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Radiolysis of Methylcyclohexane. I. Effects of Temperature and Electron Scavengers on Hydrogen Formation

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The effects of temperature and electron scavengers on the hydrogen yield in the radiolysis of methylcyclohexane have been investigated by conventional kinetic techniques. The G value for hydrogen formation from pure methylcyclohexane varied from 4.9 to 4.4 in the range from room temperature to liquid nitrogen temperature. In the iodobenzene-methylcyclohexane system, the decrease in hydrogen yield was equal to the yield of benzene produced within experimental error. It is concluded that the benzene is formed through H atom abstraction from the solvent molecules by phenyl radicals which are formed by dissociative electron attachment to iodobenzene and that the benzene yield indicates the scavenged electron yield. Furthermore, a kinetic treatment for electron scavenging in the glassy state was presented. In the N_2O-methylcyclohexane system, it was found that the ratio of the nitrogen yield, $G(N_2)$, to the decrease in hydrogen yield, $\Delta G(H_2)$, is 2 in the temperature range from room temperature to -140°C, 1 at -160°C, and increases from 1 to 4 with increasing N_2O concentration at -196°C, respectively.

The mechanism of radiolysis at -196°C has been investigated mainly by physical methods such as ESR and optical absorption measurements but rarely by chemical methods which involve product analysis. Since it is difficult to apply information obtained by physical methods at -196°C directly to the mechanism of radiolysis at room temperature, it seems useful to get information by chemical methods at -196°C. If both physical and chemical methods are applied to the same system, it can be expected that deeper understanding of the radiolysis mechanism will be obtained. For this purpose we have made a study of the radiolysis of methylcyclohexane at room temperature, -196°C, and several temperatures between room temperature and -196°C. Hitherto, the radiolysis of methylcyclohexane has been studied in the liquid(1-3) and gas phases,(4,5) but not in the glassy state at -196°C.

We studied the effects of temperature on the hydrogen yield in γ-irradiated pure methylcyclohexane, N_2O-methylcyclohexane, and iodobenzene-methylcyclohexane systems. It is well known that organic halides scavenge an electron to yield a halogen anion and a radical.(6,7)

$$RX + e^- \rightarrow R\cdot + X^- \qquad (1)$$

In the case of iodobenzene, the phenyl radical was not detected by ESR(8) in γ-irradiated organic glass at -196°C. This fact indicates that the phenyl radical in hydrocarbon glass abstracts an H atom from the solvent molecule even at -196 °C.(8) Nitrous oxide has extensively been used as an electron scavenger in irradiated gaseous,(5,9-12) liquid,(13-17) and solid(18) hydrocarbons. In this work, an attempt is made to estimate the scavenged electron yield in liquid and glassy methylcyclohexane using iodobenzene and nitrous oxide as electron scavengers and the mechanism of electron scavenging in the glassy state as well as the liquid state is considered.

Experimental

Materials. Tokyo-Kagaku-Seiki standard pure 99.9 % methylcyclohexane was used partly as received and

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17) R. A. Holroyd, *J. Phys. Chem.*, **72**, 759 (1968).
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partly after purification. Being passed through a silica gel column, methylcyclohexane was dried over calcium hydride *in vacuo* until bubbles of hydrogen gas could not be seen. Then the methylcyclohexane was transferred by vacuum distillation to a glass tube coated with a sodium mirror to remove water, passed through soda-lime which had been thoroughly dried and degassed in order to remove carbon dioxide, transferred to another glass tube with a break-seal by vacuum distillation and sealed off. The difference between the results obtained with methylcyclohexane with and without purification was negligible.

Tokyo-Kasei extra pure iodobenzene was passed through a silica gel column, and distilled *in vacuo*. The middle fraction was used. Takachiho-Shoji Co. pure reagent N_2O (99.9%) was used as received.

Sample Preparation. Amounts of methylcyclohexane and iodobenzene were measured volumetrically. Usually 1 m*l* of methylcyclohexane was used. Solutions in irradiation glass cells (equipped with a break-seal and usually 2 m*l*) were degassed by the freeze-pump-thaw technique until bubbles were hardly observed and then sealed off. Nitrous oxide was introduced into a bulb of known volume to the desired pressure and then condensed into the irradiation cell.

Irradiation. A 3000 Ci ^{60}Co source was used for irradiation. The doses used are shown in Table 1.

TABLE 1. DOSES AT VARIOUS IRRADIATION TEMPERATURES

Irradiation temperature	Dose
Room temperature	3.06×10^{20} eV/g
Dry ice - ethanol temperature	3.19×10^{20} eV/g
−123°C	7.99×10^{19} eV/g
−140°C	7.99×10^{19} eV/g
−160°C	2.86×10^{19} eV/g
−196°C	2.75×10^{20} eV/g

The dose rate was determined by Fricke dosimetry with nitrogen saturated ($G(\mathrm{Fe}^{3+})=8.07$). Irradiations were performed at room temperature (20°C), dry ice-ethanol temperature, and liquid nitrogen temperature. In addition, the experiments were performed at −123, −140, and −160°C. To keep the sample at −123 and −140°C slushy ethanol and ethanol - *n*-propanol mixture, chilled by mixing with liquid nitrogen, were used respectively. The experiments at −160°C were performed by blowing nitrogen vapor from liquid nitrogen against the samples. Blowing was controlled automatically to keept the temperature within ±2.5°C. These temperatures were measured with a chromel-alumel thermocouple during irradiation to be −123±2.5, −140±5, and −160±2.5°C, respectively.

Analysis. Gaseous products not condensable at liquid nitrogen temperature were collected by a Toepler pump and determined the volume by a gas burette. Then the gas was circulated about 20 cycles through a cupric oxide furnace heated at 220—260°C and a liquid nitrogen trap to convert hydrogen into water. The residual gas was recollected and determined the volume again. Benzene was analyzed by a Hitachi-K53 gas chromatograph with FID using a column of *n*-hexatriacontane (4 mm×2 m).

Results

Pure Methylcyclohexane. The *G* value of hydrogen from pure methylcyclohexane depended little upon the irradiation temperature and amounted to 4.9 at room temperature and 4.4 at −196°C. The *G* value at room temperature agrees with Freeman's value.1) There are no previous data on the *G* value at −196°C.

Iodobenzene - Methylcyclohexane System. The *G* values for hydrogen and benzene produced from mixtures of methylcyclohexane and iodobenzene irradiated at room temperature and −196°C are shown in Figs. 1 and 2, respectively. At both temperatures, $G(H_2)$ decreased with

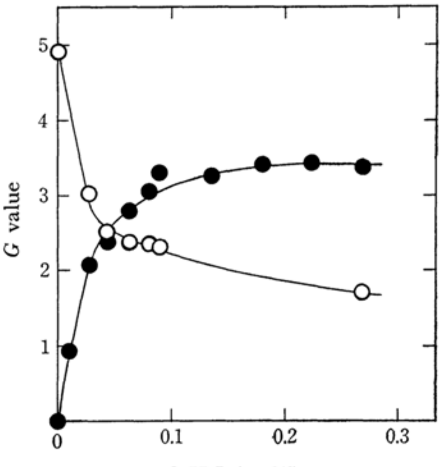

Fig. 1. Yields of hydrogen and benzene from the iodobenzene-methylcyclohexane system irradiated at room temperature.
○, $G(H_2)$; ●, $G(C_6H_6)$

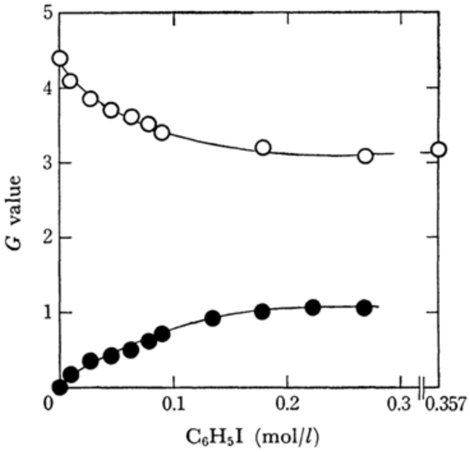

Fig. 2. Yields of hydrogen and benzene from the iodobenzene-methylcyclohexane system irradiated at −196°C.
○, $G(H_2)$; ●, $G(C_6H_6)$

increasing iodobenzene concentration more effectively than in N_2O-methylcyclohexane systems which will be described later on. This seems to indicate that iodobenzene scavenges electrons more effectively than N_2O both in the liquid and glassy states. On the other hand, $G(C_6H_6)$ increases with increasing iodobenzene concentration. Further it should be noted that the decrease in hydrogen yield is equal to the increase in benzene yield at any iodobenzene concentration within experimental error. This result indicates that one molecule of benzene is produced by quenching one precursor of hydrogen.

N_2O-Methylcyclohexane System. The yields of hydrogen and nitrogen produced from mixtures of methylcyclohexane and N_2O irradiated at room temperature, dry ice - ethanol temperature and $-196°C$ are shown in Figs. 3, 4 and 5, respectively. The G values of hydrogen and nitrogen from pure methylcyclohexane and methylcyclohexane containing 0.3 M of N_2O irradiated at various temperatures are shown in Fig. 6. The hydrogen yield from methylcyclohexane containing 0.3 M of N_2O was nearly constant in the range from room temperature to $-140°C$, changed from 2.5 to 3.8 (G unit) at a temperature between -140 to $-160°C$, and remained constant in the temperature range from -160 to $-196°C$. These results seem to indicate that the efficiency of electron scavenging in these systems changes significantly at a temperature between -140 to $-160°C$.

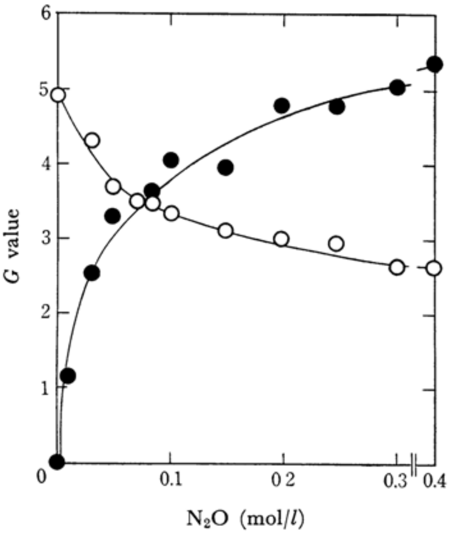

Fig. 3. Yields of hydrogen and nitrogen from the N_2O-methylcyclohexane system irradiated at room temperature.
○, $G(H_2)$; ●, $G(N_2)$

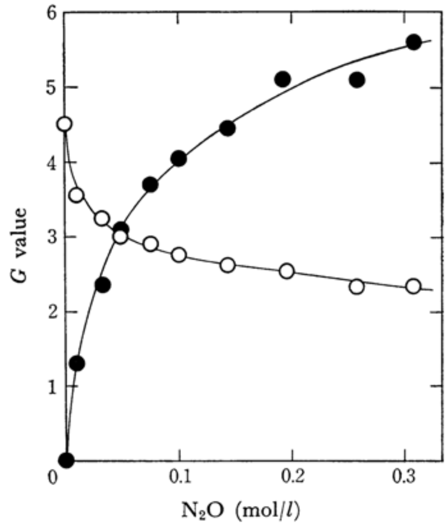

Fig. 4. Yields of hydrogen and nitrogen from the N_2O-methylcyclohexane system irradiated at dry ice-ethanol temperature.
○, $G(H_2)$; ●, $G(N_2)$

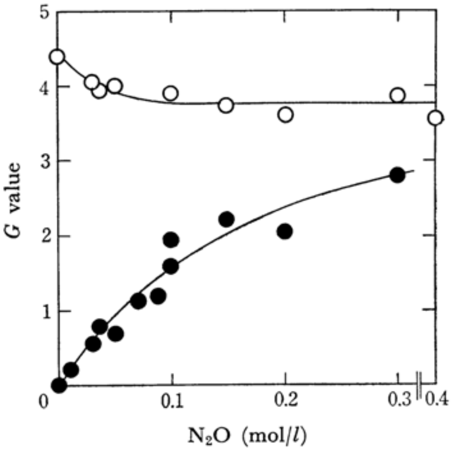

Fig. 5. Yields of hydrogen and nitrogen from the N_2O-methylcyclohexane system irradiated at $-196°C$.
○, $G(H_2)$; ●, $G(N_2)$

In the range from room temperature to $-140°C$, the following relationship holds between the nitrogen yield and the decrease in hydrogen yield at any N_2O concentration,

$$G(N_2) = 2\Delta G(H_2) \tag{2}$$

Such a relationship has been reported by other workers for the radiolysis of cyclohexane at room temperature.$^{15,16)}$ However, at $-196°C$ the ratio of the nitrogen yield to the decrease in hydrogen yield increased from 1 to about 4 with increasing N_2O concentration.

$$G(N_2)/\Delta G(H_2) = 1\text{—}4 \tag{3}$$

The mechanism of nitrogen formation from the mixtures of methylcyclohexane and N_2O in the range from room temperature to $-140°C$ differs apparently from that at $-196°C$. Furthermore, at $-160°C$ the ratio, $G(N_2)/\Delta G(H_2)$, was 1 at N_2O concentration of 0.3 M.

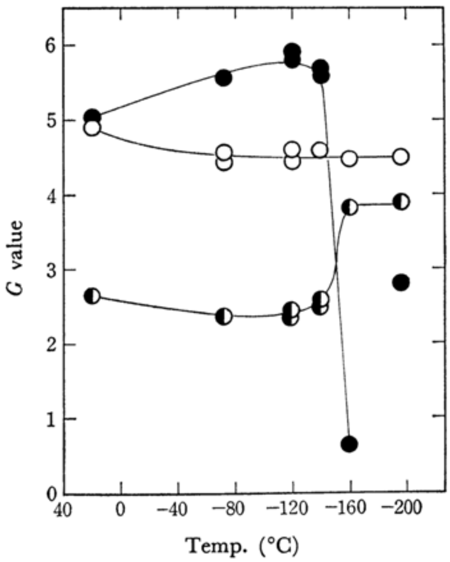

Fig. 6. Yields of hydrogen and nitrogen at various temperature.
○, $G(H_2)$ from pure methylcyclohexane; ◐, $G(H_2)$ from methylcyclohexane containing 0.3 M N_2O; ●, $G(N_2)$ from methylcyclohexane containing 0.3 M N_2O.

Discussion

Iodobenzene - Methylcyclohexane System. As is shown in Figs. 1 and 2, the hydrogen yield decreases and the benzene yield increases with increasing iodobenzene concentration. Therefore it is considered that iodobenzene scavenges electrons to produce I^- and the phenyl radical, the latter of which immediately abstracts a hydrogen atom from the solvent molecule (methylcyclohexane) to form benzene.[8,19]

$$\mathrm{MCH} \rightsquigarrow \mathrm{MCH^+} + e^- \tag{4}$$

$$\mathrm{MCH^+} + e^- \rightarrow H_2 + \text{residue} \tag{5}$$

$$C_6H_5I + e^- \rightarrow C_6H_5\cdot + I^- \tag{6}$$

$$C_6H_5\cdot + \mathrm{MCH} \rightarrow C_6H_6 + \mathrm{MCH}\cdot \tag{7}$$

Hydrogen atom abstraction from hydrocarbons by phenyl radicals was previously reported by Bennet *et al.*[19] Our experimental results also support the mechanism described above. If benzene is produced by Reactions (6) and (7), the decrease in hydrogen yield must be equal to the yield of electrons scavenged by iodobenzene and consequently equal to the benzene yield.

$$\Delta G(H_2) = G(C_6H_6) \tag{8}$$

It was found that this relationship holds both in the liquid and glassy states (Figs. 1 and 2). Thus it is concluded that the benzene yield corresponds to the scavenged electron yield. The limiting G value of benzene formation in methylcyclohexane glass at −196°C is about 1.1 which is in good agreement with $G(CH_3\cdot)$ in 3MP and MCH glasses containing CH_3I reported by Shirom and Willard.[20] It should be noted that iodobenzene may be used to measure the scavenged electron yield by the yield of benzene produced.

We now consider the kinetics of electron scavenging. Recently a kinetic treatment of electron scavenging in liquids has been presented by Freeman.[21] In the present treatment the probability of electron scavenging by solute in liquid methylcyclohexane is quoted from that calculated by Freeman. We have calculated the probability of electron scavenging in the glassy state at −196°C by extending Freeman's treatment. In these calculations the following assumptions are made: (i) In the glassy state at −196°C, the mobility of positive ions and the diffusion constant of scavenger (iodobenzene) are negligibly small compared with those of electrons, *i. e.*,

$$u_+ \ll u_- \quad \text{and} \quad D_s \ll D_- \tag{9}$$

where u_+ and u_- are the mobility of positive ion and electron respectively, and D_s and D_- are the diffusion constant of iodobenzene and an electron, respectively. In other words, electrons in the glassy state are treated as "quasifree" electrons,*[1] while electrons in the liquid state are treated as "solvated" electrons. (ii) The following equation is used:

$$u/D = \boldsymbol{k}T/e \tag{10}$$

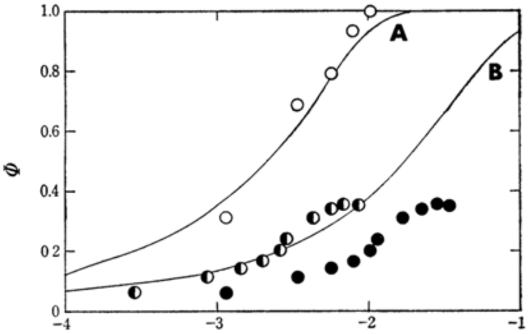

Fig. 7. Probability of electron scavenging in methylcyclohexane.
N_s, mole fraction of iodobenzene; A, calculated curve at room temperature; B, calculated curve at −196°C; ○, observed probability, $G(e^-)_s/G(e^-)_0$, at room temperature, $G(e^-)_0=3$; ●, observed probability at −196°C; ◐, observed probability, assuming aggregation, at −196°C.

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[19] J. E. Bennett, B. Mile and A. Thomas, *Proc. Roy. Soc.*, **293**, 246 (1966).

[20] M. Shirom and J. E. Willard, *J. Chem. Phys.*, **47**, 286 (1967).

[21] G. R. Freeman, *ibid.*, **46**, 2822 (1967).

*[1] The term quasifree electrons was used as those neither trapped nor solvated in rigid matrices.

where k is Boltzmann constant, T is the absolute temperature, and e is the charge on an electron. (iii) In the glassy state at $-196°C$, the initial separation distances between positive ions and electrons may be reduced to 70% of those in the liquid state at room temperature, since the density of the medium at $-196°C$ is 1.4 times that at room temperature.

The calculated curve for the probability of electron scavenging in methylcyclohexane at room temperature (quoted from Freeman's results) and that at $-196°C$ calculated here are shown in Fig. 7. The experimental values are also plotted in Fig. 7. In the liquid state at room temperature, the probabilities of electron scavenging obtained by the experiments are in good agreement with the calculated ones, but those in the glassy state at $-196°C$ are a little lower than the calculated results. The reason for this may be explained by assuming aggregation of iodobenzene molecules in nonpolar solvents. Aggregation of organic halides in hydrocarbon glasses has also been suggested by Willard *et al.*[22] and Hamill *et al.*[23] If iodobenzene molecules aggregate in methylcyclohexane glass, the effective concentration of iodobenzene would be lower than the apparent concentration. Assuming the effective concentration to be a quarter of the apparent concentration, the probabilities of electron scavenging were recalculated and plotted in Fig. 7. As is shown in Fig. 7, if it is assumed that three or four iodobenzene molecules aggregate, the probability of electron scavenging obtained by the experiments is in fairly good agreement with the calculated curve. Since the encounter efficiency, f_-, at $-196°C$ is expected to be smaller than 1, the calculated curve probably shows the maximum probability of electron scavenging. Thus it is concluded that electrons in rigid matrices at $-196°C$ may be treated as "quasifree" electrons, while electrons in the liquid state can be treated as "solvated" electrons.[21]

N_2O-Methylcyclohexane System. Nitrous oxide scavenges electrons ejected from γ-irradiated methylcyclohexane to give N_2 and O^- and therefore causes the decrease in hydrogen yield.

$$N_2O + e^- \rightarrow N_2 + O^- \qquad (11)$$

The ratio of the nitrogen yield to the decrease in hydrogen yield indicates that nitrogen is not formed only by single electron attachment process (Reaction (11)) except at $-160°C$. The other mechanisms of nitrogen formation than the single electron attachment have been proposed by some workers; (i) O atom abstraction from N_2O molecule by O^-,[9] (ii) chain reactions initiated by H atom abstraction from solvent molecules by O^-,[5] (iii) energy transfer from excited solvent molecules to nitrous oxide molecules.[17] However, at $-196°C$, it is difficult to explain the nitrogen formation by Mechanism (i) or (ii) because $G(N_2)/\Delta G(H_2)$ reaches 4. This ratio will be 2 according to Mechanism (i) and possibly 4 if the chain reactions by (ii) would more easily occur at $-196°C$ than room temperature. The energy transfer (iii) cannot explain the experimental curve shown in Fig. 6. As a possible mechanism at $-196°C$ the following reaction is considered:

$$O^- + N_2O \rightarrow O + N_2O^- \qquad (12)$$

$$N_2O^- \rightarrow N_2 + O^- \qquad (11')$$

The reaction (12) was observed by Paulson in mass spectrometric study.[24] It would be necessary for Reactions (12) and (11′) to proceed that nitrous oxide molecules aggregate at $-196°C$. Such aggregation may be possible because liquid nitrogen temperature is below the glass transition temperature of methylcyclohexane.[25] As is shown in Fig. 8, the increase of $G(N_2)/\Delta G(H_2)$ from 1 to 4 with increasing N_2O concentration seems to indicate this aggregation. However, it is also uncertain if the above reactions occur at $-196°C$, because Reaction (12) is endothermic in the gas phase.[24] Thus the mechanism for formation of nitrogen from mixtures of nitrous oxide and methylcyclohexane (as well as other hydrocarbons) is not clear at present and remains to be resolved in future.

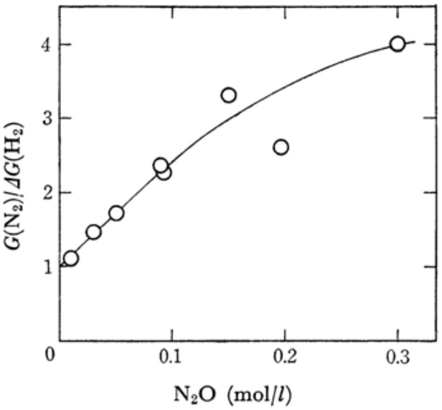

Fig. 8. The ratio of $G(N_2)/\Delta G(H_2)$ *vs.* N_2O concentration.

Mechanism of Hydrogen Formation. The mechanism of hydrogen formation may be written as follows:

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[24] J. F. Paulson, "Ion-Molecule Reactions in the Gase Phase," ed. by F. Gould, American Chemical Society Publications, Washington, D. C. (1966).

[25] M. R. Carpenter, D. B. Davies and A. J. Matheson, *J. Chem. Phys.*, **46**, 2451 (1967).

$$C_7H_{14} \rightsquigarrow \left[\begin{array}{ll} C_7H_{14}^* & (13) \\ C_7H_{14}^+ + e^- & (14) \end{array} \right.$$

$$C_7H_{14}^* \rightarrow \mathrm{H(hot)},\ \mathrm{H(thermal)},\ \text{and/or}\ H_2 \tag{15}$$

$$C_7H_{14}^+ + e^- \rightarrow \left| \begin{array}{ll} H_2 + C_7H_{12} & (16) \\ \mathrm{H(hot)} + C_7H_{13}\cdot & (17) \\ \mathrm{H(thermal)} + C_7H_{13}\cdot & (18) \end{array} \right.$$

At room temperature both hot and thermal hydrogen atoms can abstract an H atom from the solvent molecule to yield a hydrogen molecule and a solvent radical.

$$\mathrm{H(hot)} + C_7H_{14} \rightarrow H_2 + C_7H_{13}\cdot \tag{19}$$

$$\mathrm{H(thermal)} + C_7H_{14} \rightarrow H_2 + C_7H_{13}\cdot \tag{20}$$

Since thermal H atoms cannot abstract H atoms from solvent molecules at −196°C, they must combine one another or with the solvent radicals. The hydrogen yield from pure methylcyclohexane irradiated at −196°C decreases by 0.5 G unit in comparison with that at room temperature (Fig. 6). If the decrease in hydrogen yield is due to thermal H atoms, the yield of thermal H atoms may be estimated to be lower than 1.0 (G unit).

As has been described already, one molecule of benzene is formed by scavenging an electron and decreasing one hydrogen molecule at −196°C as well as room temperature. Therefore one molecule of hydrogen is formed by neutralization of a positive ion and an electron. A large fraction of hydrogen formed by neutralization will be hot, since its G value is expected to be 4 from W value and that of thermal H atoms is estimated to be about 1.0. Consequently the two solvent radicals produced by Reactions (17) and (19) seem to be very close to each other in the solid state. Then it will be suggested that the amount of trapped radicals does not increase after neutralization, since recombination or disproportionation of these two radicals may immediately occur even at −196°C. Further study on this point is being planned.