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Mechanism of Hydrogen Formation in the Vapor Phase Radiolysis of Methanol

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The yields of isotopic hydrogen in the vapor phase radiolysis of deuterated methanol(CH_3OD) were found to be $G(H_2)=6.1$, $G(HD)=5.3$ and $G(D_2)=0.2$. The molecular yields of isotopic hydrogen were also determined by adding propylene as a radical scavenger, $G_M(H_2)=1.5$, $G_M(HD)=0.6$ and $G_M(D_2)\sim0$. In order to estimate the contribution of ionic species for the formation of hydrogen, the ion-molecule reaction of CH_3OD has also been investigated by using a mass spectrometer of the differential pumping type. The product ions, such as $(CH_3OCH_3CH_3OD)D^+$ or $(CH_3OD)_3D^+$, which were considered to be formed by the higher order ion-molecule reactions were observed. The mechanism of hydrogen formation was discussed on the basis of the ionic, the molecular and the radical mechanisms.

Although extensive studies of the radiolysis of methanol have been carried out in the liquid phase, little attention has been paid to vapor phase radiolysis.[1-4]

Baxendale *et al.*[1] calculated the yields of radiolysis products of CH_3OD from mass spectral data, considering the ion-molecule reactions. In the ion-molecule reactions of CH_3OD^+ and CH_2OD^+ with CH_3OD, they assumed that only H^+ transfer from CH_3OD^+ or CH_2OD^+ occurred to form CH_3ODH^+. However this is not true, because recent studies[5-7] on ion-molecule reactions of CH_3OD indicate that D^+ transfer also occurs from OD as well as H^+ transfer from CH_3 and CH_2. Prasil[8] also calculated the relative yields of products using the quasi-equilibrium theory in semiclassical approximation, considering direct excitation as well as ionization. However, the molecular yield of hydrogen thus obtained seemed to be larger compared with the experimental values.

In order to obtain information on the vapor phase radiolysis of methanol, the ion-molecule reaction of methanol was also studied by a conventional mass spectrometer.[5] However, it is very doubtful that the mechanism of ion-molecule reactions thus obtained can be applied to the mechanism of vapor phase radiolysis of methanol, since radiolysis is usually made at considerably higher pressure compared with that in the mass spectrometer.

The present investigation has been undertaken in order to elucidate the mechanism of hydrogen formation in the vapor phase radiolysis of CH_3OD.

The following experiments were carried out.

(1) The isotopic composition of hydrogen formed by γ-radiolysis was determined by mass spectrometric analysis, and the molecular yields of isotopic hydrogen were also estimated by adding propylene as a radical scavenger.

(2) The ion-molecule reaction of CH_3OD was studied in the pressure range of $6\times10^{-3}-1\times10^{-1}$ mmHg with a mass spectrometer of the differential pumping type.

Experimental

Materials. Deuterated methanol, CH_3OD, from Showa Denko Co. (99%) was used without further purification. Before irradiation, the sample was thoroughly degassed by the freezethaw method. Propylene and nitrous oxide from Takachiho Chem. Indust. Co. were used after purification by distillation.

Irradiation and Analysis. A glass reaction vessel of about 700 *ml* with a break-seal was used. Before introducing the sample into the reaction vessel, both the sample preparation system and the reaction vessel were flamed out several times in a vacuum. Deuterated methanol vapor of about 60 mmHg was irradiated at room temperature with a ^{60}Co source of 3000 Ci. The molecular yield of hydrogen was determined by

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[1] J. H. Baxendale and R. D. Sedgwick, *Trans. Faraday Soc.*, **57**, 2157 (1961).

[2] E. Lindholm and P. Wilmenius, *Arkiv Kemi*, **20**, 255 (1962).

[3] M. Meaburn and F. W. Mellows, *Trans. Faraday Soc.*, **61**, 1701 (1965).

[4] T. Ohma and H. Sakurai, This Bulletin, **40**, 1368 (1968).

[5] T. Yamamoto, Y. Shinozaki and G. Meshitsuka, *Mass Spectroscopy*, **12**, 93 (1964).

[6] P. Wilmenius and E. Lindholm, *Arkiv Physik*, **21**, 97 (1962).

[7] D. J. Hyatt, E. A. Dodman and M. J. Henchman, "Ion-Molecule Reactions in the Gas Phase," ed. by R. F. Gould, American Chemical Society Publications, Washington D. C. (1966), p. 131.

[8] Z. Prasil, *Collect. Czech. Chem. Commun.*, **31**, 3252 (1966).

adding a few percent propylene as a hydrogen atom scavenger. Dose rate was determined with nitrous oxide of 200 mmHg on the basis of $G(N_2)=10.0$.[9] Energy absorbed by methanol was calculated from the electron densities. The dose rate was approximately 3.3×10^{18} eV·g^{-1}·hr^{-1} and the total dose was $\sim10^{20}$ eV·g^{-1}.

After irradiation, the amount and composition of products volatile at liquid nitrogen temperature were determined by gas burette and mass spectrometric analysis.

Ion-Molecule Reaction. In order to investigate the ion-molecule reaction in the higher pressure range, a Hitachi mass spectrometer, Model RMU-5, was rearranged and equipped with an ion source of the differential pumping type. The relevant dimensions of the ion soruce are: electron beam hole 0.02 cm; ion exit slit 0.02 × 0.5 cm^2; repeller electrode - ion exit slit 0.31cm and center of electron beam - ion exit slit 0.25 cm. Electron bombardment was carried out at 70 eV. Pressure of the ionization chamber could not be measured directly, but was estimated from the pressure of the sample reservoir by the conventional method[10] using methane. The revised ion source made it possible to carry out experiment at the pressure of ionization chamber up to about 0.14 mmHg.

Results

Gamma Radiolysis. The G value of each isotopic hydrogen obtained with and without propylene in the system is shown in Table 1. The total yield of isotopic hydrogen G_{total}(hydrogen), is found to be 11.6. This value is somewhat higher than that obtained by Baxendale.[1] In contrast with the results in the liquid phase radiolysis, the yield of H_2 is higher than that of HD. The yield of D_2 is very small as shown in Table 1.

TABLE 1. OBSERVED YIELDS OF ISOTOPIC HYDROGEN

	$G(H_2)$	$G(HD)$	$G(D_2)$	G(Total)
Total yield	6.1	5.3	0.2	11.6
Molecular yield	1.5	0.6	~0	2.1

Addition of propylene as a hydrogen atom scavenger reduces the total hydrogen yield from G_{total}(hydrogen)$=11.6$ to G_{total}(hydrogen)$=2.1$, which corresponds to the molecular yield of isotopic hydrogen. The molecular yield of H_2 is about 2.5 times greater than that of HD, and the molecular yield of D_2 is negligibly small.

Ion-Molecule Reaction. In the pressure range of 0.006–0.02 mmHg, the relation between the ionization chamber pressure and the ion current fraction of each ion, $(i_j/\sum i_j)$, where i_j is the ion current for jth ion and $\sum i_j$ the total ion current, is shown in Fig. 1. We see that all primary ions decrease as the ionization chamber pressure increases. These primary ions are considered to decrease by either one of the ion-molecule reactions, such as proton or deuteron transfer, hydride ion transfer or charge transfer. On the other hand, as reported by Hyatt *et. al.*[7], $i_{CH_3OD_2^+}/i_{CH_3ODH^+}$ increases with the increase in the ionization chamber pressure. Table 2 shows the results obtained at the higher pressures up to 0.14 mmHg. At 0.14 mmHg, only a trace of CH_2OD^+, which is the most abundant primary ion at low pressure, is observed and the ratio $i_{CH_3OD_2^+}/i_{CH_3ODH^+}$ exceeds 10. We see that the primary ions and the lower order product ions decrease and the higher order product ions increase with the increase in pressure. The results

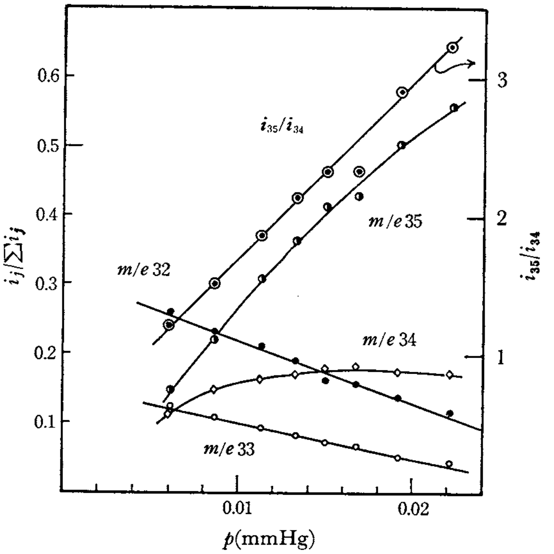

Fig. 1a

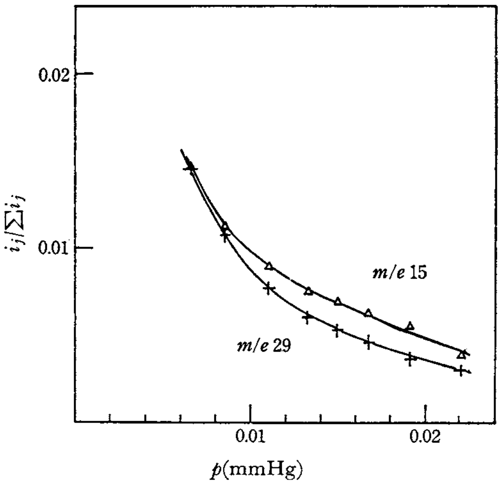

Fig. 1b

Fig. 1a, b. Relation between ionization chamber pressure and $i_j/\sum i_j$ or i_{35}/i_{34}.

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[9] F. T. Jones and T. J. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).

[10] C. E. Melton, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press, New York and London, (1963) p. 80.

indicate that the ion-molecule reactions occur successively to form the higher order product ions at a higher pressure. It is also clear that the deuteronated ions formed by the higher order ion-molecule reactions are much greater than the protonated ions. Munson[11] also observed the higher order product ions using CH_3OH and presented the mechanism of their formation.

Discussion

Ionic Mechanism. Primary processes in radiation chemistry are mostly caused by secondary electrons with energies less than 100 eV. A number of discussions for the ionic mechanism of radiolysis have been made on the basis of the results obtained by mass spectrometer at low pressure. As shown in Table 2, the higher order product ions, which do not appear in mass spectrum at low pressure, are observed remarkably at higher pressure, indicating that the contribution of these higher order product ions must be considered in the ionic mechanism of radiolysis. It can be assumed that fragment ions are formed from parent ion by the unimolecular decomposition in a much shorter time than collision time of parent ion with neutral molecule at the pressure employed in radiolysis experiments. Thus the abundance of ions formed primarily by the irradiation of ^{60}Co γ-rays should be the same as that in the usual mass spectrum. Table 3 shows the fragmentation processes and abundance of various ions in the mass spectrum of CH_3OD and the possible types of ion-molecule reactions. According to the types of ion-molecule reactions, these primary ions react with neighboring CH_3OD molecules to form the secondary ions, CH_3ODH^+ and $CH_3OD_2^+$. As the pressure increases, these secondary ions react further with CH_3OD molecules by the reactions such as.

TABLE 2. VARIATION OF RELATIVE ION CURRENT WITH IONIZATION CHAMBER PRESSURE

m/e	Ion	Relative ion current(%) Pressure (mmHg)		
		0.07	0.10	0.14
32	CH_2OD^+	4.1	0.7	0.2
34	CH_3ODH^+	9.4	5.5	3.2
35	$CH_3OD_2^+$	65.4	51.9	34.1
48	$(CHOCH_3)D^+$	9.6	11.9	9.7
67	$(CH_3OD)_2H^+$	1.0	1.6	3.3
68	$(CH_3OD)_2D^+$	10.1	26.2	36.1
81	$(CH_3OCH_3CH_3OD)D^+$	0.3	1.3	4.6
101	$(CH_3OD)_3D^+$	0.1	0.9	8.7

$$CH_3ODH^+ + CH_3OD \rightarrow CH_3OD + CH_3ODH^+ \qquad (1a)$$

$$\rightarrow CH_3OH + CH_3OD_2^+ \qquad (1b)$$

$$CH_3OD_2^+ + CH_3OD \rightarrow CH_3OD + CH_3OD_2^+ \qquad (2)$$

Secondary ion CH_3ODH^+ can transfer either a proton or a deuteron by reaction (1a) or (1b). Secondary ion $CH_3OD_2^+$ will not change its identity by reaction (2) since only a deuteron can be transferred. Therefore, the ratio $i_{CH_3OD_2^+}/i_{CH_3ODH^+}$ increases with the increase in the ionization chamber pressure. The ions, such as $(CH_3OCH_3)D^+$, $(CH_3OD)_2H^+$ and $(CH_3OD)_2D^+$, are formed by the following reactions.

$$CH_3ODH^+ + CH_3OD \rightarrow (CH_3OCH_3)D^+ + HDO \qquad (3)$$

$$CH_3OD_2^+ + CH_3OD \rightarrow (CH_3OCH_3)D^+ + D_2O \qquad (4)$$

$$CH_3ODH^+ + CH_3OD \rightarrow (CH_3OD)_2H^+ \text{ or } (CH_3ODCH_3OH)D^+ \qquad (5)$$

$$CH_3OD_2^+ + CH_3OD \rightarrow (CH_3OD)_2D^+ \qquad (6)$$

TABLE 3. FRAGMENTATION PROCESS AND ABUNDANCE IN THE MASS SPECTRUM OF CH_3OD AND POSSIBLE TYPE OF ION-MOLECULE REACTION

Fragmentation process[1]	Abundance[5] (%)	Type of ion-molecule reaction[5,9]
$CH_3OD + e \rightarrow CH_3OD^+ + 2e$	24.8	P, D
$\rightarrow CH_2OD^+ + H + 2e$	37.7	P, D
$\rightarrow CH_3O^+ + D + 2e$	2.9	P
$\rightarrow HCOD^+ + H_2 + 2e$	2.4	C
$\rightarrow COD^+ + H_2 + H + 2e$	4.5	D, H, d
$\rightarrow HCO^+ + H_2 + D + 2e$	16.1	P, H, d
$\rightarrow CO^+ + H_2 + HD + 2e$	1.6	H
$\rightarrow CH_3^+ + OD + 2e$	10.0	H

P : Proton transfer
H: Hydride ion transfer
d : Dissociative charge transfer
D: Deuteron transfer
C: Charge transfer

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[11] M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 5313 (1965).

From the fact that the higher order product ions, $(CH_3OCH_3CH_3OD)D^+$ and $(CH_3OD)_3D^+$, were also observed, it is reasonable to assume that the primary ions formed in the radiolysis are ultimately converted to deuteronated ions by successive ion-molecule reactions. These product ions recombine with electrons, and dissociate into D atoms, not H atoms, and products.

$$(CH_3OCH_3CH_3OD)D^+ + e \rightarrow D + \text{Products} \quad (7)$$

$$(CH_3OD)_3D^+ + e \rightarrow D + \text{Products} \quad (8)$$

D atom formed by reaction (7) or (8) reacts with CH_3OD and abstracts H atom from the methyl group of CH_3OD to give HD.

$$D + CH_3OD \rightarrow HD + CH_2OD \quad (9)$$

$$D + CH_3OD \rightarrow D_2 + CH_3O \quad (9')$$

The direct formation of molecular hydrogen (D_2) by neutralization reactions and the formation of D_2 by reaction, (9′), if any, are negligibly small, because of the very small observed value of $G(D_2)$. Furthermore it can not be considered that molecular hydrogen HD is formed preferentially by neutralization reactions.

Baxendale and Sedgwick[1] explained that a part of molecular hydrogen is produced from excited methanol molecule which is formed by the neutralization reaction of secondary ion, CH_3ODH^+,with electron. As shown in Table 2, higher order ions are produced by successive ion-molecule reactions. It may be reasonable to consider that hydrogen is not formed molecularly from the excited molecules by the neutralization reactions of these higher order ions with electrons. Therefore, hydrogen formed through ion-molecule reactions followed neutralization is considered to be only HD by the reactions (7), (8) and (9).

As shown in Table 3, the primary ions are also accompanied with atomic or molecular hydrogen. The yields (M_i/N) of isotopic hydrogen are shown in Table 4, where M_i is the number of molecules produced through ionization of CH_3OD and N is the number of ion pairs induced by irradiation. From these data, the total yield of isotopic hydrogen through ionization is estimated to be $M_i/N(H_2) = 0.67$ and $M_i/N(HD) = 1.21$. By the saturation current method, Ohma and Sakurai[4] obtained $M/N(H_2) = 3.00$ for the ionic yield of hydrogen from CH_3OH, where M is the number of hydrogen molecules produced. Combining $M/N(H_2) = 3.00$ with the observed $G_{total}(\text{hydrogen}) = 11.6$, the energy to produce an ion pair from methanol (W) is calculated to be 25.9 eV. Baxendale and Sedgwick obtained $W = 27.7$ eV on the assumption that molecular hydrogen was also produced by the decomposition of excited methanol molecule formed by the neutralization of $CH_3OH_2^+$ with electron. The yield of isotopic hydrogen through ionization, G_i, can then be estimated from the relation, $G_i(\text{hydrogen}) = 100/W \times [M_i/N(\text{hydrogen})]$, and $G_i(H_2) = 2.6$ and $G_i(HD) = 4.7$ were obtained.

Table 4. Yield of isotopic hydrogen calculated from data in Table 3

	H_2	HD	D_2
M_i/N	0.67	1.21	0
M_{i-m}/N	0.24_6	0.01_6	0
G_i	2.6	4.7	0
G_{i-m}	1.0	0.1	0

N: number of ion pair produced

M_i: number of isotopic hydrogen produced through the ionization of CH_3OD

M_{i-m}: number of isotopic hydrogen produced molecularly by the fragmentation of CH_3OD^+

G_i: G-value of isotopic hydrogen produced through the ionization of CH_3OD

G_{i-m}: G-value of isotopic hydrogen produced molecularly by the fragmentation of CH_3OD^+

G-values are calculated by the following equation using $W = 25.9$ eV.

$$G = \frac{100}{W} \times \frac{M}{N}$$

Molecular Mechanism. The observed molecular yields of hydrogen are $G_M(H_2) = 1.5$ and $G_M(HD) = 0.6$. On the other hand, as shown in Table 4, molecular yields by the fragmentation of CH_3OD^+ are $G_{i-m}(H_2) = 1.0$ and $G_{i-m}(HD) = 0.1$.

The fact that the value of $W = 25.9$ eV is more than twice the ionization potential(10.85 eV) suggests that directly excited CH_3OD molecule may well be formed by reaction (10) and that the excited molecule thus formed may give hydrogen by the molecular mechanism, reaction (11).

$$CH_3OD \rightsquigarrow CH_3OD^* \quad (10)$$

$$CH_3OD^* \rightarrow H_2,\ HD + \text{Formaldehyde} \quad (11)$$

The molecular yields of hydrogen formed by the dissociation of CH_3OD^*, $G_m(H_2)$ and $G_m(HD)$, can be estimated as

$$G_m(H_2) = \underset{1.5}{G_M(H_2)} - \underset{1.0}{G_{i-m}(H_2)} = 0.5$$

$$G_m(HD) = \underset{0.6}{G_M(HD)} - \underset{0.1}{G_{i-m}(HD)} = 0.5\,.$$

Porter and Noyes[12] investigated the photolysis ($\lambda < 200$ mμ) of CD_3OH vapor and obtained 80% HD and 20% H_2 as unscavengeable hydrogen. A similar result was also obtained by Hagege *et al.*[13] ($\lambda = 124$ and 185 mμ). If one considers that the excited molecules formed by radiolysis are the same as those formed by photolysis, the ratio of $\Phi(H_2)$ to $\Phi(HD)$ in the photolysis of CD_3OH must correspond to the ratio of $G_m(D_2)$ to $G_m(HD)$ in the radiolysis of CH_3OD. In the present investigation, $G_M(D_2)$ was found to be negligibly small, indicating that $G_m(D_2)$ is also negligible. There-

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[12] R. P. Porter and W. A. Noyes, Jr., *ibid.*, **81**, 2307 (1959).

[13] J. Hagege, S. Leach and C. Vermeil, *J. Chim. Phys.*, **62**, 736 (1965).

fore, it is clear that radiolysis and photolysis are quite different in the mechanism of hydrogen formation.

There is also some possibility that hot hydrogen atom may be a source of unscavengeable hydrogen, but at present no definite information concerning quantitative estimation has been achieved. However, the fact that $G_M(D_2)$ is negligibly small indicates that the contribution of hot hydrogen atom may not be so large.

Radical Mechanism. The observed total hydrogen yield, G_{total}(hydrogen)$=11.6$, can not be explained only by ionic and molecular mechanisms, because the sum of the yields by the two mechanisms, G(hydrogen)$=8.3$, is much smaller than the observed value. The difference can only be explained by assuming that hydrogen atoms formed by the dissociation of CH_3OD^* are also the precursors of hydrogen molecules. The calculated yields by the radical mechanism, $G_r(H_2)$ and $G_r(HD)$, are found to be 3.0 and 0.1 which indicates that reaction (11a) is more important than reaction (11b).

$$CH_3OD^* \rightarrow H + CH_2OD \qquad (11a)$$

$$CH_3OD^* \rightarrow D + CH_3O \qquad (11b)$$

The results obtained by direct photolysis[12,13] and by the mercury-photosensitized decomposition of methanol vapor[14] show that reaction(11b) is more important than reaction(11a). The difference between radiolysis and photolysis can be explained as follows. In the photolysis data, the energy of light applied was lower than the ionization potential of methanol molecule, but enough to excite methanol molecule electronically. The absorption band of methanol vapor is observed in the vacuum ultraviolet region λ_{max} 174 mμ, and attributed to the (n-σ^*) transition which corresponds to the excitation of the non-bonding electron of oxygen atom in methanol.[15] Therefore, the formation of hydrogen atom by the scission of O–H bond in the primary process is explained by the assumption that the excitation of methanol molecule by the absorption of ultraviolet light is limited to the oxygen atom of methanol molecule, and thus causes the scission of O–H bond of methanol molecule. In radiolysis, it is well known that most of the excited molecules are formed by the interaction of electrons. Thus, it is reasonable to consider that the induced excitation energy is not localized but distributed at random among methanol molecule. Therefore, the scission of C–H bond occurs more easily than that of O–H bond, because the bond energy of C–H is lower by about 10 kcal/mol than that of O–H.

TABLE 5. CALCULATED YIELDS OF ISOTOPIC HYDROGEN ON THE BASIS OF IONIC, MOLECULAR AND RADICAL MECHANISMS

	$G(H_2)$	$G(HD)$	$G(D_2)$
Ionic	2.6	4.7	—
Molecular	0.5	0.5	—
Radical	3.0	0.1	—
Observed	6.1	5.3	0.2

The yields are defined as follows :

Ionic : yields of isotopic hydrogen, formed molecularly as well as radically, through the ionization of CH_3OD

Molecular : yields of isotopic hydrogen formed molecularly by the dissociation of directly excited methanol molecule (CH_3OD^*)

Radical: yields of isotopic hydrogen formed radically by the dissociation of directly excited methanol molecule (CH_3OD^*)

The calculated yields of isotopic hydrogen in each radiolysis mechanism are summarized in Table 5.

The author wishes to thank Dr. Gisuke Meshitsuka and Dr. Yoshiharu Shinozaki for their useful discussions. The author is also indebted to Mr. Yukio Inokoshi for his assistance in the experimental works.

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[14] R. F. Pottie, A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **39**, 102 (1961). A. R. Knight and H. E. Gunning, *ibid.*, **39**, 1231 (1961).

[15] H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964).