BULLETIN OF THE CHEMICAL SOCEITY OF JAPAN, VOL. 44, 2619—2626 (1971)

# Effect of Phase on Hot Hydrogen Atom Abstraction Reaction with Solid Isobutane as Studied by Electron Spin Resonance Spectroscopy

Terunobu WAKAYAMA, Tetsuo MIYAZAKI, Kenji FUEKI, and Zen-ichiro KURI
*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya*

(Received March 10, 1971)

The effect of phase on the hot-hydrogen-atom abstraction reaction with isobutane at 77°K has been studied by electron spin resonance spectroscopy in the photolysis and the radiolysis of solid isobutane containing hydrogen iodide. While only the isobutyl radical is formed by the UV-illumination of isobutane–hydrogen iodide systems in the polycrystalline state, the tertiary butyl radical, accompanied with a small amount of isobutyl radicals, is produced from isobutane-methylcyclohexane-hydrogen iodide systems in the glassy state. The hot hydrogen atom produced by dissociative electron attachment to hydrogen iodide abstracts the tertiary hydrogen atom from isobutane at 77°K, independent of whether the matrix is polycrystalline or glassy. It appears that the H-abstraction reaction from isobutane by hot hydrogen atoms depends upon the energy of the hot hydrogen atoms.

The familiar atomic hydrogen-saturated hydrocarbon abstraction reaction has been extensively investigated at thermal energies under equilibrium conditions,[1] at very high kinetic energies in recoil media,[2] and at intermediate energies in photolytic systems.[3]

In the photolytic technique, hydrogen atoms of different known initial kinetic energies (7—92 kcal/mol) may be selectively generated by the photodissociation of hydrogen iodide (HI) in the presence of a reactant. For example, when activation is induced by a 2537 Å light, the kinetic energy of the hydrogen atom produced is 20 kcal/mol if the iodine atom is produced in the $^2P_{1/2}$ excited state and 41 kcal/mol if it is produced in the $^2P_{3/2}$ ground state.[4] The hot hydrogen atom produced by dissociative electron attachment to HI may have an energy of *ca.* 5—6 kcal/mol.

Although hot atom reactions have been investigated in detail in the gas phase, such reactions in condensed phases[5] are much less well understood. One of the complications in the hot atom reaction in condensed

---

[1] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth and Co., Ltd., London (1955); V. N. Kondratev, "Chemical Kinetics of Gas Reactions," Addison Wesley Co., Reading, Mass. (1964); I. Amdur and G. G. Hammes, "Chemical Kinetics: Principles and Selected Topics," McGraw-Hill Book Co., Inc., New York, N. Y. (1966).

[2] R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965); E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 897 (1963).

[3] R. J. Carter, W. H. Hamill, and R. R. Williams, Jr., *ibid.*, **77**, 6457 (1955); R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 3007 (1964).

[4] S. Aditya and J. E. Willard, *J. Amer. Chem. Soc.*, **88**, 229 (1966).

[5] J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **82**, 5974 (1960); C. D. Bass and G. C. Pimentel, *ibid.*, **83**, 3754 (1961); R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, **48**, 306 (1968).

phases is in the possible existence of the cage effect, which is absent in the gas phase. The cage effect explains the characteristically low quantum yield of primary dissociation in a condensed medium.[6] It was found in previous studies that the fragmentation of the excited molecule is an important process in the radiolysis of saturated hydrocarbons in the solid state at 77°K.[7] We reported in a previous paper that different radicals are formed in the radiolysis of solid isobutane at 77°K, depending on whether it is in the glassy or polycrystalline state.[8] In a recent stuPy with isobutane-2-$d_1$ we concluded that such a phase effect cannot be attributed to the isomerization of butyl radicals, such as $i$-$C_4H_9 \rightleftarrows t$-$C_4H_9$, but must be attributed to the primary process of the C–H bond rupture.[9]

In the present work, we shall examine, by ESR measurements, the phase effect on the hydrogen atom abstraction reaction in the photolysis and the radiolysis of isobutane-HI systems at 77°K, and shall attempt to compare these results with those of hot-hydrogen-atom reaction in the radiolysis of pure isobutane at 77°K.

In this paper, emphasis will be placed on our experimental findings rather than on their interpretation.

## Experimental

The isobutane, methylcyclohexane(MCH), and 3-methylpentane (3MP) were more than 99.9%pure. Gas-chromatographic analysis did not show any detectable impurities. They were purified by distillation on a vacuum line and were dried over a sodium mirror. Isobutane-2-$d_1$, synthesized by the Grignard reaction, was purified by passing it through a column of freshly-activated alumina and then through a column of fresh soda lime. The xenon was used as received, the stated purity being 99.9%.

The hydrogen iodide was prepared from Katayama Chemical reagent-grade aqueous HI by removing the iodine by shaking it with red phosphorus and by then allowing the frozen solution to warm twice in the presence of excess $P_2O_5$ on the vacuum line.

The samples, prepared on the vacuum line, were sealed in 4.3-mm o.d. Suprasil tubes. They were illuminated by ultraviolet light or $\gamma$-rays at 77°K, and then ESR measurements were made by means of a JES-3BX ESR spectrometer.

$\gamma$-Irradiation was provided by $^{60}$Co at a dose rate of $1.0 \times 10^6$ rads/hr, and UV-illumination, by a filtered end-window Toshiba medium-pressure mercury lamp. A Toshiba UV-25 filter was used; it cut off UV-light of wavelengths shorter than 2500 Å.

## Results and Discussion

*Effects of Phase on Hydrogen-atom Abstraction in the Photolysis of Solid Isobutane Containing HI.* Figure 1A shows the ESR spectrum of 0.2 mol% HI in isobutane at 77°K obtained after a 10-min illumination with a medium-pressure mercury lamp. The prolonged photolysis of isobutane without HI produced

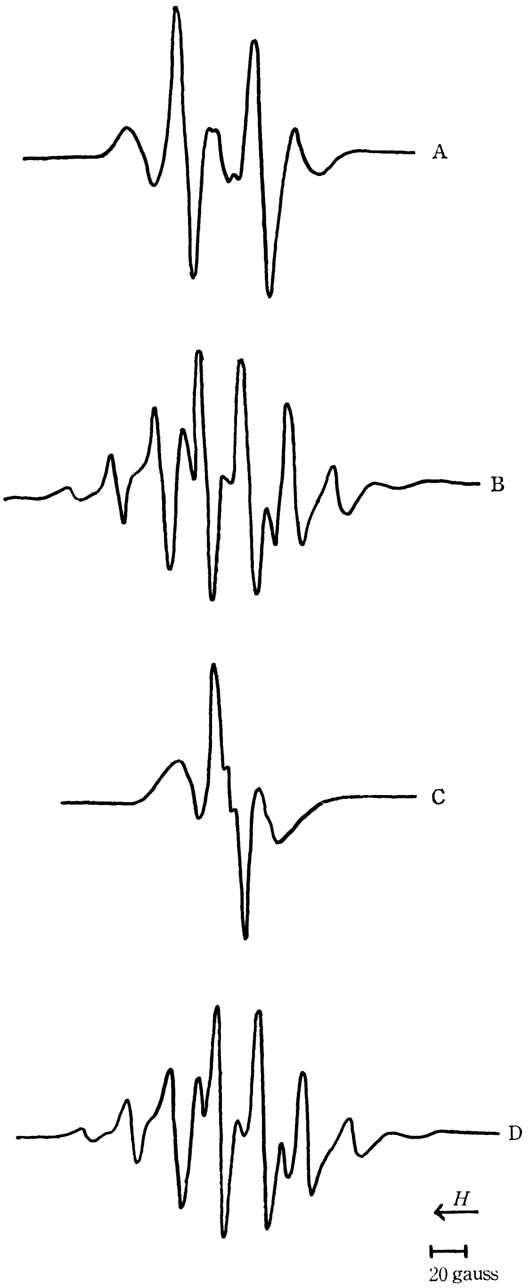

Fig. 1. (A) ESR spectrum of UV-illuminated $i$-$C_4H_{10}$-HI (0.2 mol%) at 77°K. UV-illumination time: 10 min.
(B) ESR spectrum of UV-illuminated $i$-$C_4H_{10}$-MCH (3.8 mol%)-HI (0.2 mol%) at 77°K. UV-illumination time: 2.5 min.
(C) ESR spectrum of UV-illuminated $i$-$C_4H_9D$-2-$d_1$-HI (0.2 mol%) at 77°K. UV-illumination time: 10 min.
(D) ESR spectrum of UV-illuminated Xe-$i$-$C_4H_{10}$ (4.6 mol%)-HI (0.2 mol%) at 77°K. UV-illumination time: 10 min.

---

[6] I. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[7] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **42**, 1164 (1969); T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **43**, 1017 (1970).

[8] a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **42**, 2086 (1969); b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970).

[9] Y. Saitake, T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **44**, 301 (1971).

no detectable radicals. A spectrum identical to Fig. 1A was obtained by the $\gamma$-irradiation of the isobutane. This indicates H-abstraction from the primary position in isobutane at 77°K by the photochemically-produced hot H atoms to form the isobutyl radical.

As the HI concentration in an isobutane matrix is increased, the yield of the isobutyl radical increases; it reaches a maximum at *ca.* 0.1 mol% HI concentration, and then decreases (Fig. 2). This result may be explained in terms of the competitive reactions between HI and isobutane for hot H atoms. A possible kinetic scheme is as follows:

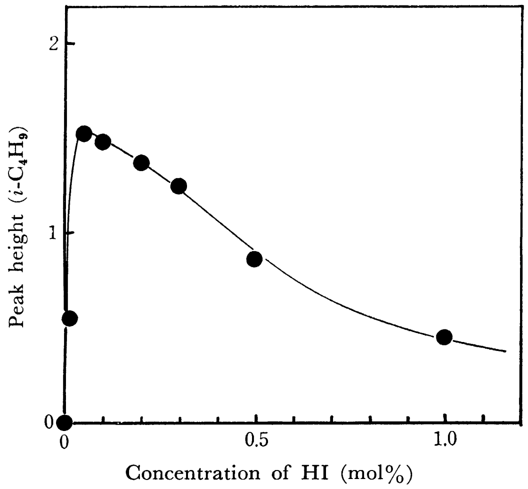

Fig. 2. Effect of HI concentration on the amounts of isobutyl radicals produced in UV-illuminated $i$-$C_4H_{10}$ at 77°K. UV-illumination time: 10 min.
●—●: $i$-$C_4H_9$

$$\mathrm{HI} \xrightarrow{\Phi I_{\mathrm{abs}}} \mathrm{H_{hot}} + \mathrm{I} \tag{1}$$

$$i\text{-}\mathrm{C_4H_{10}} + \mathrm{H_{hot}} \xrightarrow{k_2} i\text{-}\mathrm{C_4H_9} + \mathrm{H_2} \tag{2}$$

$$i\text{-}\mathrm{C_4H_{10}} + \mathrm{H_{hot}} \xrightarrow{k_3} i\text{-}\mathrm{C_4H_{10}} + \mathrm{H} \tag{3}$$

$$\mathrm{HI} + \mathrm{H_{hot}} \xrightarrow{k_4} \mathrm{H_2} + \mathrm{I} \tag{4}$$

where $I_{\mathrm{abs}}$ is the rate of light absorption by HI, $\Phi$ is the quantum yield of the photodissociation of HI, and $k$ is the rate constant. From these equations we can derive the following kinetic equation:

$$\frac{\Phi I_{\mathrm{abs}}\tau}{(\mathrm{R}\cdot)} = \left(1 + \frac{k_3}{k_2}\right) + \frac{k_4(\mathrm{HI})}{k_2(\mathrm{RH})} \tag{5}$$

where (R·), (RH), and (HI) are the concentrations of isobutyl radicals, isobutane, and HI respectively. $\tau$ is the time of light illumination. (R·) is measured by ESR, and $I_{\mathrm{abs}}$ is calculated as a function of (HI), using a value of 75[10] for the molar extinction coefficient of HI and taking the geometrical factor of the sample into account. Since $\Phi$ is constant, it can be expected from Eq. (5) that the relative value of $\Phi I_{\mathrm{abs}}\tau/(\mathrm{R}\cdot)$ also increases linearly with an increase in (HI)/(RH). Figure 3 shows the relative value of $\Phi I_{\mathrm{abs}}\tau/(\mathrm{R}\cdot)$ *vs.* the value of (HI)/(RH). It can be seem from Fig. 3 that several of the points tested fall on a straight line. This supports our interpretation presented above.

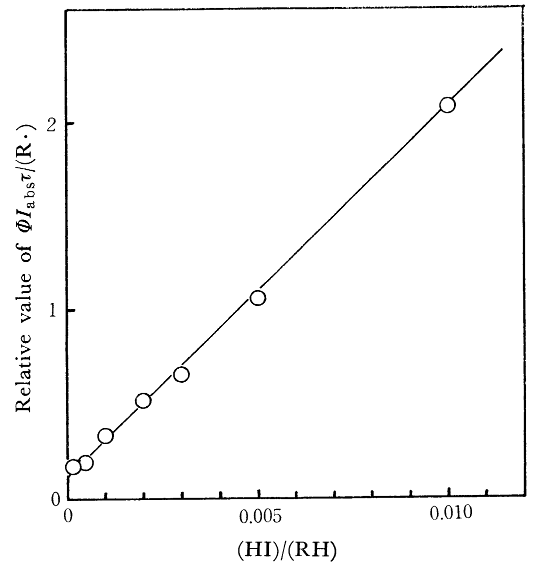

Fig. 3. Relation between $\Phi I_{\mathrm{abs}}\tau/(\mathrm{R}\cdot)$ and (HI)/(RH).

Pure isobutane is polycrystalline at 77°K, while isobutane containing 3.8 mol% MCH is glassy at 77°K. A quite different ESR spectrum was obtained by the 2.5-min photolysis of an isobutane-MCH mixture containing 0.2 mol%HI in the glassy state (Fig. 1B). This spectrum is identical with that of tertiary butyl radicals produced in $\gamma$-irradiated isobutane-3.8 mol% MCH in the glassy state at 77°K. This result indicates that the hot H atoms produced by the photolysis of isobutane-3.8 mol% MCH abstract the tertiary H atoms of isobutane to form tertiary butyl radicals.

The effect of the MCH concentration in an isobutane-0.2 mol% HI solution on the formation of radicals is shown in Fig. 4. Here, the remarkable point is the rapid increase in the yield of the tertiary butyl

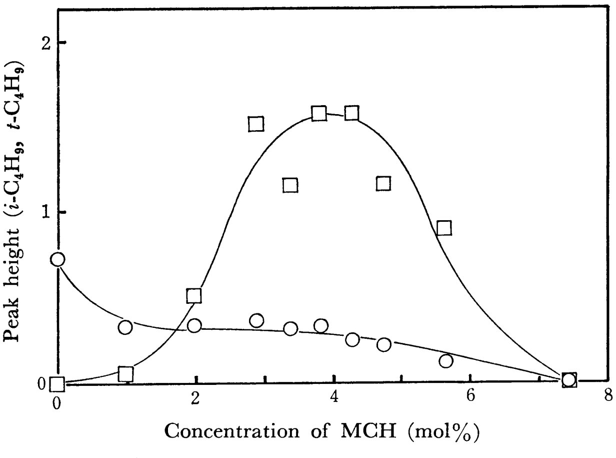

Fig. 4. Effect of MCH concentration on the amounts of butyl radicals produced in UV-illuminated $i$-$C_4H_{10}$-HI (0.2 mol%) at 77°K. UV-illumination time: 2.5 min.
○—○: $i$-$C_4H_9$
□—□: $t$-$C_4H_9$

---

[10] R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999 (1964).

radical, reaching a maximum at *ca.* 4 mol% MCH concentration. The yield of the isobutyl radical, however, does not change as much as that of the tertiary butyl radical. This result may be interpreted in terms of the following effects. As the concentration of MCH is increased, the matrix becomes glassy, so that the tertiary butyl radical is primarily produced by the hot-H-atom abstraction, while the isobutyl radical is secondarily produced by the photo-induced isomerization, $t\text{-}C_4H_9 \overset{h\nu}{\rightarrow} i\text{-}C_4H_9$. The yields of both isobutyl and tertiary butyl radicals decrease in the range of MCH concentration above *ca.* 4 mol%, where the matrix becomes so soft that the radicals are trapped less efficiently in the matrix.[11]

Figure 5 shows the dependence of the yields of butyl radicals on the UV-illumination time. As the illumination time is increased, the yield of the isobutyl radical increases almost linearly, while that of the tertiary butyl radical initially increases and then reaches a plateau after a 40-min illumination. This result indicates that the tertiary butyl radical is produced by the hot-H-atom abstraction reaction with isobutane, while the isobutyl radical arises from a secondary process, *i.e.*, the photoisomerization of the tertiary butyl radical to the isobutyl radical upon prolonged UV-illumination,[12] in an isobutane-3.8 mol% MCH solution containing 0.2 mol% HI at 77°K.

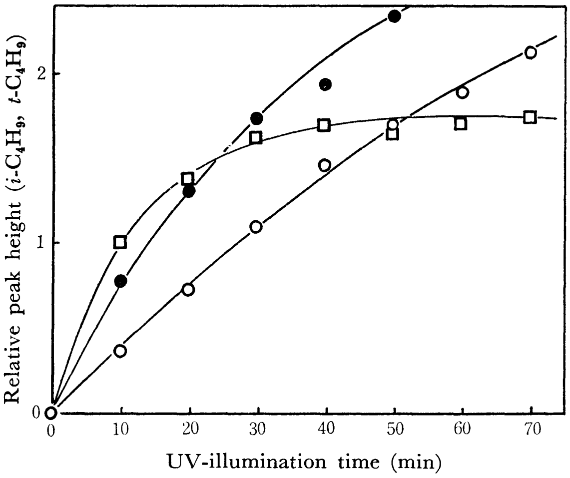

Fig. 5. Effect of UV-illumination time on the amounts of butyl radicals produced in UV-illuminated $i$-$C_4H_{10}$-HI (0.2 mol%) and $i$-$C_4H_{10}$-MCH (3.8 mol%)-HI (0.2 mol%) at 77°K.
●—●: $i$-$C_4H_9$ in an $i$-$C_4H_{10}$ matrix.
○—○: $i$-$C_4H_9$ in an $i$-$C_4H_{10}$-MCH (3.8 mol%) matrix.
□—□: $t$-$C_4H_9$ in an $i$-$C_4H_{10}$-MCH (3.8 mol%) matrix.

Table I shows the butyl radicals produced by the hot-H-atom abstraction from isobutane in various UV-illuminated systems containing HI. Since the isobutyl-2-$d_1$ radical is produced in the photolysis of isobutane-2-$d_1$-HI (Fig. 1C), reactions (6) and (7) can be ruled out and reaction (8) occurs predominantly to form the isobutyl-2-$d_1$ radical:

$$i\text{-}C_4H_9D\text{-}2\text{-}d_1 + H_{hot} \rightarrow t\text{-}C_4H_9 + HD \qquad (6)$$

$$t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_9 \qquad (7)$$

$$t\text{-}C_4H_9D\text{-}2\text{-}d_1 + H_{hot} \rightarrow i\text{-}C_4H_8D\text{-}2\text{-}d_1 + H_2 \qquad (8)$$

In order to investigate the phase effect on the hot-H-atom abstraction reaction with isobutane, we have examined both the thermal isomerization and the decay of radicals. Ayscough and Evans[12] and Iwasaki and Toriyama[13] reported that isobutyl radicals produced in $\gamma$-irradiated alkyl halides, on standing at 77°K, isomerize thermally to tertiary butyl radicals. When the isobutyl radical was produced from dissociative electron attachment to $i$-$C_4H_9Cl$ in the $\gamma$-irradiated $i$-$C_4H_{10}$-3.8 mol% MCH-1 mol% $i$-$C_4H_9Cl$ system, the $i$-$C_4H_9 \rightarrow t$-$C_4H_9$ isomerization could be observed when it stood in the dark at 77°K for 15 hr.[8b] When an isobutane-3.8 mol% MCH solution containing 0.2 mol% HI is UV-illuminated for 30 min, the isobutyl radical is produced in addition to the tertiary butyl radical. When this sample was stored in the dark at 77°K for about 30 hr, the isomerization of the isobutyl radical could not be observed at all, but both isobutyl and tertiary butyl radicals decayed. The isobutyl radical produced by the photolysis of isobutane containing HI neither isomerizes to the tertiary butyl radical nor decays at all at 77°K (Fig. 6). The same phenomena were observed in $\gamma$-irradiated glassy isobutane-3.8 mol% MCH and in polycrystalline isobutane at 77°K.[8b]

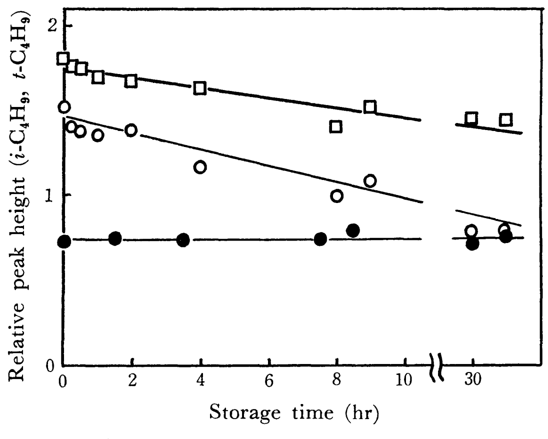

Fig. 6. Effect of storage time on the amounts of butyl radicals produced in UV-illuminated $i$-$C_4H_{10}$-HI (0.2 mol%) and $i$-$C_4H_{10}$-MCH (3.8 mol%) - HI (0.2 mol%) at 77°K. UV-illumination time: 30 min.
●—●: $i$-$C_4H_9$ in an $i$-$C_4H_{10}$ matrix.
○—○: $i$-$C_4H_9$ in an $i$-$C_4H_{10}$-MCH (3.8 mol%) matrix.
□—□: $t$-$C_4H_9$ in an $i$-$C_4H_{10}$-MCH (3.8 mol%) matrix.

An ESR spectrum was obtained for the radicals produced in the radiolysis of a Xe-3.8 mol% isobutane mixture at 77°K; these radicals are identified as tertiary butyl radicals, presumably produced by energy transfer from Xe to isobutane. These tertiary butyl radicals isomerize to isobutyl radicals upon UV-

---

[11] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **43**, 3761 (1970).

[12] P. B. Ayscough and H. E. Evans, *J. Phys. Chem.*, **68**, 3066 (1964).

[13] M. Iwasaki and K. Toriyama, *J. Chem. Phys.*, **46**, 2852 (1967).

Table 1. Butyl radicals produced in the photolysis of HI in various matrices at 77°K[a)]

| System | Phase | Radical |
|---|---|---|
| $i$-$C_4H_{10}$ | Crystal | $i$-$C_4H_9$ |
| $i$-$C_4H_9D$-2-$d_1$ | Crystal | $i$-$C_4H_8D$-2-$d_1$ |
| $i$-$C_4H_{10}$-MCH (3.8 mol%) | Glass | $t$-$C_4H_9$ |
| $i$-$C_4H_9D$-2-$d_1$-3MP (7.4 mol%) | Glass | $t$-$C_4H_9$ |
| Xe-$i$-$C_4H_{10}$ (4.6 mol%) | | $t$-$C_4H_9$ |

a) Concentration of HI: 0.2 mol%; UV-illumination time: 10 min

Table 2. Effect of matrix on butyl radical formation in the radiolysis at 77°K[a)]

| System | Phase | Radical |
|---|---|---|
| $i$-$C_4H_{10}$ | Crystal | $i$-$C_4H_9$ |
| $i$-$C_4H_9D$-2-$d_1$ | Crystal | $i$-$C_4H_8D$-2-$d_1$ |
| $i$-$C_4H_{10}$-MCH (3.8 mol%) | Glass | $t$-$C_4H_9$ |
| $i$-$C_4H_9D$-2-$d_1$-MCH (5.7 mol%) | Glass | $t$-$C_4H_9$ |
| Xe-$i$-$C_4H_{10}$ (3.8 mol%) | | $t$-$C_4H_9$ |
| X-$i$-$C_4H_9D$-2-$d_1$ (4.6 mol%) | | $t$-$C_4H_9$ |

a) $\gamma$-Irradiation dose: $2.22\times10^5$ rad

illlumination. When this sample was stored in the dark at 77°K for *ca.* 30 hr, both the isobutyl and the tertiary butyl radicals decayed. These results indicate that the physical state of a Xe-3.8 mol% isobutane mixture at 77°K is rather more similar to the glassy state of an isobutane-MCH mixture than to the polycrystalline state of pure isobutane. This is also consistent with the fact that the primary radicals produced from isobutane in the photolysis and radiolysis are isobutyl radicals in the polycrystalline matrix and tertiary butyl radicals in the glassy matrix at 77°K (Tables 1 and 2). Accordingly, the thermal isomerzation from the isobutyl to the tertiary butyl radical seems to be a phenomenon characteristic of the isobutyl radical produced from alkyl halides. The decay of butyl radicals seems to be related to the physical state of the matrix.

Figure 1D shows the ESR spectrum of radicals produced by the photolysis of 0.2 mol% in Xe-4.6 mol% isobutane at 77°K.

Kagiya *et al.* reported an empirical method of evaluating the activation energies for radical substitution reactions in the gas phase.[14)] Using their method, we have calculated the activation energies for such thermal radical substitution reactions as:

$$H_{thermal} + i\text{-}C_4H_{10} \rightarrow H_2 + t\text{-}C_4H_9 \text{ (or } i\text{-}C_4H_9) \qquad (9)$$

and

$$H_{thermal} + i\text{-}C_4H_9D\text{-}2\text{-}d_1 \rightarrow HD \text{ (or } H_2) + t\text{-}C_4H_9 \text{ (or } i\text{-}C_4H_8D\text{-}2\text{-}d_1) \qquad (10)$$

The calculated activation energies are shown in Table 3. If we assume that the activation energies for the thermal radical substitution reactions are independent of the temperature, we can say, on the basis of the activation energies estimated above, that the tertiary hydrogen atom of isobutane should be abstracted much more easily than the primary one at 77°K. However, this is inconsistent with observations on the polycrystalline samples, indicating that the hot hydrogen atom must be involved in the abstraction reaction in these systems.

Table 3. The calculated activation energies of H atom abstraction reactions with isobutanes in the gas phase

| Isobutane | Type of the bond | $D_i$[a)] (kcal/mol) | $E_a$[b)] (kcal/mol) |
|---|---|---|---|
| Isobutane | $t$-C–H | 85 | 6.8 |
| Isobutane | $i$-C–H | 89 | 7.7 |
| Isobutane-2-$d_1$ | $t$-C–D | 85.9 | 6.6 |
| Isobutane-2-$d_1$ | $i$-C–H | 89 | 7.7 |

a) The bond dissociation energy of the initial bond. The C–D bond strength is taken to be 0.9 kcal/mol greater than that of C–H: S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y. (1960), p. 666.

b) The activation energy.

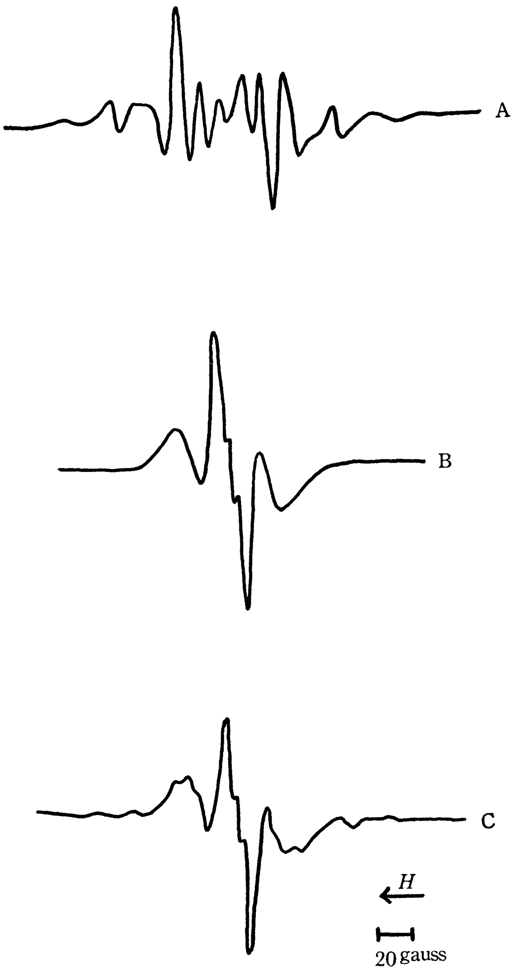

Fig. 7. (A) ESR spectrum of $\gamma$-irradiated $i$-$C_4H_{10}$-HI (1.0 mol%) at 77°K.
(B) ESR spectrum of $\gamma$-irradiated $i$-$C_4H_9D$-2-$d_1$ at 77°K.
(C) ESR spectrum of $\gamma$-irradiated $i$-$C_4H_9D$-2-$d_1$-HI (1.0 mol%) at 77°K. Irradiation dose: $2.22\times10^5$ rad.

---

[14)] T. Kagiya, Y. Sumida, T. Inoue, and F. S. Dyachkovskii, This Bulletin, **42**, 1812 (1969).

*Effects of Phase on Hydrogen-atom Abstraction in the Radiolysis of Solid Isobutane Containing HI.* γ-Irradiated pure isobutane at 77°K displays a five-line ESR spectrum with a hyperfine coupling constant of $a_{av}=20.7$ G, which can be attributed to the isobutyl radical[15] (Table 2). A quite different ESR spectrum, however, is obtained for radicals produced in the radiolysis of isobutane containing 1.0 mol% HI. This spectrum consists of two components which may be assigned to the tertiary butyl radical (a ten-line spectrum with $a_{av}=22.3$ G)[16] and the isobutyl radical (Fig. 7A) respectively.

Figure 8 shows the dependence of the peak heights of trapped radicals on the dose in γ-irradiated isobutane containing 2.0 mol% HI at 77°K. The peak intensity of isobutyl radicals is linear in doses over the entire range studied, while that of tertiary butyl radicals is linear in doses up to $1.5\times10^5$ rad, but deviates from the straight line with doses beyond it. This result can be interpreted in terms of the following reactions:

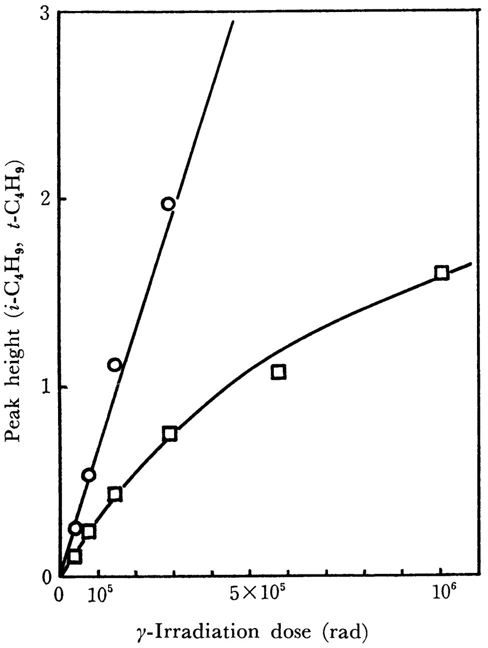

Fig. 8. Effect of dose on the amounts of butyl radicals produced in γ-irradiated $i\text{-C}_4\text{H}_{10}$-HI (2.0 mol%) at 77°K.
○—○: $i\text{-C}_4\text{H}_9$
□—□: $t\text{-C}_4\text{H}_9$

$$i\text{-C}_4\text{H}_{10} \rightsquigarrow i\text{-C}_4\text{H}_{10}^*,\ i\text{-C}_4\text{H}_{10}^+ + \text{e}^- \quad (11)$$

$$i\text{-C}_4\text{H}_{10}^* \rightarrow i\text{-C}_4\text{H}_9 + \text{H} \quad (12)$$

$$\text{HI} + \text{e}^- \rightarrow \text{H}_{\text{hot}} + \text{I}^- \quad (13)$$

$$\text{H}_{\text{hot}} + i\text{-C}_4\text{H}_{10} \rightarrow \text{H}_2 + t\text{-C}_4\text{H}_9 \quad (14)$$

The isobutyl radical is produced by the decomposition of the excited isobutane molecule (reaction (12)),[7] while the tertiary butyl radical is produced in the H-abstraction by the hot H atom which is formed in the dissociative electron attachment (reaction (13)) and has an energy of *ca.* 5—6 kcal/mol.

As the HI concentration in an isobutane matrix is increased, the yield of the isobutyl radical produced in the radiolysis decreases initially and reaches a plateau value at *ca.* a 1.0 mol% HI concentration, while that of the tertiary butyl radical increases rapidly initially and then gradually (Fig. 9). Figure 10 shows the dependence of the yields of trapped radicals on the concentration of HI in a γ-irradiated isobutane-3.8 mol% MCH matrix at 77°K. The yield of the tertiary butyl radical increases with the concentration of HI up to *ca.* 0.5 mol% and reaches a plateau value, while that of the isobutyl radical is constant over the entire range of HI concentrations studied. These results may be interpreted in terms of the energy dependence of the hot-H-atom reaction and on the basis of the electron yield in γ-irradiated hydrocarbons in the solid state; the hot H atom produced from HI by the dissociative electron attachment (reaction

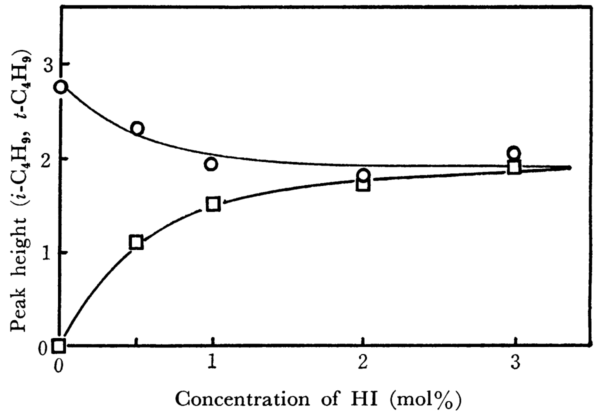

Fig. 9. Effect of HI concentration on the amounts of butyl radicals produced in γ-irradiated $i\text{-C}_4\text{H}_{10}$ at 77°K. Irradiation dose: $8.9\times10^4$ rad.
○—○: $i\text{-C}_4\text{H}_9$
□—□: $t\text{-C}_4\text{H}_9$

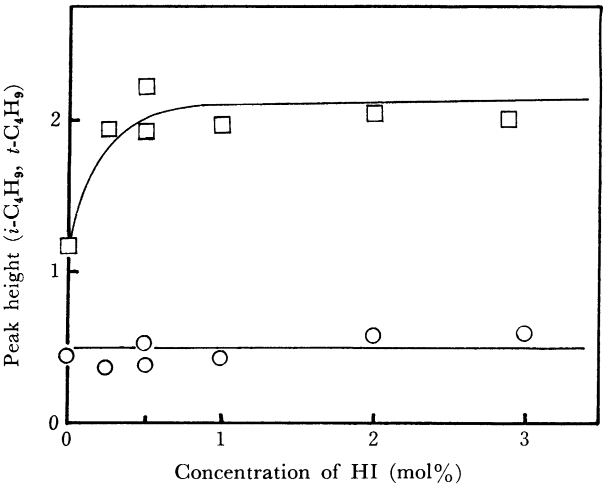

Fig. 10. Effect of HI concentration on the amounts of butyl radicals produced in γ-irradiated $i\text{-C}_4\text{H}_{10}$-MCH (3.8 mol%) at 77°K. Irradiation dose: $8.9\times10^4$ rad.
○—○: $i\text{-C}_4\text{H}_9$
□—□: $t\text{-C}_4\text{H}_9$

---

[15] J. Lin and F. Williams, *J. Phys. Chem.*, **72**, 3707 (1968).

[16] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

(13)) abstracts an H atom from the tertiary position more easily than from the primary position in isobutane at 77°K, since the hot H atom thus produced has an energy of *ca.* 5—6 kcal/mol, which is much lower than that produced by the photolysis of HI. Such an argument holds for both polycrystalline isobutane and glassy isobutane-MCH matrices (Table 4). The yield of the tertiary butyl radical produced by reaction (14) increases with HI concentration up to *ca.* 1.0 mol%, above which it remains constant, because the yield of electrons which escape from recombination with the parent positive ions in the radiolysis of condensed systems is limited and its maximum value in solid hydrocarbon matrices is $G(e^-)=2$.[17] The yield of the isobutyl radical is rather insensitive to the concentration of HI, since the isobutyl radical is produced by the decomposition of the excited isobutane molecule.

Table 4. Butyl radicals produced in the radiolysis of HI in various matrices at 77°K[a)]

| System | Phase | Radical |
|---|---|---|
| $i$-$C_4H_{10}$ | Crystal | $t$-$C_4H_9$ |
| $i$-$C_4H_9D$-2-$d_1$ | Crystal | $t$-$C_4H_9$ |
| $i$-$C_4H_{10}$-MCH (3.8 mol%) | Glass | $t$-$C_4H_9$ |

a) Concentration of HI: 1.0 mol%; γ-irradiation dose: $2.22 \times 10^5$ rad

Figure 7B shows the ESR spectrum of radicals produced in the radiolysis of pure isobutane-2-$d_1$ at 77°K, which can be attributed to the isobutyl-2-$d_1$ radical.[9] In γ-irradiated 1 mol% HI in isobutane-2-$d_1$, the tertiary butyl radical is produced in addition to the isobutyl-2-$d_1$ radical (Fig. 7C). The tertiary butyl radical may arise from D-atom abstraction from isobutane-2-$d_1$ by the hot H atom produced from HI.

*Cause of Phase Effect on H-atom-abstraction Reaction by Hot H Atoms.* When a diatomic molecule such as HI dissociated by absorbing light with more energy than the dissociation energy of the bond, the atoms produced will be hot. The main advantage of utilizing photochemically-produced hot atoms is that their initial kinetic energy is well known. In the 2537 Å photolysis of HI, hot H atoms have 20 kcal/mol or 41 kcal/mol, depending on whether the iodine atom is produced in the excited state or in the ground state. Since the first excited-state energy of the H atom is about 237 kcal/mol, the energy given to the H atom produced photochemically is the kinetic energy.

The phase effect can be discussed from the following two points of view: (i) whether the phase change affects such primary processes as the fragmentation of the excited HI molecule in the photolysis of solid isobutane containing HI at 77°K, and (ii) whether the phase change affects such secondary processes as the hot-hydrogen-atom abstraction reaction with isobutane. In a diatomic molecule such as HI, the H–I bond rupture of the excited HI molecule (HI*) may occur repulsively in the period of one vibration (less than $10^{-13}$ sec). Therefore, the phase effect has no important influence upon the primary process of the HI* fragmentation.

One plausible explanation is given by the cage effect on the radiolysis of organic solids, which was reviewed by Willard.[18] Since the C–C bond of the stable tertiary butyl radical is formed by $sp^2$-hybrid orbitals, three methyl groups construct a planar structure. Therefore, the structural rearrangement of the C–C bonds would be necessary for the formation of the stable tertiary butyl radical from the isobutane molecule, which such a rearrangement would be unnecessary for the formation of the isobutyl radical. In the radiolysis of isobutane in the polycrystalline state, the formation of the tertiary butyl radical, accompanied by the structural rearrangement of the C–C bonds, may be suppressed in the rigid crystal, and only the primary C–H bond, which is stronger than the tertiary C–H bond, may be ruptured. The effect of the matrix rigidity was observed both in the abstraction of H atom from isobutane by hot H atoms produced from the photolysis of HI and in the decomposition of the excited isobutane molecule produced by the radiolysis of isobutane (Tables 1 and 2). In the radiolysis of the polycrystalline isobutane-HI or isobutane-2-$d_1$-HI, however, it was found that the hot H atom, which is produced by dissociative attachment to HI, abstracts the tertiary H atom from isobutane or isobutane-2-$d_1$ (Table 4). Thus, only the cage effect does not explain satisfactorily this H-abstraction reaction in solid hydrocarbons at 77°K. The energy dependence of the hot-H-atom abstraction reaction must be invoked to interpret this observation.

Another effect of the hot-atom reaction is the moderator effect, which was discussed by Hamill,[19] in the photolysis of HI. On this model, hot H atoms are formed with 20 or 41 kcal/mol of translational energy, which they can lose in the subsequent moderating collisions with an inert gas. Typically, these are rare gases such as He and Ne, but such substances as A, Kr, Xe, and $H_2$ may act as moderators. We may interpret the present results for a moderator matrix, Xe (Tables 1 and 2), as follows. The hot H atoms (H**) in a Xe matrix may lose translational energy by collisions with the moderator, Xe, and then they may abstract the tertiary H atoms of isobutane to form tertiary butyl radicals (reactions (15), (16), and (17)). This interpretation is consistent with the findings on the radiolysis of isobutane-HI, where hot H atoms have only 5—6 kcal/mol and preferentially abstract the tertiary H atoms. In summary, the H-abstraction reaction by hot H atoms depends upon the energy of the hot H atoms:

---

[17] M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1968); T. Kimura, K. Fueki, and Z. Kuri, This Bulletin, **43**, 3090 (1970); T. Kimura, M. Fukaya, M. Hada, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **43**, 3400 (1970); T. Shida, *J. Phys. Chem.*, **74**, 3055 (1970).

[18] J. E. Willard, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y. (1968), p. 599.

[19] H. A. Schwarz, R. R. Williams, Jr., and W. H. Hamill, *J. Amer. Chem. Soc.*, **74**, 6007 (1952).

$$\mathrm{HI} \xrightarrow{h\nu} \mathrm{H^{**}} + \mathrm{I} \quad (15)$$

$$\mathrm{H^{**}} + \mathrm{M} \rightarrow \mathrm{H^{*}} + \mathrm{M} \quad (16)$$

$$\mathrm{H^{*}} + i\text{-}\mathrm{C_4H_{10}} \rightarrow \mathrm{H_2} + t\text{-}\mathrm{C_4H_9} \quad (17)$$

In reactions (15)—(17) H** and H* represent hot atoms with higher and lower kinetic energies respectively, and M represents a moderator such as Xe. It should be stressed that, although the efficiency of Xe as a moderator is probably lower than that of hydrocarbons, the contribution of H-abstraction by very hot atoms is more greatly reduced in a Xe matrix than in a hydrocarbon matrix, in which H-abstraction by hot atoms inevitably competes with hot-atom moderation.

The authors thank Dr. T. Kimura and Mr. Y. Saitake of Nagoya University, and Professor E. Maekawa of Nagoya Institute of Technology for their assistance in preparing isobutane-2-$d_1$.