Radiolyses of Mixtures of Ammonia and Hydrocarbons. II. Formation of Hydrogen from Mixtures of Ammonia and Olefins (Ethylene, Propylene and Butadiene)

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γ-radiolyses of gaseous mixtures of ammonia and olefins (ethylene, propylene and butadiene) have been investigated over the whole composition range of mixtures, and consideration was given on the primary processes of hydrogen formation. From the extrapolated values of $G(H_2)$ obtained in the γ-radiolyses of the mixture of ammonia and olefins, it was found that the non-scavengeable $G(H_2)$ of ammonia, ethylene, propylene and butadiene were 0.68—0.72, 1.26, 1.06, and 0.33, respectively. Gas-phase radiolyses of ammonia–perdeuterated olefin mixtures have also been investigated. From kinetic calculation on the data of isotopic mixtures of hydrogen, the following results were obtained; 1) both thermal and non-scavengeable hydrogen molecules are produced by the γ-radiolysis of ammonia, and the non-scavengeable hydrogen molecules are produced for the most part by a unimolecular process, 2) almost all the hydrogen molecules produced by the γ-radiolyses of olefins (ethylene, propylene, and butadiene) are non-scavengeable; a unimolecular process plays an important role in the case of ethylene, and in other cases a bimolecular process. $G(H_2)$ of the butadiene radiolysis is very small compared with that of other olefins and with the calculated value of butadiene, *i.e.*, $G(H_2)<1$. The discrepancies can be interpreted in terms of the addition reaction of the "hot" hydrogen radicals to butadiene to form *t*-2-butene.

The radiolyses of olefins have been studied extensively. In particular, 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 the γ-ray radiation.[1-6] They concluded that almost all the hydrogen molecules produced were non-scavengeable and produced by the decomposition of the so-called "Super-excited state" proposed by Platzman.[7-12] Generally, it is well known that thermal hydrogen radical reacts quickly with olefins to form alkyl radicals, namely, the olefins are good radical scavengers.[13] Many works have also been carried out on the radiolysis of ammonia. The results have led to the conclusion that the G values of non-scavengeable hydrogen molecules are 0.64—0.84 and those of thermal (scavengeable) hydrogen radicals are 5—12.[14-20] It can be said that ammonia is a good donor of the thermal hydrogen radical.

Thus, it is interesting to study the γ-radiolysis of the mixture of ammonia and olefin. We have reported on the radiolysis of the gaseous mixture of ethylene and ammonia.[21] In this paper we will report on the results of γ-radiolyses of gaseous mixtures of ammonia and olefins (ethylene, propylene and butadiene). Consideration is given to the primary processes of hydrogen formation.

Experimental

Matheson pure-grade ammonia, ethylene, propylene and butadiene were purified by the same method as described in part I.[21] The purity of these purified gases was determined by gas chromatographic analyses to be greater than 99.9%. Ethylene-d_4, propylene-d_6, and butadiene-d_6, were purchased from Merck, Sharp and Dohme Ltd. (isotopic purity 98 at. %D), and were subjected to trap-to-trap distillation. The reactant gas, a mixture of ammonia and olefin, was led into a 3.1 *ml* pyrex glass ampoule at constant pressure of 4 atm. Irradiation was carried out at room temperature by Co-60 γ-rays at the exposure-dose rate of 6.0×10^5 R/hr. Unless otherwise stated, samples were irradiated to a total dose of 2.88×10^7 R. Analyses of products (hydrocarbon and hydrogen) were carried out by the same method as described in part I,[21] and those of isotopic hydrogens were carried out with a Hitachi RMS-4 mass spectrometer. We confirmed the formation of ethylamine in the mixture of ammonia and ethylene. No amines were observed in the mixtures of ammonia and propylene or butadiene.

Results

In the radiolyses of pure propylene and of a mixture of ammonia and propylene or butadiene, the yields of

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hydrogen increased linearly with irradiation doses up to at least 5.0×10^7 R. The same results were obtained in the case of pure ammonia and pure ethylene by Eyre and Smithies[14] and by Hatano *et al.*[5]

Figure 1 shows the pressure dependence of hydrogen formation. Pressure effects are very small in the range 1—4 atm.

The relationship between hydrogen formation and the concentration of olefin is shown in Fig. 2. It is obvious that $G(H_2)$ of ammonia is reduced rapidly by the addition of a small amount of ethylene or propylene, and then increases linearly with increasing concentration of the olefins. In the case of butadiene, a marked decrease is also observed by the addition of a small amount of butadiene. $G(H_2)$ is then reduced monotonously by the further addition of butadiene.

Figure 3 shows the relationship between the G values of the main products which seem to be formed from thermal hydrogen radicals, and the concentration of olefins.

The gas-phase radiolyses of ammonia–perdeuterated olefins mixtures (C_2D_4, C_3D_6, C_4D_6) have also been investigated. The isotopic compositions of HD are comparatively small, *i.e.*, 7—12% at most. The relationship between the concentrations of perdeuterated olefins and D_2/HD or H_2/HD are given in Figs. 4 and 5.

Figures 6 and 7 shows the temperature dependence of hydrogen formation in a mixture of C_3H_6–NH_3 and C_4H_6–NH_3, respectively. So far no explanation has been given on the maximum values near 0°C. Bp and mp denote the boiling and melting points of ammonia, propylene and butadiene, respectively.

Table 1. Effects of scavengers on hydrogen formation

System	Scavenger (%)	$G(H_2)$
C_3H_6	0.0	1.06
C_3H_6+NO	0.6	1.06
	1.2	1.04
	2.6	1.05
	5.6	1.11
C_3H_6+N_2O	0.7	1.06
	1.6	1.00
	2.9	1.16
	5.3	1.04
C_3H_6–NH_3(C_3H_6=30%)	0.0	0.82
C_3H_6–NH_3+NO	1.0	0.80
	1.9	0.80
	4.1	0.77
	6.5	0.86
C_3H_6–NH_3+N_2O	1.3	0.81
	2.3	0.85
	4.1	0.78
	7.1	0.79
C_4H_6–NH_3(C_4H_6=30%)	0.0	0.48
C_4H_6–NH_3+NO	1.4	0.45
	2.6	0.47
	9.8	0.48
	14.0	0.47
C_4H_6–NH_3+N_2O	1.4	0.50
	2.8	0.52
	10.0	0.48
	13.6	0.44

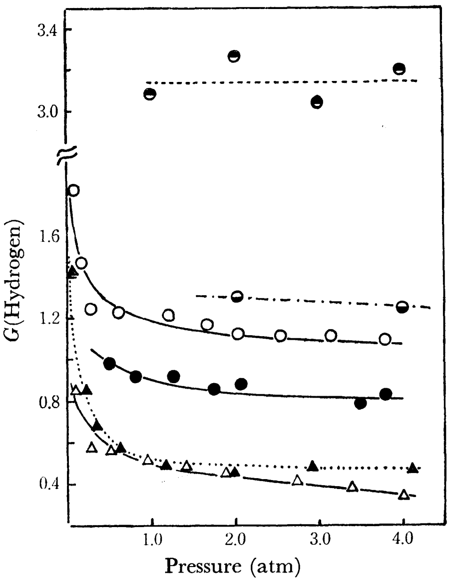

Fig. 1. Pressure-dependence of the formation of hydrogen ◓: NH_3, ◒: C_2H_4, ○: C_3H_6, ●: C_3H_6–NH_3 (C_3H_6=30%), △: C_4H_6, ▲: C_4H_6–NH_3(C_4H_6=30%).

Table 1 shows the effects of scavengers, nitric oxide and nitrous oxide, on the hydrogen formation. No effects were observed.

Discussion

It is obvious from Fig. 1 that there is little change in $G(H_2)$ in the gas-phase radiolysis of ammonia in the pressure range 1—4 atm, namely, $G(H_2)=3.14 \pm 0.11$. Willis *et al.* studied the radiolysis of ammonia by electron beams and found that $G(H_2)$ was constant, *i.e.*, $G(H_2)=3.58 \pm 0.08$, in the pressure range 1—2.25 atm.[15] The same results were obtained by Jones *et al.* in the pressure range 500—700 mmHg, but they found an increase at lower pressure.[17] Eyre and Smithies[14] studied the effects of pressure, temperature, dose and additives on the radiolysis of ammonia, and found that $G(H_2)$ is unaffected in the pressure range 100—700 mmHg. They obtained the G value of non-scavengeable hydrogen molecule and that of scavengeable hydrogen radical as follows.

$$G^*(H_2) = 0.70 \pm 0.02, \quad G(H) = 7.0 \pm 0.6,$$

where $G^*(H_2)$ is the G value of non-scavengeable hydrogen molecule.

In our experiments in the radiolyses of pure olefins or of mixtures of ammonia and olefins, small pressure dependence of $G(H_2)$ above 1 atm can be observed. Marked increase in $G(H_2)$ at a lower pressure may presumably be attributed to the enhanced decrease of the collisional deactivation of excited state.

The initial sharp fall in $G(H_2)$ caused by the addition of a small amount of olefins is consistent with the fact that the olefins are good radical scavengers (Fig. 2). In the case of ethylene or propylene, $G(H_2)$ increased linearly with the increase of the concentration of olefins.

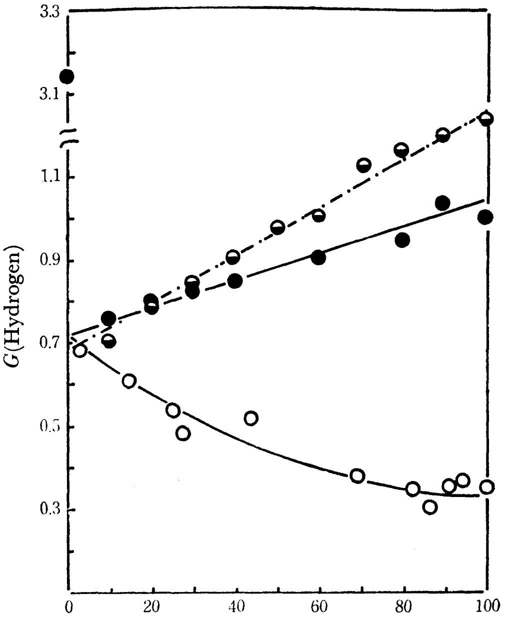

Fig. 2. Variation of hydrogen formation as a function of the concentration of C_2H_4, C_3H_6 and C_4H_6
◒: C_2H_4-NH_3, ●: C_3H_6-NH_3, ○: C_4H_6-NH_3

This suggests that they are due to non-scavengeable hydrogen from olefins. In the case of butadiene, the results is the opposite. However, the limiting values of $G(H_2)$, obtained by the extrapolation of the linear part of the curve to zero mol% olefins, namely 100 mol% ammonia, are nearly the same, *viz.*, $G_{NH_3}(H_2)=0.68$ with ethylene, 0.72 with propylene and butadiene. The values are in good agreement with the value of non-scavengeable hydrogen molecule $(G^*_{NH_3}(H_2)=0.70\pm0.02)$.[14] The values obtained by extrapolating to 100 mol% olefins are 1.26, 1.06, and 0.33 for ethylene, propylene and butadiene, respectively. The data except for butadiene are in good agreement with those formerly obtained.[4-6,14,22-24]

Hatano *et al.* investigated the mechanism of hydrogen formation in the radiolysis of liquid olefins (RH_2).[1-6] They proposed a possible role of the superexcited state (RH_2^{**}); hydrogen molecule is formed by the decomposition of RH_2^{**} by reaction (1) or (2), either by a unimolecular process directly yielding molecular hydrogen or by a bimolecular process yielding hot hydrogen radical (H^*) which abstracts hydrogen from the reactant.

$$RH_2^{**} \begin{array}{l} \nearrow H_2 + R \qquad (1) \\ \searrow H^* + RH \qquad (2) \end{array}$$

The G value of hydrogen formation by the decomposition of the superexcited state is derived by the optical approximation introduced by Platzman.[7-12]

$$G = \frac{100}{W}\frac{M_d^2}{M_i^2} \qquad (3)$$

where M_d^2 and M_i^2 are the dipole matrix elements squared for dissociation and for ionization, respectively. The calculated results show that the quantities M_d^2 and M_i^2 are directly proportional to the number of carbon atoms in the hydrocarbons. The G values were calculated from the results. The values obtained are in good agreement with those of experimental values for ethylene, propylene, butene-1 and butene-2. Thus we might conclude that the linear portion of Fig. 2 is due to non-scavengeable hydrogen molecule from olefin.

No report seems to have been published on the radiolysis of butadiene. However, if we assume that the hydrogen molecules produced by the radiolysis of butadiene are non-scavengeable like those of other olefins, then the G value, *i.e.*, $G(H_2)=0.33$, is much smaller than that of other olefins or that calculated by Hatano,[6] *i.e.*, $G(H_2)>1$. The discrepancies suggest that the "hot" hydrogen radical may partly react with butadiene to form a different product from hydrogen molecule.

In Fig. 3, it is obvious that the G values of products in the radiolyses of mixtures of ammonia and ethylene

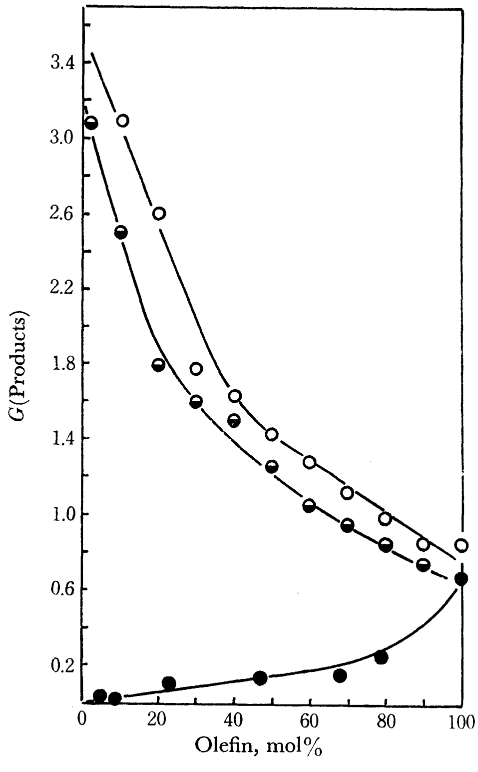

Fig. 3. Variation of the formation of major products as a function of the concentration of C_2H_4, C_3H_6 and C_4H_6
◒: $G(C_2H_6+n\text{-}C_4H_{10}+{}^1/_2C_2H_5NH_2)$ from C_2H_4-NH_3[21]
○: $G(C_3H_8)$ from C_3H_6-NH_3, ●: $G(t\text{-}2\text{-Butene})$ from C_4H_6-NH_3

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[22] Y. Hatano and S. Shida, 11th Symposium of Radiation Chemistry, p. 20, Tokyo, (1968).

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[25] The mechanism of the formation of *t*-2-butene is not known at present. Assuming that it may be formed by the following reaction in which one hot radical participates;

$C_4H_7^* + C_4H_6$ (or NH_3) $\rightarrow t$-2-butene,

then, $G^*(H_2)$ is 0.99. An alternative explanation may be that two hot radicals participate in

$C_4H_7^* + C_4H_7^* \rightarrow t$-2-butene,

in this case, $G^*(H_2)=0.33+2G(t\text{-}2\text{-butene})=1.65$.

or propylene decrease with the increase of the concentration of olefins. This can be explained from the fact that the *G* values of thermal hydrogen radical from olefins are comparatively small and from ammonia very large. In the case of propylene, the extrapolation of the curve to 100 mol% ammonia gives the value 3.5, the corresponding *G* value of hydrogen radical then being 7.0. This value agrees with the initial *G* value of hydrogen radical, $G(\mathrm{H})=7.0\pm0.6$[14] and $G(\mathrm{H})=7.2\pm0.5$.[16]

In the case of ethylene, if we take account of the formation of ethylamine, the corresponding value is 6.4 which shows also good agreement.

These results lead to the conclusion that the thermal hydrogen radicals produced by the γ-radiolysis add quickly to olefins in the case of ethylene and propylene. In the latter, the formation of amines is negligible. In contrast, the *G* value of *t*-2-butene which seems to be the main product from butadiene shows a different behaviour. If the product is formed by the reaction of thermal hydrogen radical and butadiene, *G*(*t*-2-butene) may decrease with the increase of the concentration of butadiene as in the case of ethylene and propylene. *t*-2-Butene should be formed by the reaction of hot hydrogen radical and butadiene, and the thermal hydrogen radical might react with butadiene to form higher hydrocarbon products.

Thus, we can explain the increase of *G*(*t*-2-butene) and the decrease of $G(\mathrm{H_2})$ to be due to increasing concentration of butadiene.

$G(\mathrm{H_2})$ of pure butadiene is 0.33, and it is obvious from Fig. 3 that *G*(*t*-2-butene) is 0.66. Assuming that $G^*(\mathrm{H_2})$ is equal to $G(\mathrm{H_2})+G$(*t*-2-butene), then $G^*(\mathrm{H_2})$ is 0.99,[25] which agrees well with the value calculated by Hatano[6] and with values of other olefins.

Tachikawa *et al.*,[26-28] and Tominaga and Rowland[29] investigated the hot-atom chemistry of recoil tritium, and found correlations between hot-yeilds of HT and bond-dissociation energies of hydrocarbons, halomethanes and amines. Thus it is reasonable to consider that the hydrogen abstraction reaction of hot hydrogen radicals produced by the γ-radiolyses might be affected by bond-dissociation energies.

In the radiolyses of mixtures of ammonia and perdeuterated hydrocarbons ($\mathrm{C_2D_4}$, $\mathrm{C_3D_6}$, $\mathrm{C_4D_6}$), the isotopic composition of HD is comparatively small, *i.e.*, 7—12% at most. In the mixture of $\mathrm{C_3H_6}$ and $\mathrm{C_3D_6}$ ($\mathrm{C_3H_6}$=50 mol%), the isotopic composition of HD is 15—16%. The lower value of HD in the system of $\mathrm{NH_3}$–$\mathrm{C_3D_6}$ than in the system of $\mathrm{C_3H_6}$–$\mathrm{C_3D_6}$ may indicate two posibilities; etiher a small *G* value of hot hydrogen radical from ammonia, or a larger bond-dissociation energy of ammonia than that of olefin.

Eyre and Smithies[14] proposed that the non-scavengeable hydrogen molecule probably arises for the most part from the decomposition of the excited ammonia molecule ($\mathrm{NH_3^{**}}$) *via* reaction (4):

$$\mathrm{NH_3^{**}} \longrightarrow \mathrm{NH} + \mathrm{H_2} \tag{4}$$

An alternative explanation is that some hot hydrogen radicals (H*) are formed and they may abstract hydrogen from ammonia:

$$\mathrm{NH_3^{**}} \longrightarrow \mathrm{NH_2} + \mathrm{H^*} \tag{5}$$

Thus, the hydrogen abstraction reaction in the mixed system of ammonia and olefin can be expressed as follows.

$$\mathrm{H^*} + \mathrm{NH_3} \longrightarrow \mathrm{H_2} \tag{6}$$

$$\mathrm{H^*} + \mathrm{RD_2} \longrightarrow \mathrm{HD} \tag{7}$$

On the other hand, perdeuterated olefin ($\mathrm{RD_2}$) might be decomposed by the following reactions.

$$\mathrm{RD_2^{**}} \longrightarrow \mathrm{D_2} + \mathrm{R} \tag{8}$$

$$\mathrm{RD_2^{**}} \longrightarrow \mathrm{D^*} + \mathrm{RD} \tag{9}$$

$$\mathrm{D^*} + \mathrm{RD_2} \longrightarrow \mathrm{D_2} \tag{10}$$

$$\mathrm{D^*} + \mathrm{NH_3} \longrightarrow \mathrm{HD} \tag{11}$$

Assuming the steady-state condition for the concentrations of the intermediate species H* and D*, we can derive the following equations by a simple kinetic treatment.

$$\lim_{[\mathrm{RD_2}]\to 0} \mathrm{HD/D_2} = \frac{k_9}{k_8} + \frac{k_5k_7}{k_6k_8} \tag{12}$$

$$\lim_{[\mathrm{NH_3}]\to 0} \mathrm{HD/H_2} = \frac{k_5}{k_4} + \frac{k_9k_{11}}{k_4k_{10}} \tag{13}$$

In the radiolysis of $\mathrm{C_4D_6}$–$\mathrm{NH_3}$ mixture, we have taken account of the following reaction besides reactions (10) and (11).

$$\mathrm{D^*} + \mathrm{RD_2} \longrightarrow \text{No hydrogen molecule} \tag{14}$$

In this case, $\mathrm{HD/D_2}$ is given by the same equation as that of Eq. (12), but $\mathrm{HD/H_2}$ is given by the following equation.

$$\lim_{[\mathrm{NH_3}]\to 0} \mathrm{HD/H_2} = \frac{k_5}{k_4} + \frac{k_9k_{11}}{k_4(k_{10}+k_{14})} \tag{15}$$

The results obtained from Figs. 4 and 5 and Eqs. (12), (13), and (15) are shown in Table 2. The values

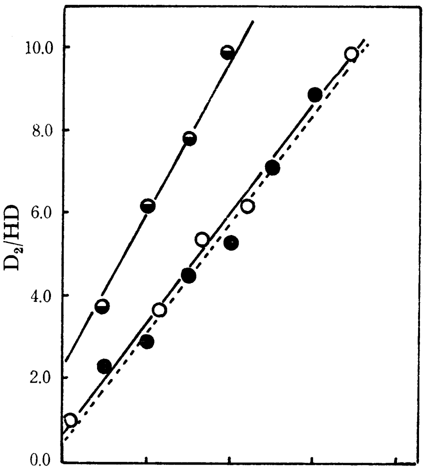

Fig. 4. $\mathrm{D_2/HD}$ *vs.* concentration of $\mathrm{C_2D_4}$, $\mathrm{C_3D_6}$ and $\mathrm{C_4D_6}$
◒: $\mathrm{C_2D_4}$–$\mathrm{NH_3}$, ●: $\mathrm{C_3D_6}$–$\mathrm{NH_3}$ ○: $\mathrm{C_4D_6}$–$\mathrm{NH_3}$

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26) E. Tachikawa and F. S. Rowland, *J. Amer. Chem. Soc.*, **90**, 4767 (1968).

27) E. Tachikawa, Y. N. Tang, and F. S. Rowland, *ibid.*, **90**, 3584 (1968).

28) E. Tachikawa and F. S. Rowland, *ibid.*, **91**, 559 (1969).

29) T. Tominaga and F. S. Rowland, *J. Phys. Chem.*, **72**, 1399 (1968).

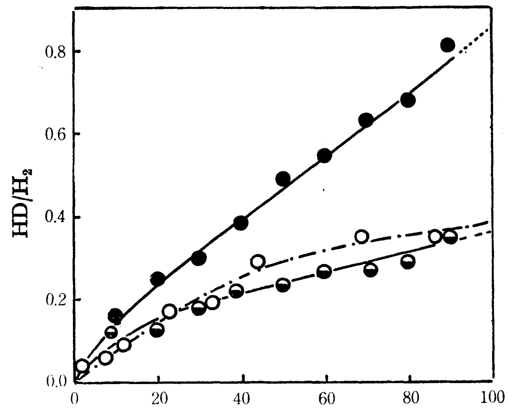

Fig. 5. HD/H$_2$ *vs.* concentration of C_2D_4, C_3D_6 and C_4D_6
◒: C_2D_4–NH_3 ●: C_3D_6–NH_3 ○: C_4D_6–NH_3

Table 2. Limiting values of D_2/HD and HD/H_2

Olefin	$\left(\frac{k_9}{k_8}+\frac{k_5k_7}{k_6k_8}\right)^{-1}$	$\frac{k_5}{k_4}+\frac{k_9k_{11}}{k_4k_{10}}$	$\frac{k_8}{k_9}$ [a)]
C_2H_4	2.4	0.36	2.4
C_3H_6	0.4	0.86	0.4
C_4H_6	0.5	0.39[b)]	

a) Ref. 5. b) $\frac{k_5}{k_4}+\frac{k_9+k_{11}}{k_4(k_{10}+k_{14})}$

of k_8/k_9 which were obtained by Hatano *et al.*[5)] in the system of RH_2–RD_2 are also listed in the last column. Comparing our results with those of Hatano *et al.*, we obtain the following equations.

$$\frac{k_9}{k_8}=\frac{k_9}{k_8}+\frac{k_5k_7}{k_6k_8} \tag{16}$$

$$k_5 \simeq 0 \tag{17}$$

$$\frac{k_5}{k_4}<0.36 \tag{18}$$

The results lead to the following conclusions.

1) Non-scavengeable hydrogen molecules produced by the radiolysis of ammonia are mainly produced by reaction (4), or by a unimolecular process. Bimolecular processes like reaction (5) are much less important.

2) Almost all the hydrogen molecules produced by the γ-radiolyses of ethylene and propylene are non-scavengeable, 71% in the former and 29% in the latter are unimolecular processes.

3) Almost all the hydrogen molecules produced by the γ-radiolysis of butadiene are also non-scavengeable, and k_8/k_9 is 0.5. Consequently, 33% is due to a unimolecular process. Hot hydrogen radicals produced can react with butadiene not only by abstraction reaction of hydrogen, but also by addition reaction to butadiene.

We have assumed that the hot hydrogen radical can add to butadiene. This indicates that the energy of the hot hydrogen radical might not be so high, and the reaction in which this hot radical participates might be temperature dependent. As shown in Figs. 6 and 7, $G(H_2)$ changes with temperature. The change includes the effect of the change of phase of the reaction system.

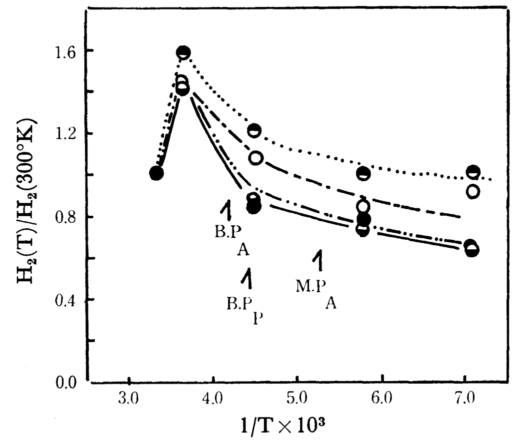

Fig. 6. Temperature-dependence of the formation of hydrogen in the mixture of C_3H_6–NH_3
●: (C_3H_6=100 mol%), ◒: (69.8%), ○: (50.0%), ◓: (30.0%)

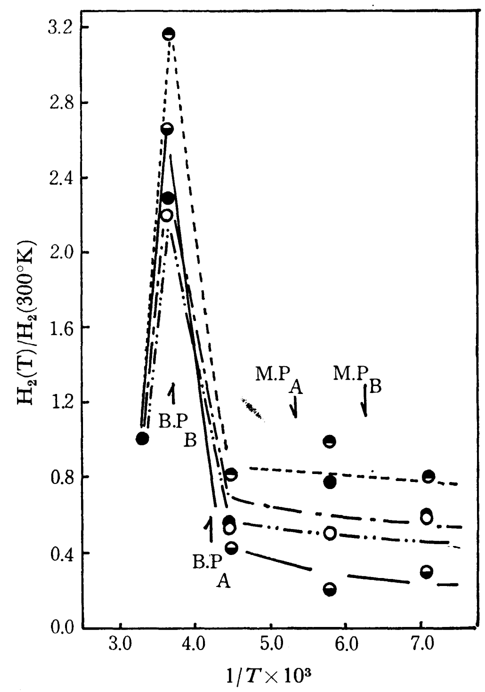

Fig. 7. Temperature-dependence of the formation of hydrogen in the mixture of C_4H_6–NH_3
◒: (C_4H_6=100 mol%), ○: (70%), ●: (50%), ◓: (30%)

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