Selective Hydrogen Atom Abstraction by Hydrogen Atoms in Photolysis and Radiolysis of Alkane Mixtures at 77 K

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A selective hydrogen atom abstraction reaction by H atoms, which are produced at 77K by radiolysis of alkane or photolysis of hydrogen halides, has been found in isobutane, 2,2,3,3-tetramethylbutane (TMB), and cyclopropane matrices as well as in the neopentane matrix. The selective hydrogen atom abstraction reaction is caused by H atoms which have initial kinetic energies in the range from 15 to 67 kcal/mol. The reaction is caused also by D atoms. The competitive reaction between *c*-C_6H_{12} and HI for H atoms has been studied in the radiolysis and photolysis of *neo*-C_5H_{12}–*c*-C_6H_{12}–HI mixture at 77K. The rate constants of these reactions in the neopentane matrix are quite different from those of a thermal H atom reaction, but similar to those of a hot H atom reaction. The importance of the selective hydrogen atom abstraction reaction by H atoms is pointed out in the radical formation in the radiolysis of pure TMB at 77K.

We can easily investigate solid-state reactions at 77 K by irradiation with ultraviolet light or γ rays. Recently quite interesting phenomena have been found in the radiolysis of a neopentane–alkane mixture in the solid phase at 77 K.1) When neopentane containing a small amount of alkane is γ-irradiated at 77 K, alkyl radicals from solute alkanes rather than neopentyl radicals are selectively formed.

Since the formation of the solute alkyl radical is not affected by the addition of an electron scavenger or a hole scavenger, it was concluded that the alkyl radical is formed by a nonionic process.1b) The following observations obtained previously showed that the solute alkyl radical is not formed by the excitation transfer from the irradiated neopentane to the solute, but by the selective hydrogen atom abstraction from the solute by H atoms.1c) (1) The mechanism of excitation transfer promotes the formation of D_2 in the radiolysis of *neo*-C_5H_{12}–*i*-C_4H_9D at 77 K. Though much HD is formed in this system, D_2 is not formed at all.1c) (2) When a *neo*-C_5H_{12}–*c*-C_6H_{12} (1 mol %) mixture is irradiated at 77 K by γ-rays, cyclohexyl radicals are mainly formed. When propylene is added to the mixture, the formation of the cyclohexyl radicals is suppressed, while C_3H_7 radicals are produced complementarily by the addition of H atoms to propylene.2) (3) H atoms, which are produced by the photolysis of hydrogen iodide in neopentane containing a small amount of alkane, react selectively with the solute slkane at 77 K.1c,3)

The selective hydrogen atom abstraction reaction by H atoms has new problems in its reaction kinetics in the solid phase at 77 K. When H atoms are hot, we must assume that they migrate a long distance at 77 K through the neopentane crystal without losing their kinetic energies. When H atoms are thermal, we must assume that the activation energy for hydrogen atom abstraction is nearly zero in the neopentane matrix at 77 K, though the value amounts to 7—10 kcal/mol in the gas phase.4,5) The research described herein was undertaken in order to obtain further information about the nature of the reactive H atoms.

The previous studies of the selective hydrogen atom abstraction have been limited only to the neopentane matrix and to the reactions of H atoms. In the present paper the study will be extended to other alkane matrices, such as isobutane, 2,2,3,3-tetramethylbutane (TMB), and cyclopropane, and to the reactions of H and D atoms.

The formation of radicals in the radiolysis of pure TMB and of a TMB–alkane mixture is discussed here in terms of the selective hydrogen atom abstraction by H atoms.

Experimental

Neopentane, isobutane, and propane were more than 99.9 mol% pure, while cyclopropane and ethane were respectively more than 99.0 and 99.7% pure. Spectrograde cyclohexane was passed through a 1-m column packed with silica gel and then distilled on a vacuum line before use. 2,2,3,3-Tetramethylbutane (TMB) was of a high purity and purified by sublimation on a vacuum line before use. To prepare hydrogen halides (HX), such as HI, HBr, DBr, and HCl, the aqueous solution of each hydrogen halide was passed through P_2O_5 and subjected to several trap-to-trap sublimations on the vacuum line.

UV illumination was provided by Toshiba medium-pressure or low-pressure mercury lamps. γ-Irradiation was done by Co-60 at a dose rate of 4.2×10^{19} eV/h.

The free radicals were measured at 77 K with a JES-3BX ESR spectrometer.

Results

Table 1 shows the yields of radicals by the reaction of hydrogen (or deuterium) atoms in the radiolysis or photolysis of alkane mixtures in the solid phase at 77 K. *t*-C_4H_9 radical is mainly formed in the photolysis of *neo*-C_5H_{12}(or TMB)–*i*-C_4H_{10}–hydrogen halide(HX), while a small amount of *i*-C_4H_9 radical is also produced. Since the ratio of the amounts of *i*-C_4H_9 radicals to those of *t*-C_4H_9 radicals increases with increasing the illumination time of ultraviolet light, *i*-C_4H_9 radical is formed by the isomerization of *t*-C_4H_9 radical, which absorbs ultraviolet light.6) The amounts of C_4H_9 radicals re-

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Table 1. Formation of solute radicals by the reaction of hydrogen (or deuterium) atoms in the radiolysis or photolysis of alkane mixtures at 77K[a]

Sample	Species of radical	Methods of production of H (or D) atoms				
		γ-Irradiation[b]	Ultraviolet illumination[c]			
			HI	HBr	DBr	HCl
neo-C_5H_{12}–*i*-C_4H_{10}(2)[d]	C_4H_9	Clearly observed[e]	10.0	4.0	3.1	0.9
neo-C_5H_{12}	*neo*-C_5H_{11}	Clearly observed[e]	10.0	3.0	4.1	$<$0.5
i-C_4H_{10}–C_3H_8(2)[d]	C_3H_7	Clearly observed[e]	10.0	2.0	1.9	
i-C_4H_{10}	*i*-C_4H_9	Clearly observed[e]	10.0	2.6	5.5	
TMB–*i*-C_4H_{10}(5)[d]	C_4H_9	Clearly observed[f]	10.0	2.1	2.6	
c-C_3H_6–C_2H_6(4)[d]	C_2H_5	Clearly observed[f]	—	—	—	

a) Yields are averages of two or more runs. b) Alkane mixtures in the absence of hydrogen halide were irradiated at 77 K with γ-rays. H atoms are produced by the radiolysis of solvent alkane. c) H (or D) atoms are produced by the photolysis of hydrogen halide with ultraviolet light. Concentrations of hydrogen halide in *neo*-C_5H_{12}, *i*-C_4H_{10}, TMB, and *c*-C_3H_6 matrices are 0.5, 0.2, 0.5, and 0.5 mol/100 mol of solvent alkane. The yield of the radical in HI system is taken as 10. Illumination times of *neo*-C_5H_{12}, *i*-C_4H_{10}, TMB, and *c*-C_3H_6 matrices with UV light from a low-pressure mercury lamp are 5, 5, 20, and 30 min respectively. d) Unit of concentration is mol/100 mol of solvent alkane. e) ESR spectra are shown in Ref. 1a. f) ESR spectra are shown in Figs. 3 and 4.

present a sum of *t*-C_4H_9 and *i*-C_4H_9 radicals, and are measured by double integration of the first-derivative ESR signal of the radicals. Since only C_4H_9 radicals are formed selectively in the photolysis of *neo*-C_5H_{12}(or TMB)–*i*-C_4H_{10}–HX, overlapping of the spectra of the solute radical and the neopentyl radical does not occur. *neo*-C_5H_{11}, C_3H_7, *i*-C_4H_9, and C_2H_5 radicals do not isomerize under the illumination by ultraviolet light. Therefore the relative yields of these radicals are obtained from the heights of their peaks in the ESR spectrum. The yields of solute radicals increase linearly with increasing irradiation time. The yield of radical in the photolysis of HI is much higher than that in the photolysis of HBr, DBr, or HCl. This is because the absorbance of the ultraviolet light by HI is stronger than that by other hydrogen halides.[7] H atoms in the previous studies have been produced only by the photolysis of HI with 253.7 nm. The present study has been undertaken in order to obtain qualitative information as to whether H atoms with various energies produced from different compounds also react selectively with solute alkanes or not. Since the absolute yields of radicals was not necessary, the effect of HX concentration on the radical yields has not been studied systematically, except for a few runs of different concentrations. The results of the photolysis in Table 1 have been obtained by the illumination in the air with UV light from a low pressure Hg lamp. It was found by using a filter that the photolysis of HI is caused mainly by light of 253.7 nm, while that of HBr or DBr is caused by light of 184.9 nm along with 253.7 nm.

In order to examine the effect of different wavelengths on the photolysis of HBr, two experiments have been undertaken. First, a filter which completely cuts off any light shorter than 190 nm has been used, and thus the photolysis was caused only by light of 253.7 nm. Second, the illumination with a low pressure Hg lamp has been done in the vacuum. The photolysis is caused mainly by light of 184.9 nm, because the decomposition of HBr by light of 253.7 nm is much smaller than that by light of 184.9 nm. Both H atoms, produced by the photolysis of HBr with the light of 184.9 nm or 253.7 nm, react selectively with the solute alkane in the *neo*-pentane matrix at 77 K.

The photolysis of HI has been done with a medium-pressure Hg lamp through a Toshiba UV31 filter, which cuts off all light shorter than 305 nm. The yields of radicals in the photolysis with the UV31 filter are much higher than those in the photolysis with a glass filter which cuts off all light shorter than 330 nm. Therefore the photolysis with the UV31 filter is caused mainly by the light from 330 nm to 305 nm. H atoms produced by the photolysis with the light from 330 nm to 305 nm also react selectively with the solute alkanes in the *neo*-pentane matrix at 77 K.

Figure 1 shows the effect of HI on the formation of cyclohexyl radicals in the radiolysis of *neo*-C_5H_{12}–*c*-C_6H_{12}–HI at 77 K. When *neo*-C_5H_{12} containing *c*-C_6H_{12} of 0.5, 1.0, and 2.0 (mol/100 mol of *neo*-C_5H_{12}) is γ-irradiated in the absence of HI, the yields of cyclohexyl radicals are approximately the same in the three systems; they are taken as 10.

Figure 2 shows the effect of HI on the formation of cyclohexyl radicals in the photolysis of *neo*-C_5H_{12}–*c*-C_6H_{12}–HI at 77 K. The yields of cyclohexyl radicals at HI concentration of 0.25 (mol/100 mol of *neo*-C_5H_{12}) are taken as 10

Figure 3a shows the ESR spectrum of γ-irradiated

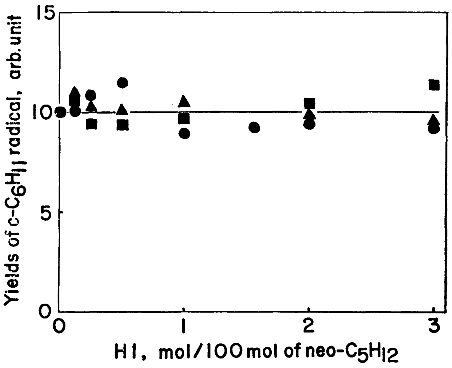

Fig. 1. Effect of HI on the yield of c-C_6H_{11} radicals in the radiolysis of neo-C_5H_{12}–c-C_6H_{12} mixture at 77 K with a dose of 2.1×10^{19} eV/g.
■, Concentration of c-C_6H_{12} is 0.5 mol/100 mol of neo-C_5H_{12}.
●, Concentration of c-C_6H_{12} is 1.0 mol/100 mol of neo-C_5H_{12}.
▲, Concentration of c-C_6H_{12} is 2.0 mol/100 mol of neo-C_5H_{12}.

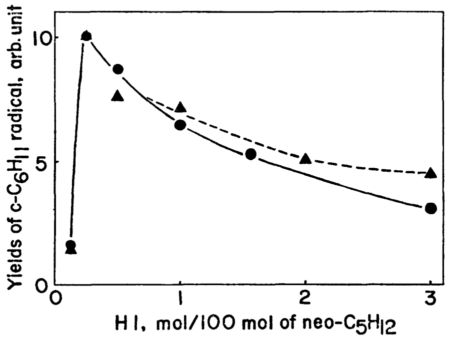

Fig. 2. Effect of HI on the yield of c-C_6H_{11} radicals in the photolysis of neo-C_5H_{12}–c-C_6H_{12}–HI mixture at 77 K.
●—●, c-C_6H_{12} concentration is 1.0 mol/100 mol of neo-C_5H_{12}.
▲---▲, c-C_6H_{12} concentration is 2.0 mol/100 mol of neo-C_5H_{12}.

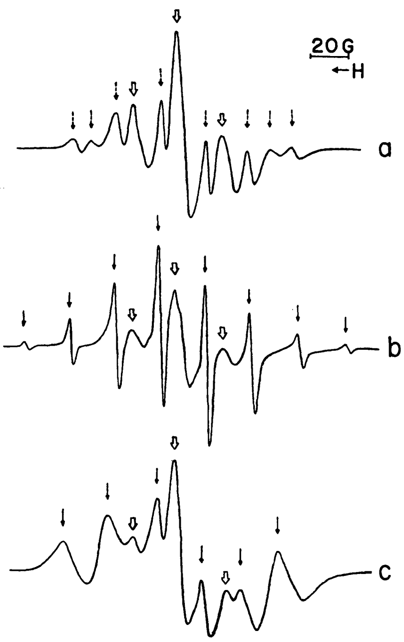

Fig. 3. ESR spectra of γ-irradiated TMB and TMB-alkane mixtures at 77 K with a dose of 1.8×10^{19} eV/g. Relative sensitivities of spectrometer for a, b, and c are approximately the ratios of 2 : 1 : 1.5 respectively. a, pure TMB; b, TMB–i-C_4H_{10}(5.4 mol/100 mol of TMB); c, TMB–c-C_6H_{12} (5.8 mol/100 mol of TMB).

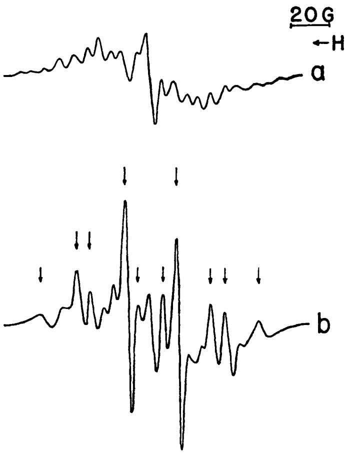

Fig. 4. ESR spectra of γ-irradiated c-C_3H_6 and c-C_3H_6–C_2H_6 mixtures at 77 K with a dose of 1.8×10^{19} eV/g. Sensitivities of spectrometer for a and b are approximately the same. a, pure c-C_3H_6; b, c-C_3H_6–C_2H_6 (4 mol/100 mol of c-C_3H_6).

pure TMB at 77 K. The spectrum is similar to that reported by Gerola *et al.*[8] The spectrum of three broad lines, indicated by ⇩, is ascribed to the $(CH_3)_3CC(CH_3)_2\dot{C}H_2$ (TMB·) radical. The other unidentified spectrum, indicated by ↓, has been ascribed to an isomerized radical, *i.e.* $(CH_3)_3CCH_2\dot{C}(CH_3)_2$,[8] or a mixture of t-C_4H_9 and $(CH_3)_3C\dot{C}(CH_3)_2$ radicals.[9] When TMB containing a small amount of isobutane or cyclohexane are γ-irradiated at 77 K, quite different spectra are obtained (Figs. 3b and c). The spectrum in Fig. 3b consists of three broad lines, which are attributable to the TMB· radical, and eight narrow lines, indicated by ↓, with a splitting constant of 22 G. The spectrum of the eight lines is consistent with the reported spectrum for the t-C_4H_9 radical.[10,11] The spectrum in Fig. 3c consists of three broad lines, which are attributable to the TMB· radical, and six broad lines, indicated by ↓, with a splitting constant of 22 G. The spectrum of the six lines is consistent with the reported spectrum for the cyclohexyl radical.[10,12] When TMB containing a small amount of C_3H_8, i-C_4H_8, or C_3H_6 is γ-irradiated at 77 K, C_3H_7, t-C_4H_9, or C_3H_7 radical is clearly observed.

Figure 4a shows the ESR spectrum of γ-irradiated pure cyclopropane at 77 K. The spectrum may be ascribed to C_3H_5 radical.[10] When cyclopropane containing a small amount of ethane is γ-irradiated at 77 K, a typical spectrum of an ethyl radical,[10,11] indicated by ↓, is clearly observed, as in Fig. 4b.[13]

Discussion

Selective Formation of Solute Radicals in the Radiolysis and Photolysis of Alkane Mixtures at 77 K. Table 1 shows that the selective formations of solute radicals in the radiolysis of alkane mixtures are observed also in isobutane, 2,2,3,3-tetramethylbutane (TMB), and cyclopropane matrices as well as in the neopentane matrix. All of the matrix alkanes are polycrystalline at 77 K. H atoms, produced by the photolysis of HI or HBr, react selectively with a small amount of the solute alkane in the *neo*-C_5H_{12}, *i*-C_4H_{10}, and TMB matrices. It is concluded that the selective hydrogen atom abstraction reaction is not limited to the neopentane matrix, but can be found also in other polycrystalline alkanes.

When H atoms are produced by the photolysis of HI with light of 330—305 nm, they react selectively with the solute alkane in the neopentane matrix. The 330—305 nm radiation corresponds to 86.6—93.7 kcal/mol, while the bond strength of HI is 71.3 kcal/mol.[14] To conserve momentum essentially all of the energy from the primary process in excess of that used in bond rupture must appear as translational energy of the H atom, because I atoms produced by the photolysis with 330—305 nm are mainly in the ground state.[15] Therefore the energies of the H atoms are 15—22 kcal/mol. The bond strength of HBr is 87.6 kcal/mol.[14] When H atoms are produced by the photolysis of HBr with light of 184.9 nm, the energies of the H atoms are 67 kcal/mol, because Br atoms produced by the photolysis are mainly in the ground state.[16] The H atoms also react selectively with the solute alkanes in the neopentane matrix. It is concluded that the H atoms, which have initial kinetic energies ranging from 15 to 67 kcal/mol, migrate a long distance through the neopentane matrix without reacting with the neopentane molecules and react selectively with the solute alkanes.

Though the C_2H_5 radical is mainly formed in the radiolysis of *c*-C_3H_6–C_2H_6 (Fig. 4), it is not observed in the photolysis of *c*-C_3H_6–C_2H_6–HI (HBr or DBr). Since the concentration of HX in cyclopropane and the method of illumination with UV light are the same as those in neopentane, the condition of the absorption of the light in cyclopropane must be the same as in neopentane, where the formation of radicals by the photolysis can be observed clearly. At present we cannot give a suitable explanation for the phenomenon that radicals are not formed by the photolysis in cyclopropane. One plausible reason would be as follows: that the amount of the H atoms produced by the photolysis of hydrogen halide in cyclopropane is extremely small. This might be because the ultraviolet light is reflected at the surface of the cyclopropane crystal and does not penetrate into the crystal, or because the decomposition of HX is suppressed by the cage effect in the cyclopropane crystal. The following results were observed during our experiments. Firstly, neither the C_3H_5 radical nor any other radical is produced by the illumination of *c*-C_3H_6–HX, where C_2H_6 does not exist, with ultraviolet light at 77 K. Secondly, when *c*-C_3H_6–C_2H_6–HI is illuminated with ultraviolet light, the color of I_2, produced by the decomposition of HI, is observed only at the surface of the crystal.

Table 1 shows that D atoms, produced by the decomposition of DBr, also react selectively with the solute alkanes. Therefore the selective hydrogen atom abstraction reaction is not limited only to H atoms.

Nature of Reactive Hydrogen Atom. In order to elucidate the mechanism of the selective hydrogen atom abstraction reaction by H atoms, it is important to get some information about the nature of the H atoms.

(I) Competitive reaction of H atoms with HI and *c*-C_6H_{12} in the *neo*-C_5H_{12} matrix at 77 K.

Figure 1 shows that the yields of cyclohexyl radicals in the radiolysis of *neo*-C_5H_{12}–*c*-C_6H_{12} mixtures are not affected by the addition of HI. As described in the Introduction, the previous studies[1] of the radiolysis of neopentane–alkane mixtures at 77 K have concluded that excited neopentane, formed by γ-irradiation, produces a H atom and a neopentyl radical. The H atom migrates through the neopentane matrix and reacts selectively with the solute cyclohexane. The ionic process and the excitation transfer are not responsible for the formation of *c*-C_6H_{11} radicals.[1] When HI is

$$neo\text{-}C_5H_{12} \rightsquigarrow neo\text{-}C_5H_{11} + H \qquad (1)$$

$$H + c\text{-}C_6H_{12} \xrightarrow{k_{c\text{-}C_6H_{12}}} c\text{-}C_6H_{11} + H_2 \qquad (2)$$

present in the *neo*-C_5H_{12}–*c*-C_6H_{12} system, occurrence of Reaction 3 is expected, because both hot and thermal H atoms react easily with HI in the gas phase. H

$$H + HI \xrightarrow{k_{HI}} I + H_2 \qquad (3)$$

atoms produced by the radiolysis of *neo*-C_5H_{12} at 77 K, however, do not react with HI, but with *c*-C_6H_{12} (Fig. 1). It can be estimated from the results in Fig. 1 that $k_{HI}/k_{c\text{-}C_6H_{12}}$ is less than 0.05; the value is given in the first line in Table 2.

Figure 2 shows that the yields of cyclohexyl radicals in the photolysis of the *neo*-C_5H_{12}–*c*-C_6H_{12}–HI mixture reach a maximum at the HI concentration of 0.25 (mol/100 mol of *neo*-C_5H_{12}) and then decrease gradually with increasing concentration of HI. Such results can be explained in terms of competitive reactions between HI and cyclohexane for H atoms. A possible kinetic scheme is as follows:

$$HI \xrightarrow{h\nu} H + I \qquad (4)$$

$$H + c\text{-}C_6H_{12} \xrightarrow{k_{c\text{-}C_6H_{12}}} c\text{-}C_6H_{11} + H_2 \qquad (5)$$

$$H + HI \xrightarrow{k_{HI}} I + H_2 \qquad (6)$$

If the rate of Reaction 4 is represented by r, the following kinetic equation is obtained:

$$\frac{1}{[c\text{-}C_6H_{11}]} = \frac{1}{r} + \frac{k_{HI}[HI]}{r\,k_{c\text{-}C_6H_{12}}[c\text{-}C_6H_{12}]}$$

The linear relationship between 1/[*c*-C_6H_{11}] and [HI]/[*c*-C_6H_{12}] is obtained for the HI concentrations higher than 0.25 (mol/100 mol of *neo*-C_5H_{12}). When concentrations of *c*-C_6H_{12} are 1.0 and 2.0 (mol/100 mol of *neo*-C_5H_{12}), $k_{HI}/k_{c\text{-}C_6H_{12}}$ are 1.2 and 1.0 respectively. The mean value for $k_{HI}/k_{c\text{-}C_6H_{12}}$ is given in the second line in Table 2.

There are many studies of the reaction of hot atoms produced by the photolysis of hydrogen halides in the gas phase. Carter *et al.*[17] reported that $k_{DI}/k_{C_3H_8}$ is

Table 2. Competitive reaction between HI and c-C_6H_{12} for H atoms at 77 K

Species of H atom	$k_{HI}/k_{c\text{-}C_6H_{12}}$
H atom produced by radiolysis of *neo*-C_5H_{12} at 77 K	<0.05
H atom produced by photolysis of HI in *neo*-C_5H_{12} matrix at 77 K	1.1
Hot H atom[a)]	0.23—1.1
Thermal H atom (A)[b)]	10^{20}—10^{23}
Thermal H atom (B)[c)]	10^{11}—10^{14}

a) Hot H atoms were produced by photolysis of HI in the gas phase. b) $k_{HI}/k_{c\text{-}C_6H_{12}}$ was estimated from the data in the gas phase. c) $k_{HI}/k_{c\text{-}C_6H_{12}}$ was estimated from the reaction of the thermal methyl radical in the solid phase at 77 K.

1.45 for reactions of hot D atoms with DI and C_2H_6. Hong *et al.*[18)] reported that $k_{HI}/k_{C_2D_5H}$ is 7.0 for reactions of hot H atoms with HI and C_2D_5H. Rebbert *et al.*[19)] reported that $k_{C_2D_6}/k_{c\text{-}C_6D_{12}}$ is 0.16 for reactions of hot CH_3 radicals with C_2D_6 and c-C_6D_{12}. Therefore $k_{HI}/k_{c\text{-}C_6H_{12}}$ ranges approximately from 1.45×0.16 (=0.23) to 7.0×0.16 (=1.1). These values are given in the third line in Table 2.

Thermal H atoms react quite easily with HI in the gas phase. According to the study by Sullivan,[20)] the rate constant of this reaction can be expressed by $k_{HI}=10^{12.05}T^{0.5}\exp(-E/RT)$. The activation energy (E) is nearly zero, 0.48 kcal/mol. The activation energy for a reaction of thermal H atoms with cyclohexane is, however, about 8 kcal/mol.[4,5)] If it is assumed that the pre-exponential factor of $k_{c\text{-}C_6H_{12}}$ is approximately the same as that of k_{HI} and that the activation energy for the reaction of H atoms with HI is 0—1 kcal/mol, $k_{HI}/k_{c\text{-}C_6H_{12}}$ at 77 K amounts to 10^{20}—10^{23}; this is given in the 4th line in Table 2.

Recently it has been reported that a thermal CH_3 radical abstracts H atoms from CH_3OH[21)] and 3-methylpentane[22,23)] at 77 K by quantum mechanical tunneling. The rate constant of the reaction can be estimated from the decay time of the CH_3 radical to be about 10^{-1} mol^{-1} ml s^{-1} at 77 K. Assuming that the thermal H atom reacts with cyclohexane by the quantum mechanical tunneling and that the rate constant of the thermal H atom is the same order of magnitude as that of the thermal CH_3 radical, $k_{HI}/k_{c\text{-}C_6H_{12}}$ at 77 K may be 10^{11}—10^{14}; this is given in the 5th line in Table 2.

Though a number of studies of the reaction rate have been undertaken in the gas and liquid phases at temperatures higher than room temperature, studies in the solid phase at 77 K are quite few. At present we have no information about the possibility that the activation energy changes drastically in the solid alkane at 77 K, as compared with the gas or liquid phases. If the activation energy obtained in the gas phase may be used also in the solid phase, the following discussion may be fruitful. The results in Table 2 show that $k_{HI}/k_{c\text{-}C_6H_{12}}$ of H atoms produced by the radiolysis or photolysis in the neopentane matrix at 77 K are quite different from the values expected from the reaction of thermal H atoms, but approximately similar to the value expected from the hot H atom reaction.

If the activation energy in the gas phase is quite different from that in the solid phase at 77 K, we cannot exclude the possibility that the H atoms produced by the radiolysis or photolysis in the neopentane matrix at 77 K are thermal. In this case, the thermal H atoms react more easily with cyclohexane than with hydrogen halide, though the activation energy for the former reaction is 8 kcal/mol and that for the latter reaction is nearly zero.

(II) Possibility of H atom abstraction by a thermal radical in the neopentane matrix at 77 K.

Since the activation energies for the hydrogen atom abstraction reaction from alkanes by thermal atoms or radicals are 7—10 kcal/mol,[4,5)] it may be concluded from the previous theory of reaction kinetics that the reaction does not occur at all at 77 K.

Recent findings,[21–23)] however, indicate that thermal methyl radicals abstract hydrogen atoms from the solvent molecules even at 77 K. We have examined here the possibility that thermal methyl radicals react in *neo*-C_5H_{12}–alkane mixtures at 77 K. When *neo*-C_5H_{12}–C_2H_6(2 mol/100 mol of *neo*-C_5H_{12})–CH_3Br(0.1 mol/100 mol of *neo*-C_5H_{12}) is irradiated with UV light at 77 K, a CH_3 radical is formed by the photolysis of CH_3Br. The thermal CH_3 decays very slowly at 77 K. The half-life for decay is about 150 h, which is extremely long as compared with 0.2—0.3 h in 3-methylpentane at 77 K.[22,23)] When the CH_3 radicals decrease, the formation of *neo*-C_5H_{11} or C_2H_5 radicals cannot be observed at all, while unknown radicals increase complementarily. Therefore it is concluded that the hydrogen atom abstraction reaction from alkane by thermal methyl radicals does not occur in the *neo*-C_5H_{12}–C_2H_6 mixture at 77 K.

(III) Selective hydrogen atom abstraction by H atoms in the i-C_4H_{10}–C_3H_8 mixture at 77 K.

When i-C_4H_{10} containing HI is irradiated with UV light at 77 K, the H atom produced by the photolysis of HI abstracts a hydrogen atom from the primary C–H bond of i-C_4H_{10} to form an i-C_4H_9 radical. When a small amount of C_3H_8 is added to the mixture, the H atom react selectively with the solute propane (Table 1 and Ref. 3) and the formation of the i-C_4H_9 radical is suppressed.

$$HI \xrightarrow{h\nu} H + I \tag{4}$$

$$H + i\text{-}C_4H_{10} \longrightarrow i\text{-}C_4H_9 + H_2 \tag{7}$$

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \tag{8}$$

The H atom produced by the photolysis of HI has an initial kinetic energy of 20 or 41 kcal/mol, depending on whether the iodine atom is produced in the excited state or in the ground state. In the radiolysis of i-C_4H_{10}–HI, it was found that the H atom, which is produced by dissociative electron attachment to HI, preferentially abstracts the tertiary H atom from i-C_4H_{10}.[24)]

$$e^- + HI \longrightarrow H + I^- \tag{9}$$

$$H + i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9 + H_2 \tag{10}$$

The H atom produced by dissociative electron attachment has a kinetic energy of 5—6 kcal/mol, if HI captures a thermal electron. Therefore it can be concluded that the hot H atom with high energy abstracts a primary H atom from i-C_4H_{10}, while the H atom with low energy abstracts a tertiary H atom. The hot H atom reacts selectively with C_3H_8 when C_3H_8 is present in the system.

(IV) Migration of H atoms in the crystal.

It can be summarized from the present and previous studies[1)] that the reactive H atoms in the crystalline alkane at 77 K have the following characteristics: (a) The activation energy for the reaction of the H atoms with solute alkane is nearly zero, though that in the gas phase is 7—10 kcal/mol. The H atoms produced by radiolysis of neopentane at 77 K do not react with HI, though the activation energy for this reaction is nearly zero in the gas phase. (b) The selective reaction of H atoms in the neopentane-isobutane mixture occurs efficiently in the solid phase at 77 K, while it does not occur at all in the liquid phase.[1c)] The selective reaction has been found only in polycrystalline matrices (Table 1).

At present we cannot give a clear answer to the question whether the reactive H atoms are thermal or hot. Though the possibility of hot H atoms cannot be excluded a priori, only the reaction of thermal H atoms has been discussed in the previous paper.[1c)] The possibility of hot H atoms will be described here in order to supplement the previous discussion.[1c)]

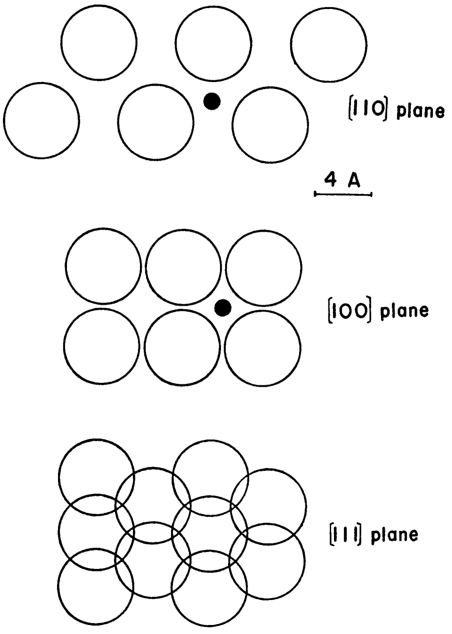

Fig. 5. Molecular arrangement of the three principal planes of fcc lattice of crystalline neopentane at 77 K.

One plausible explanation will be given by the idea of "channeling."[25—27)] The crystalline structure of neopentane at 77 K consists of face-centered cubic unit cells with a lattice constant of 11.4 Å.[28)] Since the chemical structure of neopentane is symmetrical, the structure is depicted here as a sphere. Projections of the molecular arrangements of the three principal planes of the fcc lattice of neopentane are shown in Fig. 5. A neopentane molecule is represented by a large circle, where a line of the circle is the most probable position of the electrons of H atoms in neopentane molecules. Top and second layers are depicted in the projections of the [110] and [100] planes, because the third and fourth layers are repetitions of the top and second layers. Top, second, and third layers are depicted in the projection of the [111] plane. A smaller circle, depicted by ●, represents a hot hydrogen atom with a Bohr radius. It is clear that the surface layers of the [110] and [100] orientations exhibit transparent regions to the incident hot H atoms. When hot H atoms produced by the radiolysis of neopentane or by the photolysis of hydrogen halide are incident upon the transparent regions of [110] and [100] planes, the hot H atoms may travel a long distance by a succession of glancing collisions with the channel walls of neopentane molecules and then react with a solute alkane which may exist as a defect in the neopentane crystal.

The selective hydrogen atom abstraction reaction by hot H atoms in neopentane–alkane mixtures is not observed in the liquid phase.[1c)] This phenomenon can be explained by the channeling hypothesis. Since a random arrangement of molecules in the liquid phase does not contain transparent regions, *i.e.* channels, the hot H atom collides head-on with a solvent molecule in the liquid phase and loses its energy by chemical reaction or deactivation. It is expected from this hypothesis that the selective reaction will be found in the crystal, but not in the glass.

Radical Formation in the Radiolysis of Pure 2,2,3,3-Tetramethylbutane(TMB) and TMB–Alkane Mixture at 77 K. Gerola *et al.*[8)] reported the ESR spectrum of γ-irradiated TMB at 77 K. Since $(CH_3)_3CC(CH_3)_2\dot{C}H_2$ (TMB·) and $(CH_3)_3CCH_2\dot{C}(CH_3)_2$ radicals are formed, they considered that first a C–H bond rupture occurs in the radiolysis of TMB and then the isomerization of the TMB· radical produces the $(CH_3)_3CCH_2\dot{C}(CH_3)_2$ radical. Shiraishi *et al.*[9)] reported t-C_4H_9, $(CH_3)_3C\dot{C}(CH_3)_2$, and TMB· radicals in the radiolysis of solid TMB. They considered that the free radicals are formed by C–C bond ruptures as well as C–H bond ruptures in the radiolysis of TMB.

The ESR spectrum in Fig. 3a consists of TMB· and an unidentified radical which has been ascribed to $(CH_3)_3CCH_2\dot{C}(CH_3)_2$[8)] or a mixture of t-C_4H_9 and $(CH_3)_3C\dot{C}(CH_3)_2$.[9)] When a small amount of alkane or olefin is added to TMB, the formation of the unidentified radical is suppressed and the solute alkyl radical is formed complementarily (Fig. 3b and c). Therefore it seems that the unidentified radical is neither formed by the isomerization of the TMB· radical nor by the direct C–C bond rupture, but by a secondary process of some active species which reacts also with the solute alkane or olefin.

The following observations obtained here show that the solute alkyl radical is not formed by the energy transfer from the irradiated TMB to the solute, but by the selective hydrogen atom abstraction by H atoms from the solute alkane.

(1) When TMB containing a small amount of propane is γ-irradiated at 77 K, the propyl radical is formed. The ionization potential of TMB has not been reported previously. But if we assume that the value is approximately the same as that of 2,2,4-trimethyl-

pentane, which is an isomer of TMB and has a structure similar to that of TMB, the ionization potential of TMB may be 9.86 eV,[29] which is lower than the ionization potential (11.07 eV)[29] of propane. The energy level of the first excited state of TMB is 8.0 eV,[30] which is lower than that (8.9 eV)[30] of propane. Therefore, assuming that the relative magnitude of the ionization potential and the first excited state is kept in the solid phase, the ordinary charge or excitation transfer from TMB to C_3H_8 cannot occur.

(2) When TMB containing a small amount of isobutene or propylene is irradiated with γ-rays at 77 K, the formation of the unidentified radical is suppressed, while t-C_4H_9 or C_3H_7 radical is produced complementarily by the addition of H atoms to isobutene or propylene.

(3) When TMB–i-C_4H_{10} (5 mol/100 mol of TMB)–HX (0.5 mol/100 mol of TMB) is irradiated with UV light at 77 K, the H atoms produced by the photolysis of hydrogen halide react selectively with i-C_4H_{10} to form the t-C_4H_9 radical (Table 1).

Therefore the mechanism of radical formation in the radiolysis of TMB at 77 K can be represented as follows:

$$\text{TMB} \rightsquigarrow \text{TMB}\cdot + \text{H} \tag{11}$$

$$\text{H} + \text{S} \longrightarrow (CH_3)_3CCH_2\dot{C}(CH_3)_2,\ t\text{-}C_4H_9,\ \text{or}\ (CH_3)_3C\dot{C}(CH_3)_2 \tag{12}$$

$$\text{H} + \text{RH} \longrightarrow \text{R}\cdot + H_2 \tag{13}$$

Reactive H atoms produced by the decomposition of TMB (Reaction 11) react selectively with impurities (S) to form $(CH_3)_3CCH_2\dot{C}(CH_3)_2$, t-C_4H_9, or $(CH_3)_3C\dot{C}(CH_3)_2$ in the radiolysis of pure TMB. When an alkane (RH), such as C_3H_8, i-C_4H_{10}, or c-C_6H_{12}, is added to TMB, the H atoms react selectively with the solute to form an alkyl radical (R·).

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