4 \times 10^{-3}$  mol

yield of ethylamine increases with the increasing concentration of ammonia and the maximum yield  $3.7 \times 10^{-7}$  mol or  $G(\text{C}_2\text{H}_5\text{NH}_2) = 0.89$  is obtained at 98 mol% ammonia. In the case of pure ammonia, a small of ethylamine  $0.25 \times 10^{-7}$  mol was also obtained. This seems to be due to the elution of ethylamine by ammonia which was absorbed on the columns of the gas chromatograph.

Oxygen and nitric oxide are often used as radical scavengers in radiation chemistry. Table 1 shows the variations of the yields of ethylamine and *n*-butane by the addition of these scavengers. Both products were reduced completely by the addition of more than 0.15 mol% oxygen or by the addition of more than 0.6 mol% nitric oxide. It can be concluded that ethylamine and *n*-butane are formed through the radical processes.

11) G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

12) F. W. Lampe, *Radiat. Res.*, **10**, 691 (1959).

TABLE 1. EFFECTS OF ADDITIVES (NO, O<sub>2</sub>)

NO, %	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> , (10 <sup>-7</sup> mol)	<i>n</i> -C <sub>4</sub> H <sub>10</sub> , (10 <sup>-7</sup> mol)	O <sub>2</sub> , %	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> , (10 <sup>-7</sup> mol)	<i>n</i> -C <sub>4</sub> H <sub>10</sub> , (10 <sup>-7</sup> mol)
0	3.0	7.0	0	3.0	7.0
0.15	1.5	2.5	0.15	0	0
0.3	0.9	1.5	0.6	0	0
0.56	0	0	1.0	0	0
1.0	0	0	1.6	0	0
1.5	0	0			

C<sub>2</sub>H<sub>4</sub>: NH<sub>3</sub>=1:9, dose; 1.0×10<sup>7</sup> rad

Figure 4 shows the dependence of the yields of hydrocarbon products (methane, ethane, acetylene, and *n*-butane) on the composition of the mixture. The yields of *n*-butane and ethane increased with the increasing concentration of ammonia, and were reduced by addition of nitric oxide. On the other hand, the yield of acetylene, one of the main products, was not only independent of the concentration of ammonia but also was unaffected by the addition of nitric oxide. This fact shows that acetylene was formed through the ionic decomposition or the unimolecular decomposition process of an excited ethylene molecule.

The yield of methane was very small, and the data were not accurate. However, it can be qualitatively concluded that no effect of the addition of ammonia are observed as in the case of acetylene.

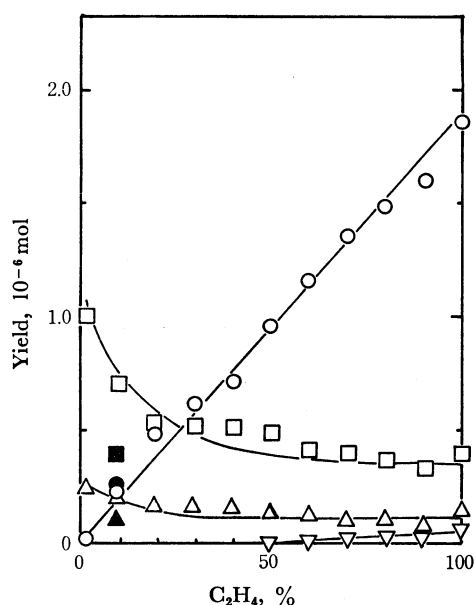


Fig. 4. Composition dependence of the yields of acetylene, *n*-butane, ethane, and methane.

dose; 1×10<sup>7</sup> rad, C<sub>2</sub>H<sub>4</sub>+NH<sub>3</sub>=2.4×10<sup>-3</sup> mol

—○—; C<sub>2</sub>H<sub>2</sub> : ● } 0.14 mol% NO  
 —□—; *n*-C<sub>4</sub>H<sub>10</sub> : ■ }  
 —△—; C<sub>2</sub>H<sub>6</sub> : ▲ }  
 —▽—; CH<sub>4</sub>

### Discussion

The radiolysis of ammonia has been studied in detail by many investigators. Willis *et al.* found by electron beams that  $G(\text{H}_2)$  was constant, *i.e.*,  $G(\text{H}_2)=3.58\pm$

0.08, in the pressure range 1—2.25 atm.<sup>13)</sup> Recently we have obtained  $G(\text{H}_2)$  to be  $3.14\pm 0.11$  in the pressure range 2—4 atm in the  $\gamma$ -radiolysis of ammonia.<sup>14)</sup>

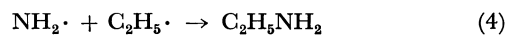
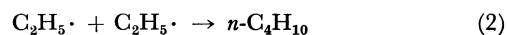
As shown in Fig. 1, it is obvious that  $G(\text{H}_2)$  is reduced rapidly by the addition of a small amount of ethylene and then increases linearly with the increasing concentration of ethylene. It is well-known that olefins are effective scavengers of thermal hydrogen radicals, and that almost all the hydrogen formed in the radiolysis of olefins is non-scavengeable. Consequently, the value obtained by extrapolating the straight line (A) in Fig. 1 to 100 mol% ammonia corresponds to the  $G$ -value of the so-called non-scavengeable hydrogen or hot hydrogen, which might be produced in the radiolysis of pure ammonia, *i.e.*,  $G_{\text{hot}}(\text{H}_2)^{15})=0.68$ . The value is in good agreement with our results in the radiolysis of a mixture of ammonia and propylene or 1,3-butadiene,<sup>14)</sup> and with the result of Eyre and Smithies.<sup>1)</sup>

It can be deduced that the difference between  $G(\text{H}_2)$  which is the value of hydrogen produced in the radiolysis of pure ammonia and  $G_{\text{hot}}(\text{H}_2)$ , *viz.*,  $G(\text{H}_2) - G_{\text{hot}}(\text{H}_2)=2.46$  corresponds to the  $G$ -value of hydrogen formed from the thermal hydrogen radicals.

In Fig. 1 is given the relationship between the  $G$ -values of products which seem to be formed from thermal hydrogen radicals, and the composition of the mixture. The value obtained by extrapolating curve B to 100 mol% ammonia is 3.2. The value corresponds to 6.4 which is the  $G$ -value ( $G_{\text{H}}$ ) of hydrogen radicals. This agrees approximately with the initial  $G$ -value of hydrogen radical  $G_{\text{H}}=7.0\pm 0.6$  obtained by Eyre and Smithies<sup>1)</sup> and  $G_{\text{H}}=7.2\pm 0.5$  by Johnson and Simic in the radiolysis of pure ammonia.<sup>16)</sup>

As shown in Table 1, the yields of *n*-butane and ethylamine are reduced by the addition of oxygen or nitric oxide. The yields of products except acetylene are reduced by the addition of nitric oxide (Fig. 4).

It can be deduced that ethane, *n*-butane, and ethylamine are formed by the following radical processes:



The relation between ethane/*n*-butane and the composition of the mixture is shown in Table 2. It is obvious that the ratio is independent of the composition, and the constant value is found to be  $0.30\pm 0.06$ . This value is about twice 0.14 which is the ratio of the rate

13) C. Willis, A. W. Boyd, and O. A. Miller, *Can. J. Chem.*, **47**, 3007 (1969).

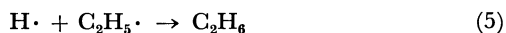
14) K. Hamanoue, J. Okamoto, O. Tokunaga, and A. Danno, to be published; 24th Annual Meeting of the Chemical Society of Japan, vol. 1, p. 52 (1971).

15) In this paper,  $G_{\text{hot}}(\text{H}_2)$  denotes the yield of non-scavengeable hydrogen.

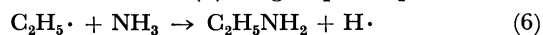
16) G. R. A. Johnson and M. Simic, "Radiation Chemistry," Vol. 2, p. 197, Am. Chem. Soc., (Washington D. C.) (1968).

17) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. 1, p. 105, Pergamon Press (Oxford) (1961).

constant of the disproportionation reaction of ethyl radicals to that of the combination reaction.<sup>17)</sup> This suggests that some processes other than reaction (3) might participate in the formation of ethane. Smith *et al.*<sup>18)</sup> and Rabinovich *et al.*<sup>19)</sup> reported that reaction(5) as well as reaction(3) takes part in the formation of ethane:



For the formation of ethylamine, the following reaction as well as reaction(4) might participate.

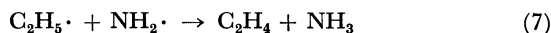


However, from the bond energies of ammonia and of ethylamine<sup>20)</sup>, we can calculate the heat of reaction of (6) to be  $-2.4$  kcal/mol, that is, the reaction is endothermic. Consequently, reaction(4) is considered to be more favorable than reaction(6).

TABLE 2. RELATIONSHIP BETWEEN THE CONCENTRATION OF ETHYLENE AND  $\text{C}_2\text{H}_6/n\text{-C}_4\text{H}_{10}$

$\text{C}_2\text{H}_4$ , %	$\frac{\text{C}_2\text{H}_6}{n\text{-C}_4\text{H}_{10}}$
2	0.24
10	0.27
20	0.29
30	0.31
40	0.31
50	0.30
60	0.34
70	0.25
80	0.31
90	0.30
100	0.35
mean	$0.30 \pm 0.06$

Schurath *et al.* have investigated the photolysis of a mixture of ethylene and ammonia, and reported that the following reaction competes with reaction(4) and that the ratio of  $k_7$  to  $k_4$  is about 0.4.<sup>21)</sup>



Thus, in our reaction system we have to take the contribution of reaction(7) into consideration.

It is obvious that the higher the yields of ethyl radical, the higher the concentration of ammonia. That is to say, the quantity of hydrogen radicals scavenged by ethylene increases with the increasing concentration of ammonia. On the other hand, it is reasonable to consider that the yield of amino radical increases with increasing concentration of ammonia. Consequently, the composition which gives the maximum yield of ethylamine lies so far to the high con-

18) M. J. Smith, P. M. Beatty, J. A. Pinder, and D. J. Le Roy, *Can. J. Chem.*, **33**, 821 (1955).

19) B. S. Rabinovitch, D. H. Dillis, W. H. McLain, and J. H. Current, *J. Chem. Phys.*, **32**, 493 (1960).

20) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, p. 16, Pergamon Press, (London) (1958).

21) U. Schurath, P. Tiedemann, and R. N. Schindler, *J. Phys. Chem.*, **73**, 456 (1969).

TABLE 3. G-VALUES OF PRODUCTS AND ETHYL RADICAL

Products	G-value	$G(\text{C}_2\text{H}_5\cdot)$ consumed
$\text{CH}_4$	0.01	
$\text{C}_2\text{H}_6$	0.52	(3) <sup>a)</sup> 0.60 (5) 0.22
$\text{C}_2\text{H}_2$	1.73	
$n\text{-C}_4\text{H}_{10}$	2.12	(2) 4.24
$\text{C}_2\text{H}_5\text{NH}_2$	0.89	(4) 0.89 (7) 0.27
Total		6.22

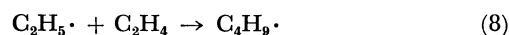
2 mol%  $\text{C}_2\text{H}_4$ , dose;  $1.0 \times 10^7$  rad

a) Number in parentheses indicates reaction number.

centration of ammonia.

Table 3 shows the G-values of products at 2 mol% ethylene. From them we can calculate the G-value of each ethyl radical consumed by reactions(2), (3), (4), (5), and (7). The values thus obtained are also given in Table 3. The total G-value of ethyl radical consumed is seen to be 6.22 which corresponds to the G-value of hydrogen radical consumed by the same processes. On the other hand, the G-value of thermal hydrogen radical in the radiolysis of pure ammonia is 6.4 to 7.0. In the radiolysis of pure ammonia, the difference between  $G(\text{H}_2)=3.14$  and  $G_{\text{hot}}(\text{H}_2)=0.68$  is 2.46. Thus, the apparent G-value of thermal hydrogen radical is 4.92. Consequently, the value 6.22 is reasonable and  $G(\text{C}_2\text{H}_5\cdot)$  is considered to be nearly equal to  $G_{\text{H}}$ .

In the radiolysis of ethylene, ethyl radicals formed might be consumed not only by reactions(2), (3), and (5), but also by reaction(8).



Reaction(8) might give hydrocarbons of more than  $\text{C}_4$ . As shown in Table 3, the  $G(\text{C}_2\text{H}_5\cdot)$  consumed by reactions(2), (3), (4), (5), and (7) is 6.22.  $k_2$ ,  $k_3$ , and  $k_8$  are the order of  $10^{11}$ ,  $10^{11}$ , and  $10^4$  (l/mol sec), respectively.<sup>14)</sup> Thus, the concentration of ethyl radical in the steady state can be estimated by the following equation using these values.

$$\frac{G(\text{C}_2\text{H}_5\cdot) \times I}{100} \simeq (k_2 + k_3)[\text{C}_2\text{H}_5\cdot], \quad (9)$$

where  $I$  is dose-rate in eV/ml sec. The value thus obtained is  $0.7 \times 10^{-9}$  mol/ml. Using these values, the ratio of the reaction rate of reaction(8) to that of reactions (2) plus (3) is as follows.

$$\frac{v_8}{v_2 + v_3} = \frac{10^4[\text{C}_2\text{H}_4][\text{C}_2\text{H}_5\cdot]}{10^{11}[\text{C}_2\text{H}_5\cdot]^2} = 2.3 \times 10^{-4} \quad (10)$$

Consequently,  $v_8 \ll (v_2 + v_3)$  and the quantity of ethyl radical consumed by reaction(8) may be negligible. It can be concluded that the thermal hydrogen radicals (scavengeable hydrogen radicals), formed in the radiolysis of a mixture of ethylene and ammonia, react mainly with ethylene and the resulting ethyl radical leads to ethane, *n*-butane, and ethylamine.

The G-value of thermal hydrogen radical in the radiolysis of pure ammonia is 6.4 to 7.0. This value must be equal to the G-value of amino radical. Con-

sidering the  $G$ -values of hydrazine, ethylamine, and that of reaction(7), amino radical must be also consumed by some other reactions.

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