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Hydrogen Formation in the Gas-Phase Radiolysis of C_2H_4-D_2O Mixtures

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The total hydrogen yields and their isotopic compositions have been measured in the gas-phase radiolysis of C_2H_4–D_2O mixtures at room temperature. A mixture of D_2O (<10 mol %) with a large amount of C_2H_4 was used to avoid the effect of the wall on the decomposition of D_2O. The contribution of thermal hydrogen atoms to the hydrogen formation may reasonably be excluded in this system. The kinetic treatment of D_2 and HD formation suggests the decomposition mechanism of D_2O. No important contribution of hot hydrogen atoms was observed. The yield of hydrogen from the D_2O formed by the unimolecular process, $G_{1D}=0.4$, was nearly equal to the molecular hydrogen yield reported previously.

In the radiolysis of pure water vapor, the hydrogen yield is very small.[1,2] The radiolysis in the presence of various organic additives, however, has shown a fairly large yield of hydrogen atoms.[3-9] The importance of excited hydrogen atoms in the physicochemical stage of the radiation effect on water vapor has been predicted by Platzman.[10] He suggested that such atoms might be electronically excited and pro-

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[1] R. Firestone, *J. Amer. Chem. Soc.*, **79**, 5593 (1957).

[2] A. R. Anderson, B. Knight, and J. A. Winter, *Trans. Faraday Soc.*, **62**, 359 (1966).

[3] J. H. Baxendale and G. P. Gilbert, *Discuss. Faraday Soc.*, **36**, 186 (1963).

[4] J. H. Baxendale and G. P. Gilbert, *J. Amer. Chem. Soc.*, **86**, 516 (1964).

[5] G. R. A. Johnson and M. Simic, *Nature*, **212**, 1570 (1966).

[6] J.Y. Yang and I. Marcus, *J. Amer. Chem. Soc.*, **88**, 1625 (1966).

[7] G. R. A. Johnson and M. Simic, *Nature*, **210**, 1356 (1966).

[8] G. R. A. Johnson and M. Simic, *J. Phys. Chem.*, **71**, 1118 (1967).

[9] G. R. A. Johnson and M. Simic, "The Chemistry of Ionization and Excitation," ed. by G. R. A. Johnson and G. Scholes, Taylor and Francis, London (1967), p. 211.

[10] R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

duced *via* excitation from superexcitation. Actually, the measurement of the Lyman and Balmer radiation has been made in the collisions of fast electrons on water vapor, in which the possible role of superexcited water molecules as important precursors of electronically-excited hydrogen atoms has been discussed.[11] The yield of superexcited water molecules has been theoretically estimated by Santer and Bednar.[12] In the radiation chemistry of water vapor, however, few experiments have been made to examine this hydrogen atom.[13]

Recently, in the radiolysis of various hydrocarbons, evidence has been presented of the important role of hydrogen atoms with excess energy, called "hot hydrogen atoms".[14] That is, bimolecular hydrogen formation in the radiolysis of olefins or paraffins with a radical and an electron scavenger has been interpreted in terms of the hydrogen atom abstraction by hot hydrogen atoms formed by direct excitation, which must at least partially involve superexcitation.

The present investigation has been made in order to examine the nature of hydrogen atoms produced in the radiolysis of water vapor.

Experimental

Research-grade ethylene supplied by the Takachiho Shoji Co. was condensed at 77 K and degassed several times before use. Gas-chromatographic analysis using a silica gel column showed a purity of more than 99.95%, most of the impurities consisted of ethane. Deuterium oxide (>99.8 D%) stored in a nitrogen atmosphere was used without further purification except for the usual degassing at 77 K.

Cylindrical glass vessels about 300 ml in volume and fitted with break-off seals were baked in air at about 400 °C and then evacuated at less than about 10^{-5} mmHg for several hours. After this treatment, the required amounts of deuterium oxide and ethylene were introduced into the vessel. The total pressure for each sample was about 300 mmHg.

The samples were irradiated by ^{60}Co γ-rays at room temperature. The dose rate was 5.2×10^{19} eV/g·hr, and the total dose was 5.2×10^{20} eV/g of ethylene. The dose rate was based on the yield of hydrogen from ethylene, using $G(H_2)=1.31$.[15]

After irradiation the samples were attached to a vacuum line and the seals were broken. The product gases noncondensable at 77 K were collected by means of a Toepler pump. The total hydrogen yield was determined by gas chromatography using a molecular sieve-5A column. The isotopic composition of hydrogen was determined by means of a Hitachi RMU-5 mass spectrometer.

Results and Discussion

In the radiolysis of water vapor the wall has a large effect on the hydrogen formation.[2] The hydrogen yield depends considerably on the cleanliness of the vessel surface. In our case, however, the partial pressure of water vapor is less than 10% of the total, which is about 300 mmHg and which is formed mainly by ethylene. The effect of the wall mentioned above may be of lesser importance for the hydrogen formation in this experiment.

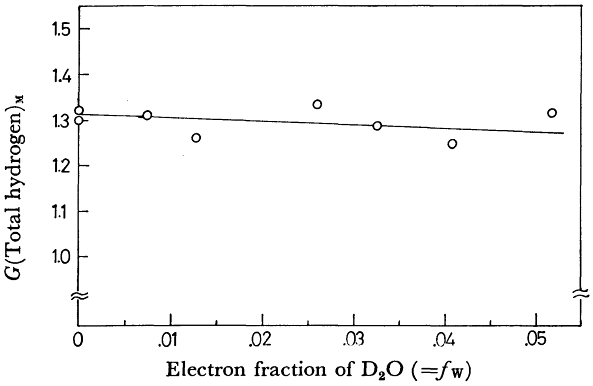

Fig. 1. Yields of hydrogen in the radiolysis of C_2H_4–D_2O mixtures.

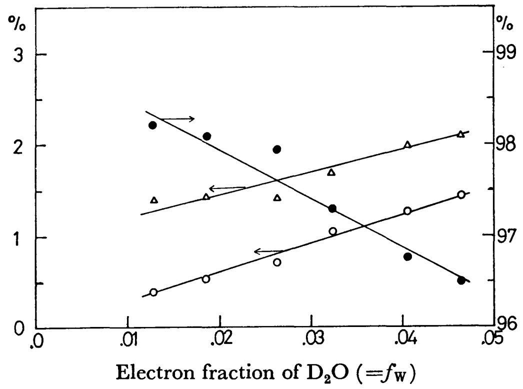

Fig. 2. The isotopic composition of hydrogen produced in the radiolysis of C_2H_4–D_2O mixtures.
●: H_2, △: HD, ○: D_2.

In Fig. 1, G(total hydrogen)$_M$, the number of hydrogen molecules formed per 100 eV of the energy absorbed by the C_2H_4–D_2O mixtures, is plotted against the electron fraction of D_2O ($=f_W$). G(total hydrogen)$_M$ decreases only a little with an increase in the D_2O concentration. Figure 2 shows the isotopic composition of the total hydrogen as a function of f_W. Both the D_2 and HD contents increase linearly with an increase in the f_W. By the extrapolation to zero concentration of D_2O, the D_2 content becomes zero, whereas the HD content has an intercept.

Now, let us consider the hydrogen formation from the C_2H_4–D_2O mixtures. In the first place, the contribution of thermal hydrogen atoms will be considered. Ethylene has a high reactivity for them[16] and the addition reaction (1) may be dominant compared with the abstraction reactions, (2) and (3):

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[11] D. A. Vroom and F. J. de Heer, *J. Chem. Phys.*, **50**, 1883 (1969).

[12] I. Santer, "Progress and Problems in Contemporary Radiation Chemistry," Vol. 1, ed. by J. Teply (1971), p. 51 and references cited therein.

[13] R. S. Dixson, *Radiation Res. Rev.*, **2**, 237 (1970).

[14] Y. Hatano and S. Shida, *J. Chem. Phys.*, **46**, 4784 (1967); Y. Hatano, S. Shida, and M. Inokuti, *ibid.*, **48**, 940 (1968); Y. Hatano, S. Shida, and S. Sato, This Bulletin, **41**, 1120 (1968); Y. Hatano, *ibid.*, **41**, 1126 (1968).

[15] G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

[16] K. R. Jennings and R. J. Cvetanovic, *ibid.*, **35**, 1233 (1961).

$$\text{H(or D)} + C_2H_4 \longrightarrow C_2H_5\text{(or } C_2H_4D) \qquad (1)$$

$$\text{H(or D)} + C_2H_4 \longrightarrow H_2\text{(or HD)} + C_2H_3 \qquad (2)$$

$$\text{H(or D)} + D_2O \longrightarrow \text{HD (or } D_2) + OD \qquad (3)$$

Thus, the contribution of the abstraction reaction of thermal hydrogen atoms to hydrogen formation must be excluded. The ethyl radicals in Reaction (1) are vibrationally excited at first and possibly dissociate again. Under these experimental conditions, however, such as a total pressure of about 300 mmHg at room temperature, these excited radicals are changed predominantly to thermal ethyl radicals by collisional deactivation and are not responsible for the hydrogen formation. Thus, thermal hydrogen atoms may be unimportant for the hydrogen formation in this system.

Secondly, the possibility of hydrogen formation through various ion-molecule reactions may also be eliminated on the basis of the following discussion.[17)]

Positive-charge or proton transfer from $C_2H_4^+$ to D_2O and hydrogen-atom transfer from D_2O to $C_2H_4^+$ seems to be energetically impossible.

$$C_2H_4^+ + D_2O \longrightarrow C_2H_4 + D_2O^+; \quad \Delta H = 47\text{ kcal/mol} \qquad (4)$$

$$C_2H_4^+ + D_2O \longrightarrow C_2H_3 + HD_2O^+; \quad \Delta H = 11\pm4\text{ kcal/mol} \qquad (5)$$

$$C_2H_4^+ + D_2O \longrightarrow C_2H_4D^+ + OD; \quad \Delta H = 32\pm4\text{ kcal/mol} \qquad (6)$$

However, secondary ions which are known to exist in the high-pressure mass spectrometry of ethylene[19)] can possibly undergo proton transfer to D_2O to produce D_2HO^+.

The formation of D_2O^+ *via* the direct effect of ionizing radiation on D_2O will invoke the following ion-molecule reactions:

$$D_2O^+ + C_2H_4 \longrightarrow D_2O + C_2H_4^+; \quad \Delta H = -47\text{ kcal/mol} \qquad (7)$$

$$D_2O^+ + C_2H_4 \longrightarrow OD + C_2H_4D^+; \quad \Delta H = -15\pm4\text{ kcal/mol} \qquad (8)$$

$$D_2O^+ + C_2H_4 \longrightarrow D_2HO^+ + C_2H_3; \quad \Delta H = -37\pm4\text{ kcal/mol} \qquad (9)$$

$$D_2O^+ + D_2O \longrightarrow D_3O^+ + OD; \quad \Delta H = -22\pm4\text{ kcal/mol} \qquad (10)$$

Even if D_3O^+ was present in this system, it seems that, on energetic grounds, we can exclude the possibility of the hydrogen formation through ion-molecule reactions (11) and (12) between D_3O^+ and C_2H_4.

$$D_3O^+ + C_2H_4 \longrightarrow D + D_2O + C_2H_4^+; \quad \Delta H = 94\pm4\text{ kcal/mol} \qquad (11)$$

$$D_3O^+ + C_2H_4 \longrightarrow HD + D_2O + C_2H_3^+; \quad \Delta H = 68\pm6\text{ kcal/mol} \qquad (12)$$

The possibility of the hydrogen formation through ion-molecule reactions between D_2HO^+ and C_2H_4 may similarly be excluded.

The HD formation *via* the neutralization of $C_2H_4D^+$ in Reaction (8) might be considered, but such a possibility may be excluded because of the experimental finding in the radiolysis of ethylene that hydrogen formation is not affected by the addition of electron scavengers. Such a neutralization would produce thermal hydrogen atoms to be scavenged by ethylene itself.

The hydrogen observed in this experiment might be formed by the molecular detachment from C_2H_4 and D_2O, or by the hydrogen-atom-abstraction reaction of the hot hydrogen atoms, H′ and D′, produced from C_2H_4 and D_2O respectively *via* direct excitation. Hot hydrogen atoms might also be produced *via* the neutralization of D_3O^+ or D_2HO^+ with an electron.[20)] In the next scheme, however, this possibility is excluded; it will be discussed later.

$$C_2H_4 \rightsquigarrow H_2(+\cdots) \qquad G_{1H} \qquad (13)$$

$$ \rightsquigarrow H'(+\cdots) \qquad G_{2H} \qquad (14)$$

$$D_2O \rightsquigarrow D_2(+\cdots) \qquad G_{1D} \qquad (15)$$

$$ \rightsquigarrow D'(+\cdots) \qquad G_{2D} \qquad (16)$$

$$H' + C_2H_4 \longrightarrow H_2 + C_2H_3 \qquad k_1 \qquad (17)$$

$$H' + D_2O \longrightarrow HD + OD \qquad k_2 \qquad (18)$$

$$D' + C_2H_4 \longrightarrow HD + C_2H_3 \qquad k_3 \qquad (19)$$

$$D' + D_2O \longrightarrow D_2 + OD \qquad k_4 \qquad (20)$$

Assuming the energy absorbed by each component in a mixture of C_2H_4 and D_2O to be proportional to the electron fraction of C_2H_4 and D_2O, one can estimate the yield of HD on the basis of the amount of energy absorbed in the mixture:

$$G(\mathrm{HD})_\mathrm{M} = G_{2\mathrm{H}}(1-f_\mathrm{w})\frac{1.6f_\mathrm{w}k_2}{(1-f_\mathrm{w})k_1+1.6f_\mathrm{w}k_2} + G_{2\mathrm{D}}f_\mathrm{w}\frac{(1-f_\mathrm{w})k_3}{(1-f_\mathrm{w})k_3+1.6f_\mathrm{w}k_4} \qquad (\mathrm{I})$$

Similarly, the yields of D_2 and H_2 are given, respectively, by:

$$G(\mathrm{D_2})_\mathrm{M} = G_{1\mathrm{D}}f_\mathrm{w} + G_{2\mathrm{D}}f_\mathrm{w}\frac{1.6f_\mathrm{w}k_4}{(1-f_\mathrm{w})k_3+1.6f_\mathrm{w}k_4} \qquad (\mathrm{II})$$

$$G(\mathrm{H_2})_\mathrm{M} = G_{1\mathrm{H}}(1-f_\mathrm{w}) + G_{2\mathrm{H}}(1-f_\mathrm{w})\frac{(1-f_\mathrm{w})k_1}{(1-f_\mathrm{w})k_1+1.6f_\mathrm{w}k_2} \qquad (\mathrm{III})$$

Now, assuming that $k_2/k_1 = k_4/k_3$ $(=\alpha)$, we obtain the following equations:

[17)] The exothermic direction of the processes is examined assuming the following heats of formation;[18)]
$\Delta H_f(C_2H_4) = 12.5$ kcal/mol, $\Delta H_f(H_2O) = -57.8$ kcal,
$\Delta H_f(C_2H_4^+) = 255$ kcal/mol, $\Delta H_f(H_2O^+) = 232$ kcal/mol,
$\Delta H_f(C_2H_5^+) = 220\pm4$ kcal/mol, $\Delta H_f(H_3O^+) = 143\pm4$ kcal/mol,
$\Delta H_f(C_2H_3^+) = 281\pm2$ kcal/mol,
$\Delta H_f(H) = 52.1$ kcal/mol, $\Delta H_f(OH) = 9.3$ kcal/mol,
$\Delta H_f(H_2) = 0$, and $\Delta H_f(C_2H_3) = 65$ kcal/mol.
It is also assumed that no isotope effect exists.

[18)] J. L. Beauchamp and S. E. Buttrell Jr., *J. Chem. Phys.* **48**, 1783 (1968).

[19)] P. Kebarle, R. M. Haynes, and S. Searles, "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series 58, American Chemical Society, Washington, D. C. (1966), p. 210.

[20)] It has already been suggested that D_2 or HD may not be formed directly *via* neutralization of D_3O^+ or D_2HO^+ with an electron.[7)]

$$\frac{(1-f_w)f_w}{G(\mathrm{HD})_M} = \frac{1}{1.6G_{2H}\alpha+G_{2D}} + \frac{1.6\alpha-1}{1.6G_{2H}\alpha+G_{2D}} \times f_w \quad (\mathrm{I'})$$

$$\frac{G(\mathrm{D_2})_M}{f_w} = G_{1D} + 1.6G_{2D}\alpha f_w \quad (\mathrm{II'})$$

$$\frac{G(\mathrm{H_2})_M}{1-f_w} = (G_{1H}+G_{2H}) - 1.6G_{2H}\alpha f_w \quad (\mathrm{III'})$$

where Eqs. (II)′ and (III)′ apply to the case of $f_w \ll 1$. The (II)/(I) ratio gives;

$$\frac{G(\mathrm{D_2})_M(1-f_w)}{G(\mathrm{HD})_M} = \frac{G_{1D}}{1.6G_{2H}\alpha+G_{2D}} + \frac{1.6\alpha(G_{1D}+G_{2D})-G_{1D}}{1.6G_{2H}\alpha+G_{2D}} \times f_w \quad (\mathrm{IV})$$

Plots of the left-hand side of these equations, (I)′, (II)′, (III)′, and (IV), against f_w should give straight lines. The intercepts and the slopes of these lines will give G_{1H}, G_{2H}, G_{1D}, G_{2D}, and α. They are shown in Figs. 3 and 4.

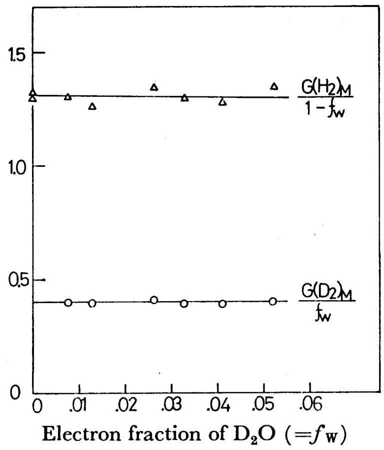

Fig. 3. $G(\mathrm{H_2})_M/(1-f_W)$ and $G(\mathrm{D_2})_M/f_W$ as a function of f_W.

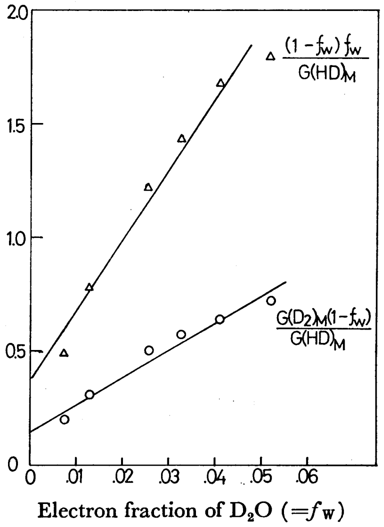

Fig. 4. $(1-f_W)f_W/G(\mathrm{HD})_M$ and $G(\mathrm{D_2})_M(1-f_W)/G(\mathrm{HD})_M$ as a function of f_W.

The yield of unimolecular hydrogen from C_2H_4, $G_{1H}=1.28$. The yield of the hot hydrogen atom from C_2H_4, $G_{2H}=0.03\pm0.01$. The yield of unimolecular hydrogen from D_2O, $G_{1D}=0.4$. The yield of the hot hydrogen atom from D_2O, $G_{2D}=0.0\pm0.1$. The value of α is nearly equal to 50.

These results apparently do not show that hot hydrogen atoms have an important role in this system. The conclusion does not necessarily follow, however, that they are not formed in the radiolysis of pure water vapor, where a fairly large amount of hydrogen atoms, $G(\mathrm{H})\cong 8$, has already been detected and divided into the following two kinds in a ratio of 3 to 5; hydrogen atoms formed *via* the neutralization process and those formed *via* direct excitation.[5,7,8] The above experimental results show that at least the latter kind of hydrogen atoms may not be hot. To describe the former, the possibility of the formation of H′ or D′ *via* the neutralization of D_3O^+ or D_2HO^+ mentioned above must be discussed here. By including this possibility in the above schemes (13)—(20) one may not easily establish the kinetic equations as (I)—(III). The yields of hot hydrogen atoms may not easily be estimated on the basis of the amount of the energy absorbed in each component. Similar experiments have been undertaken in the presence of 0.5 mol % SF_6, where the possibility of the above neutralization processes may reasonably be excluded. The same kinetic treatment as Eqs. (I)—(III) leads to exactly the same results for G_{1H}, G_{2H}, G_{1D}, G_{2D} as those obtained in the absence of SF_6.[21] On the basis of this fact, it seems that, the possibility of the formation of D′ or H′ *via* neutralization is not large. The hydrogen atoms formed *via* neutralization, however, can not be completely described; further investigations will be required.

A hot hydrogen atom here corresponds to the precursor of the bimolecular formation of hydrogen, which is non-scavengeable by ethylene. If a hot hydrogen atom reacts with ethylene such as:

$$\mathrm{D'} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_3D} + \mathrm{H}$$

to form a thermal hydrogen atom which is scavenged by ethylene itself, the yield of hot hydrogen atoms estimated here will indicate the lower limit.

The value of $G_{1D}=0.4$ is nearly equal to the "molecular" hydrogen yield, which is unaffected by an electron scavenger.[2,4–6,8,22] The most reasonable process for the formation of "molecular" hydrogen is the molecular detachment of hydrogen from the excited state formed *via* direct excitation.

The authors wish to thank Professor Shoji Shida and Dr. Satoshi Takao for their valuable suggestions.

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[21] The value of α is nearly half of that in the absence of SF_6. The value of α itself and the decrease of α by the addition of SF_6 may not reasonably be explained here.

[22] A. R. Anderson, B. Knight, and J. A. Winter, *Nature*, **201**, 1026 (1964).