BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1657—1661 (1970)

Hydrogen Formation in the Radiolysis of Saturated Hydrocarbons in the Liquid and Solid Phases. Effect of Temperature

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(Received November 24, 1969)

Hydrogen yields have been determined for thirteen saturated hydrocarbons (*n*-pentane, cyclopentane, methylcyclopentane, 3-methylpentane, *n*-hexane, cyclohexane, methylcyclohexane, *n*-heptane, *n*-octane, 2,2,4-trimethylpentane, *n*-nonane, *n*-decane and polyethylene) γ-irradiated at 20°C, −72°C and −196°C. The decrease in hydrogen yield with decreasing temperature from 20°C to −196°C has been correlated with the yield of thermal hydrogen atoms, which was obtained by adding ethylene as a scavenger at 20°C; the decrease in most cases was nearly equal to a half of the thermal hydrogen atom yield. Evidence of thermal hydrogen atom production at −196°C has also been demonstrated by ESR measurement. It has been concluded that thermal hydrogen atoms abstract hydrogen atoms from solvent molecules at 20°C, but they mostly recombine with each other to form hydrogen molecules at −196°C. An empirical formula based on the C–H bond parameter has been presented which is adapted for the hydrogen yield from normal alkanes.

One of the major products from γ-irradiated hydrocarbons is hydrogen and in most cases its yield depends upon the irradiation temperature. Dewhurst showed in the 800 Kvp electron radiolysis of *n*-hexane that the hydrogen yield was 5.0 (*G* unit) at 30°C and 3.0 (*G* unit) at −196°C.[1]

Recently we reported the hydrogen yield from γ-irradiated methylcyclohexane in the temperature range from 20°C to −196°C.[2] In contrast to Dewhurst's result, the decrease in hydrogen yield in our case was only 0.5 (*G* unit). Several workers[3-5] also reported results similar to those obtained by us; the decrements of hydrogen yield were lower than 1.0 (*G* unit). Only the result by Dewhurst is significantly different from the others. In this paper, we will report the hydrogen yields from thirteen γ-irradiated saturated hydrocarbons at 20°C, −72°C and −196°C and attempt to give a semiquantitative explanation for the yields.

A few studies have been made to explain the yields of products in the radiolysis of hydrocarbons from the view point of their chemical structure.[6-8] We will propose an empirical formula from which the hydrogen yield from *n*-alkanes can be evaluated fairly well.

Experimental

The experimental procedure was almost the same as that described earlier.[2] *n*-Pentane, cyclopentane, methylcyclopentane, *n*-hexane, cyclohexane ,methylcyclohexane, *n*-heptane, and 2,2,4-trimethylpentane were Tokyo Kagaku Seiki 99.9% standard pure materials and used as received. Tokyo Kagaku Seiki 99.0% 3-methylpentane was shaken with concentrated sulfuric acid in a separating flask, washed with distillated water and dried over Galuber's salt. Passing through a silica gel column, 3-methylpentane was fractionally distillated. *n*-Octane, *n*-nonane and *n*-decane were Nakarai Kagaku 99% guaranteed reagents and purified in the same procedure as for 3-methylpentane. Polyethylene was "Takasen" made by ^{60}Co γ-irradiation at the Japan Atomic Energy Research Institute (Takasaki) and used without further purification.

Irradiations at −196°C were performed in a Dewar filled with liquid nitrogen and the absorbed dose was determined by correcting for the shielding effect of Dewar and liquid nitrogen. This shielding effect was measured with two Fricke dosimeters; one was settled in a position in the radiating field and the other in a Dewar filled with liquid ethanol, which has almost the same density as liquid nitrogen, in the same position as the first one. This shielding effect was 11.1%; the dose rate at −196°C decreased to 88.9% of that at 20°C.

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The dose absorbed at −72°C was estimated assuming that the shielding effect of dry-ice is proportional to its density.

ESR measurements were performed using a JES 3BX ESR spectrometer.

Results

The hydrogen yields from thirteen hydrocarbons irradiated at 20°C, −72°C and −196°C are listed in Table 1. The doses were 2.28×10^{19}, 1.43×10^{20} and 1.62×10^{20} eV/g at the irradiation temperatures of 20, −72 and −196°C, respectively. From Table 1, the following three features can be pointed out: (1) the decrease in hydrogen yield $\{G(H_2)_{20^\circ C}-G(H_2)_{-196^\circ C}\}$ is low in the cases of *n*-pentane, methylcyclopentane and 3-methylpentane, (2) the hydrogen yield from 2,2,4-trimethylpentane increases at −196°C, although it decreases at −72°C, and (3) the decrease in hydrogen yield from the other hydrocarbons is ≤1. The results differ considerably from those of Dewhurst.[1)]

TABLE 1. HYDROGEN YIELDS AT EACH IRRADIATION TEMPERATURE

Substance	Temperature		
	20°C	−72°C	−196°C
n-Pentane	5.13	4.58	4.70
Cyclopentane	5.60	5.30	4.46
Methylcyclopentane	4.18	4.40	4.10
3-Methylpentane	4.25	4.40	3.90
n-Hexane	5.50	5.00	4.30
Cyclohexane	5.60	5.60	5.00
Methylcyclohexane	4.85	4.50	4.40
n-Heptane	5.45	4.70	4.40
n-Octane	5.36	5.26	4.36
2,2,4-Trimethylpentane	2.72	2.34	2.87
n-Nonane	5.30	4.80	4.40
n-Decane	5.20	5.20	4.25
Polyethylene	4.40	4.20	3.40

It seemed that the decrease in hydrogen yield could be explained in terms of "thermal" hydrogen atom, so we measured the yields of thermal hydrogen atoms from hydrocarbons excepting polyethylene. For this purpose, ethylene was added to the hydrocarbons, which were γ-irradiated at 20°C at a dose of 2.74×10^{20} eV/g. Figure 1 shows the effect of ethylene on the hydrogen yield from *n*-pentane. The curve was drawn to fit the experimental data. The hydrogen decrease is almost completed at about 0.3M. The limiting value of the decrement in hydrogen yield in Fig. 1 can be taken as the yield of thermal hydrogen atoms, $G(H_{\text{thermal}})$. In the same manner as for *n*-pentane, the yields

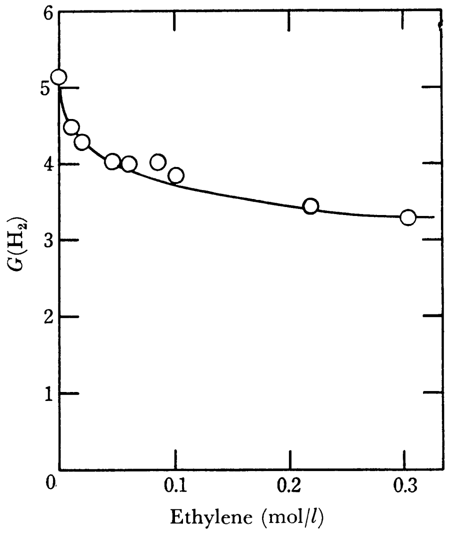

Fig. 1. Effect of ethylene on the hydrogen formation from γ-irradiated *n*-pentane at 20°C.

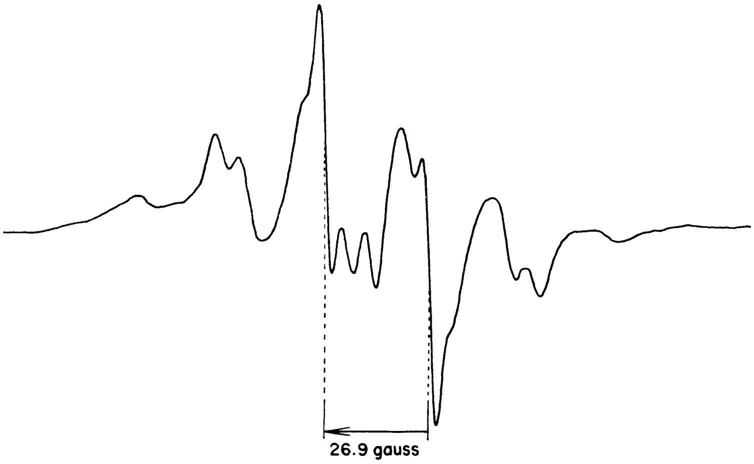

Fig. 2. ESR spectrum of γ-irradiated 3-methylpentane glass containing 3.73 mol% of ethylene at −196°C.

of thermal hydrogen atoms from the other hydrocarbons were obtained and are listed in Table 2. These thermal hydrogen atom yields are between 1 and 2 (G unit).

To ascertain whether thermal hydrogen atoms are produced at $-196°C$, ESR measurements were performed for γ-irradiated 3-methylpentane glass which contains 3.74 mol% of ethylene. In Fig. 2, we can see 3-methylphentyl radicals mixed with ethyl radicals the splitting constant of which is 26.9 gauss.

Discussion

The mechanism of hydrogen formation from γ-irradiated hydrocarbons has been investigated by many workers and are described as follows:

$$RH \rightsquigarrow \begin{cases} RH^+ + e^- & (1) \\ RH^* & (2) \end{cases}$$

$$\left.\begin{array}{l} RH^+ + e^- \\ RH^* \end{array}\right\} \longrightarrow \begin{cases} H\ (\text{thermal}) + R\cdot & (3) \\ H\ (\text{hot}) + R\cdot & (4) \\ H_2 + \text{Olefin} & (5) \end{cases}$$

The molecular hydrogen detachment (Eq. (5)) needs a lower energy than that of atomic hydrogen detachment (Eqs. (3) and (4)).[9] Thus the molecular detachment process does not seem to be affected by temperature. Hot H atoms abstract hydrogen atoms from solvent molecules to form H_2 molecules and solvent radicals both at 20°C and $-196°C$.

$$H(\text{hot}) + RH \longrightarrow H_2 + R\cdot \qquad (6)$$

Thermal H atoms abstract H atoms from solvent molecules to produce H_2 molecules at room temperature, but in the presence of an H atom scavenger such as olefin, they are scavenged and the total hydrogen yield decreases.[10-12]

$$H(\text{thermal}) + RH \longrightarrow H_2 + R\cdot \qquad (7)$$

$$H(\text{thermal}) + C_2H_4 \longrightarrow C_2H_5\cdot \qquad (8)$$

However, up to the present, the formation of thermal H atom in solid hydrocarbons at $-196°C$ has not been confirmed.

We have reported the effect of ethylene on the hydrogen formation from γ-irradiated methylcyclohexane at $-196°C$ as well as 20°C[13] and ascribed it to thermal H atom scavenging.

On the other hand, Timm *et al.*[14] have shown in the ESR measurements at 4°K that no thermal H atom can be observed in solid hydrocarbons except methane. However, as is shown in Fig. 2, H atoms are captured by ethylene to form ethyl radicals. Therefore it can be said that thermal H atoms are probably produced not only at room temperature, but also at liquid nitrogen temperature. The reason for the absence of H atoms in the ESR spectra may be that thermal H atoms cannot be trapped by solid hydrocarbons except methane, but recombine with each other to form hydrogen molecules, as was suggested previously.[13]

$$2H(\text{thermal}) \longrightarrow H_2 \qquad (9)$$

Molecularly detached hydrogen and hot H atoms do not affect the total hydrogen yield when the irradiation temperature decreases from 20°C to $-196°C$. Only thermal H atoms can affect the total hydrogen yield. From Eqs. (7) and (9), it seems that the total hydrogen yield decreases by $0.5\,G(H_{\text{thermal}})$ when the irradiation temperature decreases from 20°C to $-196°C$. Thus we can describe the hydrogen yields at 20°C and $-196°C$ as follows:

$$G(H_2)_{20°C} = G(H_2)_{\text{molecular}} + G(H)_{\text{hot}} + G(H)_{\text{thermal}} \qquad (10)$$

$$G(H)_{-196°C} = G(H_2)_{\text{molecular}} + G(H)_{\text{hot}} + 0.5G(H)_{\text{thermal}} \qquad (11)$$

Table 2. Yields of thermal H atoms in hydrocarbons irradiated at 20°C

	$G\ (H_{\text{thermal}})$
n-Pentane	1.8
Cyclopentane	1.6
Methylcyclopentane	1.1
3-Methylpentane	1.3
n-Hexane	2.0
Cyclohexane	1.0
Methylcyclohexane	1.0
n-Heptane	1.7
n-Octane	1.8
2,2,4-trimethylpentane	1.1
n-Nonane	1.7
n-Decane	1.4

Substracting Eq. (11) from Eq. (10), we obtain

$$\Delta G(H)_2 = G(H_2)_{20°C} - G(H_2)_{-196°C} = 0.5G(H)_{\text{thermal}} \qquad (12)$$

To see if Eq. (12) holds for our results or not, we compared $\Delta G(H_2)$, obtained from Table 1, with $0.5\,G(H_{\text{thermal}})$ from Table 2. The results are listed in Table 3. Although $\Delta G(H_2)$ is not exactly equal to $0.5\,G(H_{\text{thermal}})$ because thermal H atoms cannot be completely scavenged by ethylene, the results shown in Table 3 illustrate the validity of Eq. (12) except in the cases of *n*-pentane, methyl-

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TABLE 3. COMPARISON BETWEEN $\Delta G(H_2)$ AND $0.5G$ ($H_{thermal}$).
$\Delta G(H_2) = G(H_2)_{20°C} - G(H_2)_{-196°C}$

	$\Delta G(H_2)$	$0.5G$-($H_{thermal}$)
n-Pentane	0.43	0.9
Cyclopentane	1.14	0.8
Methylcyclopentane	0.08	0.6
3-Methylpentane	0.35	0.6
n-Hexane	1.20	1.0
Cyclohexane	0.60	0.8
Methylcyclohexane	0.50	0.5
n-Heptane	1.05	0.9
n-Octane	1.00	0.9
2,2,4-Trimethylpentane	−0.15	0.6
n-Nonane	0.90	0.9
n-Decane	0.95	0.7

cyclopentane, 3-methylpentane and 2,2,4-trimethylpentane. In the case of these four hydrocarbons, Eq. (12) does not hold and $\Delta G(H_2)$ is considerably less than $0.5\,G(H_{thermal})$ (2,2,4-trimethylpentane gives a negative value of $\Delta G(H_2)$).

It is not easy to explain the exceptions, but we might consider the difference in intramolecular energy partition in the liquid and solid states, which may change the relative contribution of the C–C and C–H bond cleavage.

To investigate the relation between the hydrogen yield and the chemical structure, we have made the following calculation. Denoting the number of hydrogen molecules formed per unit absorbed energy (eV), per 1 g of hydrocarbon, by P_i, we can express the G value of hydrogen as

$$G(H_2) = 100P_i \tag{13}$$

Denoting the number of hydrogen molecules formed per 1 eV energy absorbed, per 1 molecule of hydrocarbon, by p_i, we can write as

$$p_i = P_i(M/N) \tag{14}$$

where M is the molecular weight of a hydrocarbon and N is the Avogadro number. Combining Eqs. (13) and (14), we obtain p_i as a function of $G(H_2)$;

$$p_i = \frac{M}{100N}G(H)_2 \tag{15}$$

Here we restrict our discussion to normal alkanes and make the following assumption; the number of hydrogen molecules per 1 eV, per 1 molecule of normal alkane is given by

$$p_i = n_pX_p + n_sX_s, \tag{16}$$

where n_p and n_s are the number of primary and secondary hydrogen atoms, respectively, and X_p X_s are parameters associated with the primary and secondary C–H bonds, respectively. From Eqs. (15) and (16), the hydrogen yield from each normal alkane is expressed as

$$G(H_2) = 100N\left(\frac{n_p}{M}X_p + \frac{n_s}{M}X_s\right) \tag{17}$$

If Eq. (17) holds, the hydrogen yield from a normal alkane can be calculated substituting the numbers of primary and secondary hydrogen atoms and the molecular weight into Eq. (17).

Using the data in Table 1, we obtain the values of X_p and X_s; $X_p = 5.40 \times 10^{-25}$ and $X_s = 5.78 \times 10^{-25}$ at 20°C, and $X_p = X_s = 4.57 \times 10^{-25}$ at −196°C. Using these values, we calculated the hydrogen yields for normal alkanes. The calculated and observed yields at 20°C and −196°C are listed in Tables 4 and 5, respectively. The calculated values at 20°C (Table 4) are in good agreement with the observed values except for *n*-pentane. The observed hydrogen yield for *n*-pentane is somewhat lower than the calculated one. A possible reason for this is that the C–C bond cleavage in *n*-pentane is more favorable than that in higher normal alkanes, resulting in suppression of hydrogen formation to some extent. Equation (17) appears to be valid for normal alkanes which are larger than *n*-pentane. We also calculated the hydrogen yield from the normal alkane, whose C–C chain is infinitely long, which was 4.97 (G unit). The observed hydrogen yield from polyethylene was 4.40 (G unit). This difference between the calculated and the observed yield may be due to terminal double bonds or branching methyl (or other) groups in polyethylene which reduce the hydrogen yield.

TABLE 4. CALCULATED AND OBSERVED HYDROGEN YIELDS AT 20°C

	Calcd. $G(H_2)$	Obs. $G(H_2)$
n-Pentane	5.60	5.13
n-Hexane	5.49	5.50
n-Heptane	5.42	5.45
n-Octane	5.36	5.36
n-Nonane	5.32	5.30
n-Decane	5.28	5.25

$X_p = 5.40 \times 10^{-25}$ $X_s = 5.78 \times 10^{-25}$

TABLE 5. CALCULATED AND OBSERVED HYDROGEN YIELDS AT −196°C

	Calcd. $G(H_2)$	Obsd. $G(H_2)$
n-Pentane	4.57	4.70
n-Hexane	4.46	4.30
n-Heptane	4.39	4.40
n-Octane	4.33	4.36
n-Nonane	4.29	4.40
n-Decane	4.25	4.25

$X_p = X_s = 4.57 \times 10^{-25}$

Equation (17) also holds for non-branching cyclic alkanes, if we use $X_s = 6.51 \times 10^{-25}$ which is higher than that for normal alkanes. We need more data for further investigation on this class of hydrocarbons. Equation (17) does not hold for branching alkanes which involve the tertiary C–H bond. Taking 3-methylpentane as an example, Eq. (17) must be changed to

$$G(\mathrm{H_2}) = 100N\left(\frac{n_p}{M}X_p + \frac{n_s}{M}X_s + \frac{n_t}{M}X_t\right) \qquad (17')$$

where subscript t is associated with the tertiary C–H bond.

Even if we use $X_t=0$, the calculated value is higher than the observed one.

It should be noted that the branching methyl group decreases the hydrogen yield which is easily recognizable if we compare the yield from cyclopentane with that from methylcyclopentane, and the yield from cyclohexane with that from methylcyclohexane.

The effect of this branching methyl group on the hydrogen yield will not be due to the increase in the fraction of primary H atoms, but the branching methyl group itself, which would affect the decomposition pattern of the molecule.

Polyethylene used in the present work has 2.1 methyl groups per 1000 units of $-\mathrm{CH_2}-$, and the deviation of the hydrogen yield from the expected value may partly be due to these branching methyl groups.

We now consider the physical meaning of the parameters, X_p and X_s. These are interpreted as representing contributions of a hydrogen atom at a specified position to the total hydrogen yield. In other words, these parameters indicate the overall probability of C–H bond cleavage, including detachment of H atom, H atom abstraction by the detached H atom, and molecular $\mathrm{H_2}$ detachment. Since X_p and X_s do not differ very much from one another, the C–H bond cleavage seems to occur almost equally at the primary and secondary C–H bonds for normal alkanes. However, our results are not consistent with those of Gäumann,[15] who used isotopic compounds to determine the scission probability of bonds. This discrepancy might be ascribed to the isotope effect.

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[15] T. Gäumann, "Aspect of Hydrocarbon Radiolysis," ed, by T. Gäumann and J. Hoigné, Academic Press, London (1968) p. 226.