

BR7700969



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ATOMS IN PHOTOLYSIS AND RADIOLYSIS  
OF ALKANE MIXTURES AT 77° K"**

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**PUBLICAÇÃO IEA 462  
COUR-ARG 70**

**JANEIRO/1977**

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# "SELECTIVE HYDROGEN ATOM ABSTRACTION BY HYDROGEN ATOMS IN PHOTOLYSIS AND RADIOLYSIS OF ALKANE MIXTURES AT 77°K"

Tetsuo Miyazaki\*, Kazuhisa Kinugawa\*\*,  
Masao Eguchi\*\* and Selma M. L. Guedes\*\*\*

## ABSTRACT

Selective hydrogen atom abstraction reaction by H atoms which are produced at 77 K by radiolysis of alkane or photolysis of hydrogen halides, has been found in isobutane, 2,2,3,3-tetramethylbutane (TMB), cyclopropane matrices besides neopentane matrix. The selective hydrogen atom abstraction reaction in neopentane-isobutane mixture is affected by the difference of kinetic energies of H atoms. The reaction occurs more favorably with decreasing the kinetic energy of H atoms. Competitive reaction between  $n\text{-C}_5\text{H}_{12}$  and  $\text{H}_2$  for H atoms has been studied in the radiolysis and photolysis of neo- $\text{C}_5\text{H}_{12}$ - $\text{H}_2$  mixture at 77 K. The rate constants of these reactions in neopentane matrix are quite different from those of thermal H atom reaction, but similar to those of hot H atom reaction. 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 77 K.

## INTRODUCTION

We can easily investigate solid-state reactions at 77 K by irradiation with ultraviolet light or  $\gamma$ -rays. Recently quite interesting phenomena have been found in the radiolysis of neopentane-alkane mixture in the solid phase at 77 K<sup>(1,4)</sup>. When neopentane containing a small amount of alkane is  $\gamma$ -irradiated at 77 K, alkyl radicals from solute alkanes rather than neopentyl radical 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 the nonionic process<sup>(10)</sup>. 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<sup>(13)</sup>. (1) The mechanism of excitation transfer expects the formation of  $\text{D}_2$  in the radiolysis of neo- $\text{C}_5\text{H}_{12}$ - $\text{C}_4\text{H}_9\text{D}$  at 77 K. Though HD is formed remarkably in this system,  $\text{D}_2$  is not formed at all<sup>(13)</sup>. (2) When neo- $\text{C}_5\text{H}_{12}$ - $n\text{-C}_6\text{H}_{14}$  (1 mol%) mixture is irradiated at 77 K by  $\gamma$  rays, cyclohexyl radicals are mainly formed. When propylene is added to the mixture, the formation of the cyclohexyl radicals is suppressed, while  $\text{C}_3\text{H}_7$  radicals are produced complementarily by the addition of H atoms to propylene<sup>(9)</sup>. (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 alkane at 77 K<sup>(13,27)</sup>.

The selective hydrogen atom abstraction reaction by H atoms has proposed new problems in a 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

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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<sup>(8,25)</sup>. The research described herein was undertaken in order to obtain further informations about the nature of the reactive H atoms.

The previous studies of the selective hydrogen atom abstraction have been limited only to neopentane matrix and to the reaction 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 reaction of H and D atoms.

The formation of radicals in the radiolysis of pure TMB and 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%. Cyclopropane and ethane were more than 99.0 and 99.7% respectively. 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 halide (HX), such as HI, HBr, DBr, and HCl, the aqueous solution of the hydrogen halide was passed through  $P_2O_5$  and subjected to several trap-to-trap sublimation on the vacuum line.

UV illumination was provided by Toshiba medium-pressure or low-pressure mercury lamps.  $\gamma$ -Irradiation was done by Co-60 at a dose rate of  $4.2 \times 10^{19}$  eV/g hr.

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

## RESULTS

Table I shows the yields of radical by the reaction of hydrogen (or deuterium) atom in the radiolysis or photolysis of alkane mixtures in the solid phase at 77 K.  $t\text{-C}_4\text{H}_9$  radical is mainly formed in the photolysis of neo- $\text{C}_5\text{H}_{12}$  (or TMB)- $i\text{-C}_4\text{H}_{10}$ -hydrogen halide (HX), while a small amount of  $i\text{-C}_4\text{H}_9$  radical is also produced. Since the ratio of amounts of  $i\text{-C}_4\text{H}_9$  radicals to those of  $t\text{-C}_4\text{H}_9$  radicals increases with increasing the illumination time of ultraviolet light,  $i\text{-C}_4\text{H}_9$  radical is formed by the isomerization of  $t\text{-C}_4\text{H}_9$  radical which absorbs ultraviolet light<sup>(7)</sup>. The amounts of  $\text{C}_4\text{H}_9$  radicals represent a sum of  $t\text{-C}_4\text{H}_9$  and  $i\text{-C}_4\text{H}_9$  radicals, and are measured by double integration of the first-derivative esr signal of the radicals. Since only  $\text{C}_4\text{H}_9$  radicals are formed selectively in the photolysis of neo- $\text{C}_5\text{H}_{12}$  (or TMB)- $i\text{-C}_4\text{H}_{10}$ -HX, overlapping of the spectra of the solute radical and the neopentyl radical does not occur. neo- $\text{C}_5\text{H}_{11}$ ,  $\text{C}_3\text{H}_7$ ,  $i\text{-C}_4\text{H}_9$ , and  $\text{C}_2\text{H}_5$  radicals do not isomerize in the illumination of ultraviolet light. Therefore the relative yields of these radicals are obtained from the height of peaks in the esr spectrum. 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 halide.

The ratio of the yield of  $\text{C}_4\text{H}_9$  radical in the photolysis of neo- $\text{C}_5\text{H}_{12}$ - $i\text{-C}_4\text{H}_{10}$ -HX to that of neo- $\text{C}_5\text{H}_{11}$  radical in the photolysis of neo- $\text{C}_5\text{H}_{12}$ -HX is plotted in figure 1 against the kinetic energy of H atom. Plots, indicated by a, b, and c, represent the reactions of H atoms formed by the photolysis of HCl, HBr, and HI respectively. The photolysis was done with light of 253.7 nm from low pressure mercury lamp. The 253.7 nm radiation corresponds to 112.6 Kcal/mol, while the bond strengths of HCl, HBr, and HI are 103.1, 87.6, 71.3 Kcal/mol respectively. 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, if halogen atoms produced by photolysis are in ground states. When HI is

decomposed by 253.7 nm radiation, both a ground state I atom and an excited I atom are produced<sup>(1,2)</sup>. Therefore the energies of H atom are 41 or 20 Kcal/mol. Only the maximum energy of the H atom is shown in figure 1. d, e, and f represent the reactions due to H atoms produced by the photolysis of HI with a medium-pressure mercury lamp through Toshiba ultraviolet filters, such as UV31, UV29, and UV27 filters, respectively. When UV31 filter is used, the photolysis is caused by the light longer than 305 nm. The yields of radicals in the photolysis with UV31 filter are much higher than those in the photolysis with glass filter which cuts off the light shorter than 330 nm. Therefore the photolysis with UV31 filter is caused mainly by the light from 330 nm to 305 nm. It is determined by the similar fashion that the photolysis with UV29 or UV27 filters is caused mainly by the light from 330 to 280 nm, or the light from 290 to 255 nm, respectively.

Figure 2 shows the effect of HI on the formation of cyclohexyl radical in the radiolysis of neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub>-HI at 77 K. When neo-C<sub>5</sub>H<sub>12</sub> containing c-C<sub>6</sub>H<sub>12</sub> of 0.5, 1.0, and 2.0 (mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>) is  $\gamma$ -irradiated in the absence of HI, the yields of cyclohexyl radical are approximately the same in the three systems and they are taken as 10.

Figure 3 shows the effect of HI on the formation of cyclohexyl radicals in the photolysis of neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub>-HI at 77 K. The yields of cyclohexyl radicals at HI concentration of 0.25 (mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>) are taken as 10.

Figure 4a shows esr spectrum of  $\gamma$ -irradiated pure TMB at 77 K. The spectrum is similar to that reported by Gerola et al<sup>(5)</sup>. The spectrum of three broad lines, indicated by  $\Rightarrow$ , is ascribed to (CH<sub>3</sub>)<sub>3</sub>CC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub> (TMB $\cdot$ ) radical. The other unidentified spectrum, indicated by  $\ddagger$ , has been ascribed to an isomerized radical, i.e. (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub><sup>(5)</sup>, or a mixture of t-C<sub>4</sub>H<sub>9</sub> and (CH<sub>3</sub>)<sub>3</sub>CC(CH<sub>3</sub>)<sub>2</sub> radicals<sup>(21)</sup>. When TMB containing a small amount of isobutane or cyclohexane are  $\gamma$ -irradiated at 77 K, quite different spectra are obtained (figure 4b and c). The spectrum in figure 4b consists of three broad lines, which are attributable to TMB $\cdot$  radical, and eight narrow lines, indicated by  $\downarrow$ , with a splitting constant of 22 G. The spectrum of the eight lines is consistent with the reported spectrum for t-C<sub>4</sub>H<sub>9</sub> radical<sup>(1,4)</sup>. The spectrum in figure 4c consists of three broad lines, which are attributable to TMB $\cdot$  radical, and six broad lines, indicated by  $\downarrow$ , with a splitting constant of 22 G. The spectrum of the six lines is consistent with the reported spectrum for cyclohexyl radical<sup>(4,22)</sup>. When TMB containing a small amount of C<sub>3</sub>H<sub>8</sub>, i-C<sub>4</sub>H<sub>8</sub>, or C<sub>3</sub>H<sub>6</sub> is  $\gamma$ -irradiated at 77 K, C<sub>3</sub>H<sub>7</sub>, t-C<sub>4</sub>H<sub>9</sub>, or C<sub>3</sub>H<sub>7</sub> radical is clearly observed respectively.

Figure 5a shows esr spectrum of  $\gamma$ -irradiated pure cyclopropane at 77 K. The spectrum may be ascribed to C<sub>3</sub>H<sub>5</sub> radicals<sup>(4)</sup>. When cyclopropane containing a small amount of ethane is  $\gamma$ -irradiated at 77 K, a typical spectrum of ethyl radical<sup>(1,4)</sup>, indicated by  $\downarrow$ , is clearly observed in figure 5b.

## DISCUSSION

### Selective Formation of Solute Radical in the Radiolysis and Photolysis of Alkane Mixture at 77 K.

Table I shows that the selective formations of solute radicals in the radiolysis of alkane mixture are observed also in isobutane, 2,2,3,3-tetramethylbutane (TMB), and cyclopropane matrices besides neopentane matrix. H atoms, produced by the photolysis of HI or HBr, react selectively with a small amount of the solute alkane in neo-C<sub>5</sub>H<sub>12</sub>, i-C<sub>4</sub>H<sub>10</sub>, and TMB matrices. The H atoms migrate a long distance through the matrix without reacting with the matrix alkane. Though C<sub>2</sub>H<sub>5</sub> radical is mainly formed in the radiolysis of c-C<sub>3</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>6</sub> (figure 5), the C<sub>2</sub>H<sub>5</sub> radical is not observed in the photolysis of c-C<sub>3</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>6</sub>-HI (HBr or DBr). It is probable that the ultraviolet light does not enter into the polycrystal of cyclopropane and that the amount of the decomposition of hydrogen halide is extremely small. This is based on the following observation. Firstly, C<sub>3</sub>H<sub>5</sub> radical or any radical is not produced at all by the illumination of c-C<sub>3</sub>H<sub>6</sub>-HI (HBr or DBr) with ultraviolet light at 77 K. Secondly, when c-C<sub>3</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>6</sub>-HI is illuminated with ultraviolet light, the color of I<sub>2</sub>, produced by the decomposition of HI, is observed only at the surface of the crystal.

All of the matrix alkanes in Table I are polycrystalline at 77 K. It is concluded that the selective hydrogen atom abstraction reaction is not limited to the neopentane matrix, but the reaction can be found also in other polycrystalline alkanes. Table I shows that D atoms, produced by the decomposition of DBr, also react selectively with the solute alkane.

#### 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 informations about the nature of the H atoms. The following results have been obtained here.

##### I) Effect, of kinetic energy of H atoms on the hydrogen atom abstraction reaction.

When neo-C<sub>5</sub>H<sub>12</sub>-i-C<sub>4</sub>H<sub>10</sub>-HX mixture is illuminated with ultraviolet light at 77 K, t-C<sub>4</sub>H<sub>9</sub> radicals are formed by the following reactions.



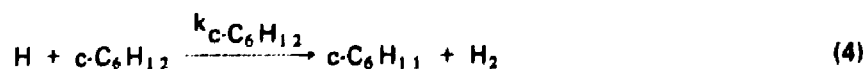
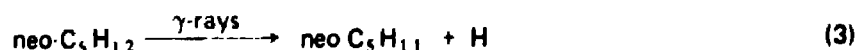
The absorbance and decomposition efficiency in the illumination of ultraviolet light may be different in various hydrogen halides and various wavelengths. In order to take these factors into consideration, the yields of neopentyl radical in the photolysis of neo-C<sub>5</sub>H<sub>12</sub>-HX were used tentatively as relative standard values. The ratio of the yield of t-C<sub>4</sub>H<sub>9</sub> radical in neo-C<sub>5</sub>H<sub>12</sub>-i-C<sub>4</sub>H<sub>10</sub>-HX system to that of neo-C<sub>5</sub>H<sub>11</sub> radical in neo-C<sub>5</sub>H<sub>12</sub>-HX system is plotted in figure 1 against the kinetic energy of H atoms. The reactions are affected remarkably by the difference of the kinetic energy of H atoms. The reaction (2) occurs more favorably with decreasing the kinetic energy of H atoms.

If H atoms in reaction (2) are thermal, the results in figure 1 can be explained by the following mechanisms. Since H atoms, produced by photolysis, has initially some kinetic energy, the initial hot H atoms are thermalized at 77 K and then react with i-C<sub>4</sub>H<sub>10</sub> in reaction (2). The thermalization process may be more favorable with decreasing the initial kinetic energy of the H atoms.

If H atoms in reaction (2) are hot, the results in figure 1 can be explained by the ability to get into "channel" which is described fully in the last part of this section.

##### II) Competitive reaction of H atoms with HI and c-C<sub>6</sub>H<sub>12</sub> in neo-C<sub>5</sub>H<sub>12</sub> matrix at 77 K.

Figure 2 shows that the yields of cyclohexyl radicals in the radiolysis of neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub> mixture are not affected by the addition of HI. As described in a section of Introduction, the previous studies<sup>(14)</sup> on the radiolysis of neopentane-alkane mixture at 77 K have concluded that excited neopentane, formed by  $\gamma$ -irradiation, produces a H atom and a neopentyl radical. The H atom migrates through 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<sub>6</sub>H<sub>11</sub> radicals<sup>(14)</sup>.



**Table I**  
**Formation of Solute Radical by the Reaction of Hydrogen**  
**(or Deuterium) Atoms in the Radiolysis or Photolysis of Alkane**  
**Mixtures at 77 K<sup>a</sup>.**

Sample	Species of Radical	Methods of production of H (or D) atoms				
		$\gamma$ -Irradiation <sup>b</sup>	Ultraviolet illumination <sup>c</sup>			
			HI	HBr	DBr	HCl
neo - C <sub>5</sub> H <sub>12</sub> - i - C <sub>4</sub> H <sub>10</sub> (2) <sup>d</sup>	C <sub>4</sub> H <sub>9</sub>	Clearly observed <sup>e</sup>	10.0	4.0	3.1	0.9
neo - C <sub>5</sub> H <sub>12</sub>	neo - C <sub>5</sub> H <sub>11</sub>	Clearly observed <sup>e</sup>	10.0	3.0	4.1	< 0.5
i - C <sub>4</sub> H <sub>10</sub> - C <sub>3</sub> H <sub>8</sub> (2) <sup>d</sup>	C <sub>3</sub> H <sub>7</sub>	Clearly observed <sup>e</sup>	10.0	2.0	1.9	
i - C <sub>4</sub> H <sub>10</sub>	iso - C <sub>4</sub> H <sub>9</sub>	Clearly observed <sup>e</sup>	10.0	2.6	5.5	
TMB - i - C <sub>4</sub> H <sub>10</sub> (5) <sup>d</sup>	C <sub>4</sub> H <sub>9</sub>	Clearly observed <sup>f</sup>	10.0	2.1	2.6	
c - C <sub>3</sub> H <sub>6</sub> - C <sub>2</sub> H <sub>6</sub> (4) <sup>d</sup>	C <sub>2</sub> H <sub>5</sub>	Clearly observed <sup>f</sup>	—	—	—	

- a) Yields are averages of two or more runs.
- b) Alkane mixtures in the absence of hydrogen halide was irradiated at 77 K with  $\gamma$ -ray. H atoms are produced by the radiolysis of solvent alkane.
- c) H (or D) atoms are produced by the photolysis of hydrogen halide with light of 253.7 nm. Concentrations of hydrogen halide in neo-C<sub>5</sub>H<sub>12</sub>, i-C<sub>4</sub>H<sub>10</sub>, TMB, and c-C<sub>3</sub>H<sub>6</sub> matrices are 0.5, 0.2, 0.5, and 0.5 mol/100 mol of solvent alkane. Yield of radical in HI system is taken as 10. Illumination times of neo-C<sub>5</sub>H<sub>12</sub>, i-C<sub>4</sub>H<sub>10</sub>, TMB, and c-C<sub>3</sub>H<sub>6</sub> matrices with UV light from 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 figures 4 and 5

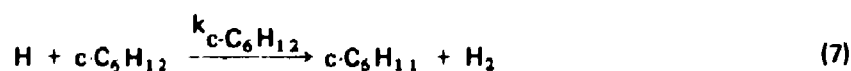


When HI is present in neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub> system, occurrence of the reaction (5) is expected, because both hot and thermal H atoms react easily with HI in the gas phase.



H atoms produced by the radiolysis of neo-C<sub>5</sub>H<sub>12</sub> at 77 K, however, do not react with HI, but with c-C<sub>6</sub>H<sub>12</sub> (figure 2) It can be estimated from the results in figure 2 that  $k_{\text{HI}}/k_{\text{c-C}_6\text{H}_{12}}$  is less than 0.05 and is given in the first line in Table II.

Figure 3 shows that the yields of cyclohexyl radical in the photolysis of neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub>-HI mixture reach a maximum at HI concentration of 0.25 (mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>) and then decrease gradually with increasing the concentration of HI. This results can be explained in terms of competitive reactions between HI and cyclohexane for H atoms. A possible kinetic scheme is as follows:



If the rate of reaction (6) is represented by  $r$ , the following kinetic equation is obtained:

$$\frac{1}{[\text{c-C}_6\text{H}_{11}]} = \frac{1}{r} + \frac{k_{\text{HI}}}{r k_{\text{c-C}_6\text{H}_{12}}} \frac{[\text{HI}]}{[\text{c-C}_6\text{H}_{12}]}$$

The linear relationship between  $1/[\text{c-C}_6\text{H}_{11}]$  and  $[\text{HI}]/[\text{c-C}_6\text{H}_{12}]$  is obtained in the HI concentration higher than 0.25 (mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>). When concentrations of c-C<sub>6</sub>H<sub>12</sub> are 1.0 and 2.0 (mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>),  $k_{\text{HI}}/k_{\text{c-C}_6\text{H}_{12}}$  are 1.2 and 1.0 respectively. The mean value for  $k_{\text{HI}}/k_{\text{c-C}_6\text{H}_{12}}$  is given in the second line in Table II.

There are many studies on the reaction of hot atom produced by the photolysis of hydrogen halides in the gas phase. Carter et al.<sup>(3)</sup> reported that  $k_{\text{DI}}/k_{\text{C}_2\text{H}_6}$  is 1.45 for reactions of hot D atom with DI and C<sub>2</sub>H<sub>6</sub>. Hong et al.<sup>(6)</sup> reported that  $k_{\text{HI}}/k_{\text{C}_2\text{D}_5\text{H}}$  is 7.0 for reaction of hot H atom with HI and C<sub>2</sub>D<sub>5</sub>H. Rebert et al.<sup>(19)</sup> reported that  $k_{\text{C}_2\text{D}_6}/k_{\text{c-C}_6\text{D}_{12}}$  is 0.16 for reactions of hot CH<sub>3</sub> radical with C<sub>2</sub>D<sub>6</sub> and c-C<sub>6</sub>D<sub>12</sub>. Therefore  $k_{\text{HI}}/k_{\text{c-C}_6\text{H}_{12}}$  is ranged approximately from 1.45 x 0.16 (= 0.23) to 7.0 x 0.16 (= 1.1). These values are given in the third line in Table II.

Thermal H atoms react quite easily with HI in the gas phase. According to the study by Sullivan<sup>(24)</sup>, the rate constant of this reaction can be expressed by  $k_{\text{HI}} = 10^{12.05} T^{0.5} \exp(-E/RT)$ . The activation energy (E) is nearly zero or 0.48 Kcal/mol. The activation energy for a reaction of thermal H atom with cyclonexane is, however, about 8 Kcal/mol<sup>(8,25)</sup>. If it is assumed that the pre-exponential factor of  $k_{\text{c-C}_6\text{H}_{12}}$  is approximately the same as that of  $k_{\text{HI}}$  and the activation energy for the reaction of H atom with HI is 0 - 1 Kcal/mol,  $k_{\text{HI}}/k_{\text{c-C}_6\text{H}_{12}}$  at 77 K amounts to  $10^{20} - 10^{23}$  which is given in the 4th line in Table II.

**Table II**  
Competitive Reaction between HI and  
c-C<sub>6</sub>H<sub>12</sub> for H atom at 77 K.

Species of H atom	$k_{HI}/k_{c-C_6H_{12}}$
H atom produced by radiolysis of neo-C <sub>5</sub> H <sub>12</sub> at 77 K	< 0.05
H atom produced by photolysis of HI in neo C <sub>5</sub> H <sub>12</sub> matrix at 77 K	1.1
Hot H atom <sup>a</sup>	0.23 - 1.1
Thermal H atom (A) <sup>b</sup>	$10^{20} - 10^{23}$
Thermal H atom (B) <sup>c</sup>	$10^{11} - 10^{14}$

a. Hot H atom was produced by photolysis of HI in the gas phase.

b.  $k_{HI}/k_{c-C_6H_{12}}$  was estimated from the data in the gas phase.

c.  $k_{HI}/k_{c-C_6H_{12}}$  was estimated from the reaction of thermal methyl radical in the solid phase at 77 K.

Recently it has been reported that thermal CH<sub>3</sub> radical abstracts H atom from CH<sub>3</sub>OH<sup>(2)</sup> and 3-methylpentane<sup>(16,23)</sup> at 77 K by quantum mechanical tunneling. The rate constant of the reaction can be estimated from the decay time of CH<sub>3</sub> radical to be about  $10^{-1} \text{ mol}^{-1} \text{ cc sec}^{-1}$  at 77 K. Assuming that thermal H atom reacts with cyclohexane by the quantum mechanical tunneling and the rate constant of thermal H atom is the same order of magnitude as that of thermal CH<sub>3</sub> radical,  $k_{HI}/k_{c-C_6H_{12}}$  at 77 K may be  $10^{11} - 10^{14}$  which is given in the 5th line in Table II.

Though a number of studies on the reaction rate have been undertaken in the gas and liquid phases at temperature 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 activation energy changes drastically in the solid alkane at 77 K as compared with in 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 II show that  $k_{HI}/k_{c-C_6H_{12}}$  of H atoms produced by the radiolysis or photolysis in neopentane matrix at 77 K are quite different from the values expected from the reaction of thermal H atom, 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 H atoms, produced by the radiolysis or photolysis in neopentane matrix at 77 K, are thermal. In this case, the thermal H atoms react more easily with cyclohexane than hydrogen halide, though the activation energy for the former reaction is 8 Kcal/mol and that for the latter reaction is nearly zero.

### III) Possibility of H atom abstraction by thermal radical in neopentane matrix at 77 K.

Since activation energies for hydrogen atom abstraction reaction from alkane by thermal atom or radical are 7 - 10 Kcal/mol<sup>(8,25)</sup>, it may be concluded from the previous theory of reaction kinetics that the reaction does not occur at all at 77 K.

Recent findings<sup>(2,16,23)</sup>, however, indicate that thermal methyl radical abstract hydrogen atom from the solvent molecule even at 77 K. We have examined here the possibility that thermal methyl radicals react in neo-C<sub>5</sub>H<sub>12</sub>-alkane mixtures at 77 K. When neo-C<sub>5</sub>H<sub>12</sub>-C<sub>2</sub>H<sub>6</sub> (2 mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>)-CH<sub>3</sub>Br (0.1 mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>) is irradiated with UV light at 77 K, CH<sub>3</sub> radical is formed by the photolysis of CH<sub>3</sub>Br. The thermal CH<sub>3</sub> decays very slowly at 77 K. The half-life for decay is about 150 hr, which is extremely large as compared to 0.2–0.3 hr in 3-methylpentane at 77 K<sup>(16,23)</sup>. When CH<sub>3</sub> radical decreases, the formation of neo-C<sub>5</sub>H<sub>11</sub> or C<sub>2</sub>H<sub>5</sub> 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 neo-C<sub>5</sub>H<sub>12</sub>-C<sub>2</sub>H<sub>6</sub> mixture at 77 K.

#### IV) Selective hydrogen atom abstractions by H atoms in i-C<sub>4</sub>H<sub>10</sub>-C<sub>3</sub>H<sub>8</sub> mixture at 77 K.

When i-C<sub>4</sub>H<sub>10</sub> containing HI is irradiated with UV light at 77 K, H atom produced by the photolysis of HI abstracts hydrogen atom from primary C-H bond of i-C<sub>4</sub>H<sub>10</sub> to form i-C<sub>4</sub>H<sub>9</sub> radical. When a small amount of C<sub>3</sub>H<sub>8</sub> is added to the mixture, the H atom react selectively with the solute propane (Table I and ref.<sup>(27)</sup>) and the formation of i-C<sub>4</sub>H<sub>9</sub> radical is suppressed.



The H atom produced by the photolysis of HI has initial kinetic energy of 20 or 41 Kcal/mol, depending on whether iodine atom is produced in the excited state or in the ground state. In the radiolysis of i-C<sub>4</sub>H<sub>10</sub>-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<sub>4</sub>H<sub>10</sub><sup>(28)</sup>.



The H atom produced by dissociative electron attachment has 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 primary H atom from i-C<sub>4</sub>H<sub>10</sub>, while the H atom with low energy abstracts tertiary H atom. The hot H atom reacts selectively with C<sub>3</sub>H<sub>8</sub>, when C<sub>3</sub>H<sub>8</sub> is present in the system.

#### V) Migration of H atoms in the crystal.

It is concluded by the above discussions 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 hydrogen atom abstraction reaction of H atoms in the

neopentane-isobutane mixture at 77 K occurs more easily with decreasing the kinetic energy of the H atoms. (c) The selective reaction of the 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<sup>(1c)</sup>. The selective reaction has been found only in polycrystalline matrices (Table II).

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<sup>(1c)</sup>. The possibility of hot H atoms will be described here in order to compensate the previous discussion<sup>(1c)</sup>.

One plausible explanation will be given by the idea of "channelling"<sup>(11,17,20)</sup>. Crystalline structure of neopentane at 77 K consists of face-centered cubic unit cells with a lattice constant of 11.4 Å<sup>(15)</sup>. Since a chemical structure of neopentane is symmetrical, the structure is depicted here as a sphere. Projection of molecular arrangement of the three principal planes of f.c.c. lattice of neopentane are shown in Figure 6. A neopentane molecule is represented by a large circle where a line of the circle is the most probable position of electrons of H atoms in neopentane molecules. Top and second layers are depicted in the projections of [110] and [100] planes. Because third, fourth layers are repetitions of the top and second layers. Top, second, and third layers are depicted in the projection of [111] plane. A smaller circle, depicted by ●, represents a hot hydrogen atom with 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 [100] 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.

According to the channelling theory, the critical angle that the hot H atoms get into the channel increases with decreasing the kinetic energy of the H atoms, that is to say, channelling occurs more easily with decreasing the kinetic energy. Therefore the yields of the solute alkyl radicals increase with decreasing the kinetic energy of the H atoms, as shown in Figure 1.

The selective hydrogen atom abstraction reaction by hot H atom in neopentane-alkane mixture is not observed in the liquid phase<sup>(1c)</sup>. This phenomenon can be explained by the channelling 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.<sup>(5)</sup> reported the esr spectrum of  $\gamma$ -irradiated TMB at 77 K. Since  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\dot{\text{C}}\text{H}_2$  (TMB $\cdot$ ) and  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{C}}(\text{CH}_3)_2$  radicals are formed, they considered that firstly C-H bond rupture occurs in the radiolysis of TMB and then the isomerization of TMB $\cdot$  radical produces  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{C}}(\text{CH}_3)_2$  radical. Shiraishi et al.<sup>(21)</sup> reported  $t\text{-C}_4\text{H}_9$ ,  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2$ , and TMB $\cdot$  radicals in the radiolysis of solid TMB. They considered that the free radicals are formed by C-C bond rupture as well as C-H bond rupture in the radiolysis of TMB.

The esr spectrum in Figure 4a consists of TMB $\cdot$  and the unidentified radical which has been ascribed to  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{C}}(\text{CH}_3)_2$ <sup>(5)</sup> or a mixture of  $t\text{-C}_4\text{H}_9$  and  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2$ <sup>(21)</sup>. 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 (Figure 4b and c). Therefore it seems that the unidentified radical is neither formed by the isomerization of TMB $\cdot$  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.

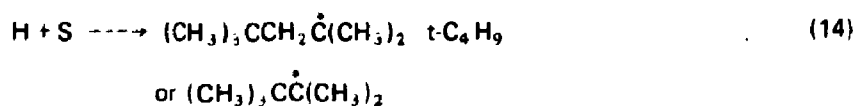
The following observations obtained here show that the solute alkyl radical is not formed by the energy transfer from the irradiated TMB to the solute, but by the selective hydrogen atom abstraction by H atoms from the solute alkane.

1) When TMB containing a small amount of propane is  $\gamma$ -irradiated at 77 K, propyl radical is formed. An ionization potential of TMB has not been reported previously. If we assume that the value is approximately the same as that of 2,2,4-trimethylpentane 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<sup>(28)</sup> which is lower than the ionization potential (11.07 eV)<sup>(28)</sup> of propane. The energy level of the first excited state of TMB is 8.0 eV<sup>(18)</sup> which is lower than that (8.9 eV)<sup>(18)</sup> of propane. Therefore, assuming that the relative magnitude of the ionization potential and the first excited state is held in the solid phase, the ordinary charge transfer from TMB to C<sub>3</sub>H<sub>8</sub> cannot occur.

2) When TMB containing a small amount of isobutene or propylene is irradiated with  $\gamma$ -ray at 77 K, the formation of the unidentified radical is suppressed, while t-C<sub>4</sub>H<sub>9</sub> or C<sub>3</sub>H<sub>7</sub> radical is produced complementarily by the addition of H atoms to isobutene or propylene.

3) When TMB (i-C<sub>4</sub>H<sub>10</sub> (5 mol/100 mol of TMB)-HX (0.5 mol/100 mol of TMB)) is irradiated with UV light at 77 K, H atoms produced by the photolysis of hydrogen halide react selectively with i-C<sub>4</sub>H<sub>10</sub> to form t-C<sub>4</sub>H<sub>9</sub> radical (Table I).

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



Reactive H atoms produced by the decomposition of TMB (reaction (13)) react selectively with impurities (S) to form  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{C}}(\text{CH}_3)_2$ , t-C<sub>4</sub>H<sub>9</sub> or  $(\text{CH}_3)_3\dot{\text{C}}(\text{CH}_3)_2$  in the radiolysis of pure TMB. When alkane (RH), such as C<sub>3</sub>H<sub>8</sub>, i-C<sub>4</sub>H<sub>10</sub>, and n-C<sub>5</sub>H<sub>12</sub>, is added to TMB, the H atoms react selectively with the solute to form alkyl radical (R·).

## ACKNOWLEDGEMENT

The authors wish to express their appreciation to Professor Fausto W. Lima of Instituto de Energia Atômica in São Paulo for his encouragement. The authors wish to express their appreciation to Professor Noriaki Ito and Dr. Kenji Morita of Nagoya University for their fruitful discussions.

## RESUMO

A reação seletiva de abstração do átomo de hidrogênio por átomos de H, os quais são produzidos a 77°K na radiólise de alcanos ou na fotólise de haletos de hidrogênio, tem sido observado em matrizes como isobutano, 2,2,3,3-tetrametilbutano (TMB) ciclopropano além da matriz de neopentano. A reação seletiva de abstração do átomo de H no sistema neopentano (matriz)/isobutano(soluto) é afetada pela diferença de energia cinética dos átomos de H. A reação ocorre favoravelmente com decréscimo de energia cinética dos átomos de H. A reação competitiva entre n-C<sub>5</sub>H<sub>12</sub> e HI por átomos de H tem sido estudada na radiólise e fotólise dos sistemas neoC<sub>5</sub>H<sub>12</sub>/n-C<sub>5</sub>H<sub>12</sub>/HI a 77°K. As constantes de velocidade destas reações em matrizes de neopentano são muito diferentes daquelas onde participa o átomo de H "thermal", mas são similares às reações com átomos de H "hot". A importância da reação seletiva de abstração do átomo de H por átomos de H é assinalada na formação do radical na radiólise de TMB puro a 77°K.

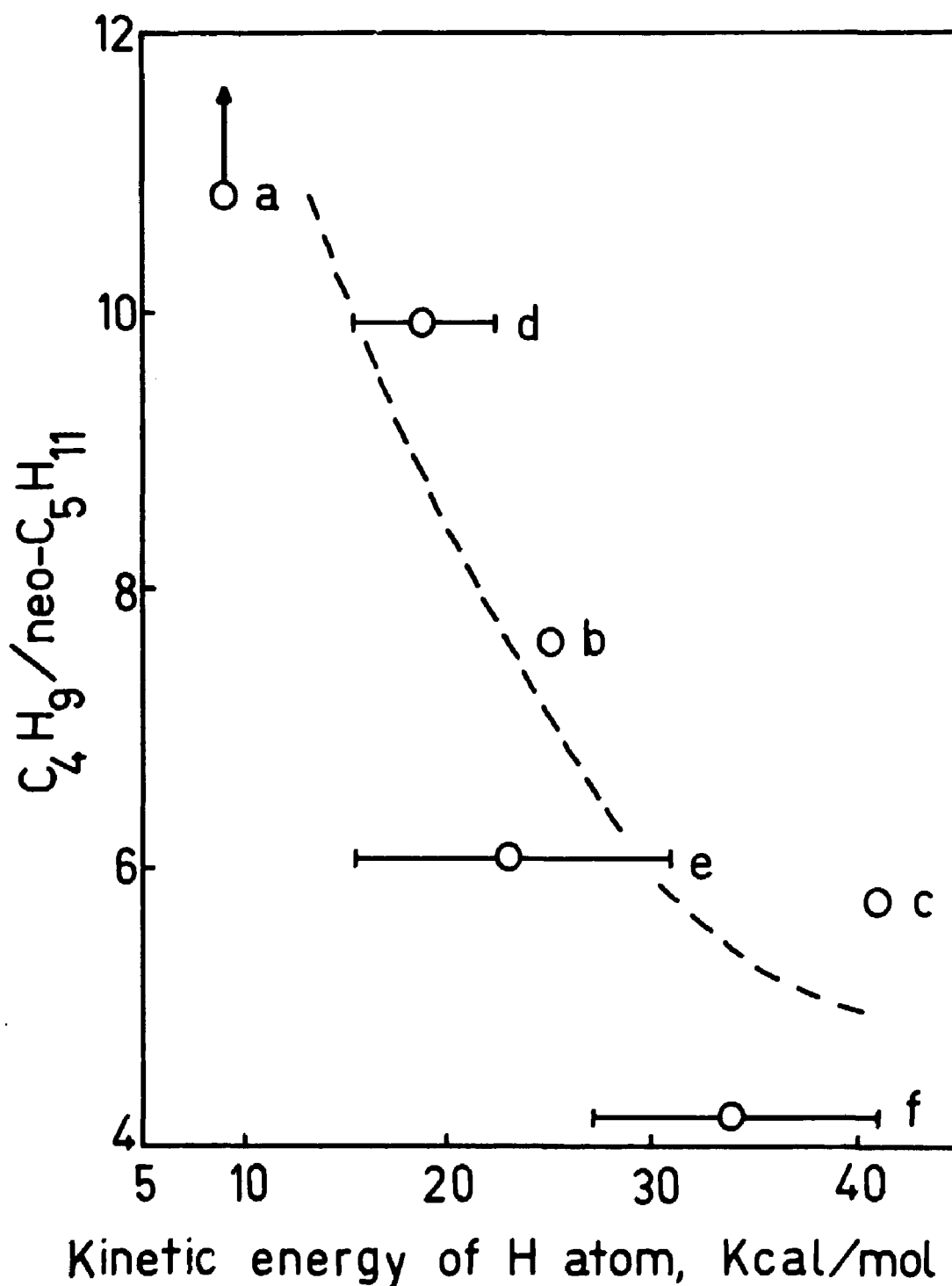


Figure 1 - Effect of kinetic energy of H atom on the ratio of the yield of  $C_4H_9$  radicals in the photolysis of  $neo-C_5H_{12}$ - $i-C_4H_{10}$ -HX to that of  $neo-C_5H_{11}$  radicals in the photolysis of  $neo-C_5H_{12}$ -HX at 77 K. Concentrations of  $i-C_4H_{10}$  and HX are 2 and 0.5 mol/100 of  $neo-C_5H_{12}$ .

- a) H atom produced by the photolysis of HCl with 253.7 nm radiation.
- b) H atom produced by the photolysis of HBr with 253.7 nm radiation.
- c) H atom produced by the photolysis of HI with 253.7 nm radiation.
- d) H atom produced by the photolysis of HI with 330 - 305 nm radiation.
- e) H atom produced by the photolysis of HI with 330 - 280 nm radiation.
- f) H atom produced by the photolysis of HI with 290 - 255 nm radiation.

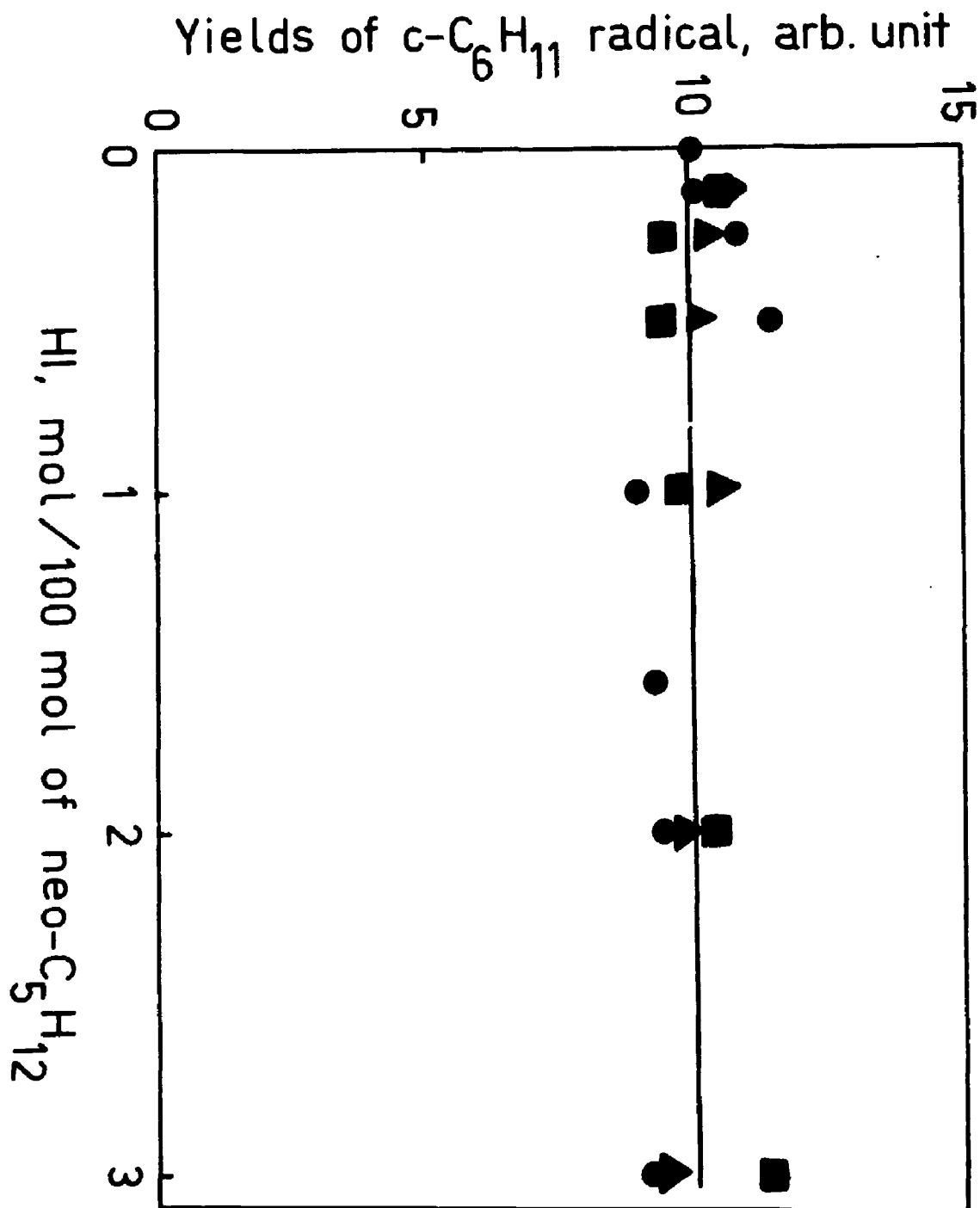


Figure 2 - Effect of HI on the yield of  $c\text{-C}_6\text{H}_{11}$  radicals in the radiolysis of neo-C<sub>5</sub>H<sub>12</sub>-c-C<sub>6</sub>H<sub>12</sub> mixture at 77 K with a dose of  $2.1 \times 10^{19}$  eV/g.

- , Concentration of  $c\text{-C}_6\text{H}_{12}$  is 0.5 mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>.
- , Concentration of  $c\text{-C}_6\text{H}_{12}$  is 1.0 mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>.
- ▲, Concentration of  $c\text{-C}_6\text{H}_{12}$  is 2.0 mol/100 mol of neo-C<sub>5</sub>H<sub>12</sub>.

(30)

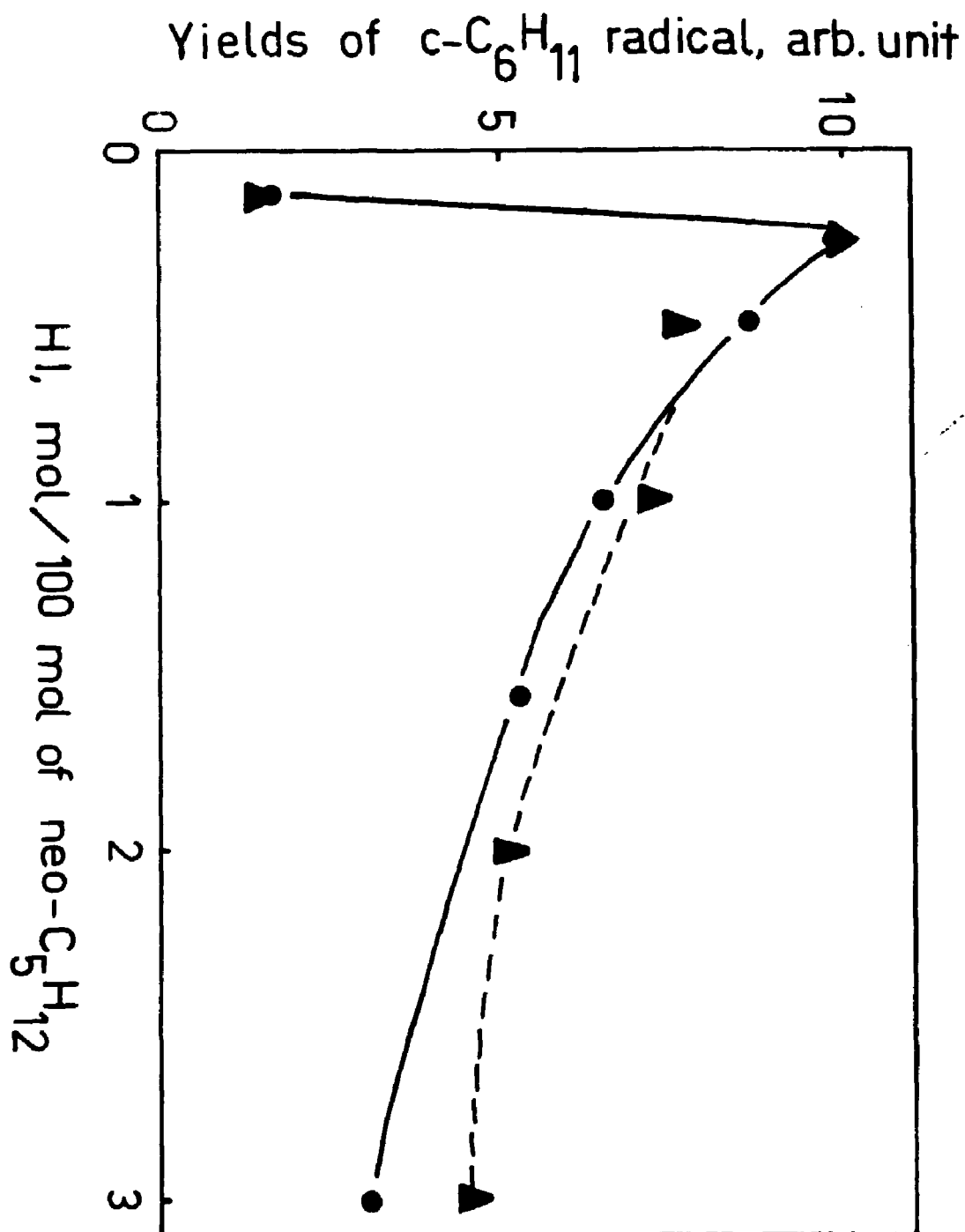


Figure 3 – Effect of HI on the yield of  $c\text{-C}_6\text{H}_{11}$  radicals in the photolysis of  $\text{neo-C}_5\text{H}_{12}\text{-}c\text{-C}_6\text{H}_{12}\text{-HI}$  mixture at 77 K.

- ,  $c\text{-C}_6\text{H}_{12}$  concentration is 1.0 mol/100 mol of  $\text{neo-C}_5\text{H}_{12}$ .
- ▲—▲,  $c\text{-C}_6\text{H}_{12}$  concentration is 2.0 mol/100 mol of  $\text{neo-C}_5\text{H}_{12}$ .



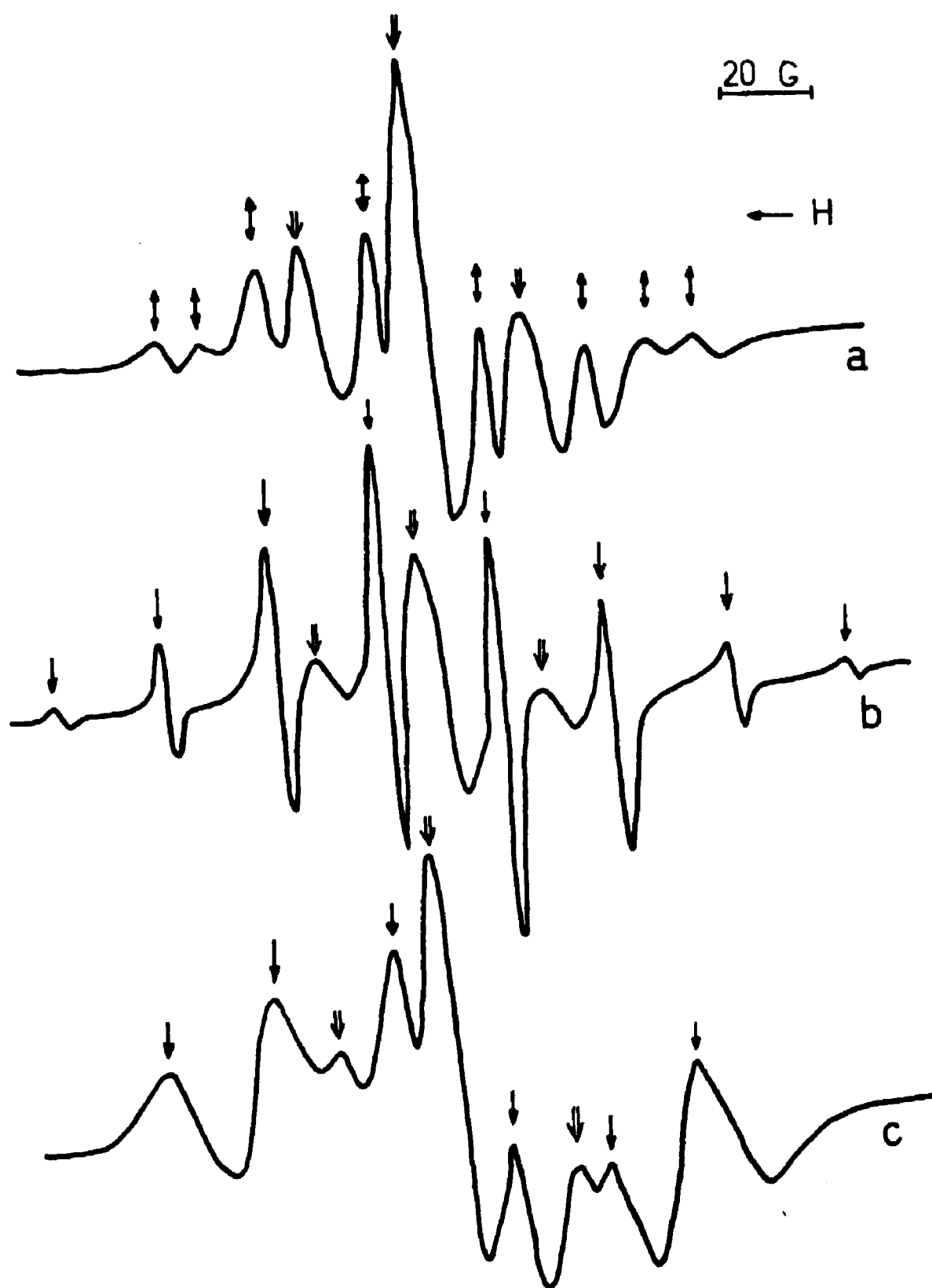


Figure 4 - ESR spectra of  $\gamma$ -irradiated TMB and TMB-alkane mixtures at 77 K with a dose of  $1.8 \times 10^{19}$  eV/g. Relative sensitivities of spectrometer for a, b and c are approximately the ratios of 2 : 1 : 1.5 respectively. a) pure TMB; b) TMB- $i$ -C<sub>4</sub>H<sub>10</sub> (5.4 mol/100 mol of TMB); c) TMB- $c$ -C<sub>6</sub>H<sub>12</sub> (5.8 mol/100 mol of TMB).

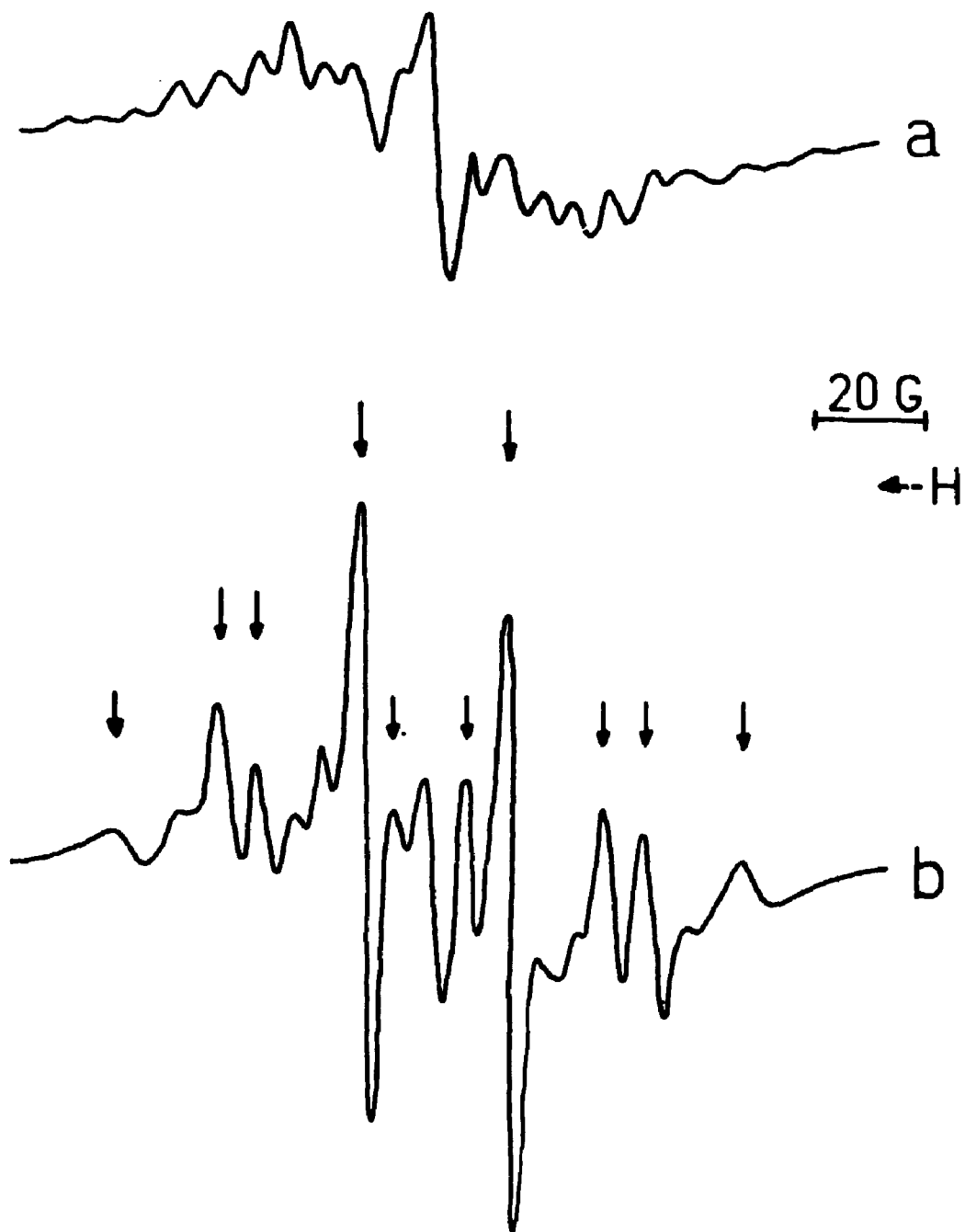


Figure 6 - ESR spectra of  $\gamma$ -irradiated  $c\text{-C}_3\text{H}_6$  and  $c\text{-C}_3\text{H}_6\text{-C}_2\text{H}_6$  mixtures at 77 K with a dose of  $1.8 \times 10^{19}$  eV/g. Sensitivities of spectrometer for a and b are approximately the same. a) pure  $c\text{-C}_3\text{H}_6$ ; b)  $c\text{-C}_3\text{H}_5\text{-C}_2\text{H}_6$  (4 mol/100 mol of  $c\text{-C}_3\text{H}_6$ ). This spectrum was done by M. Fukaya and T. Miyazaki previously.

(33)

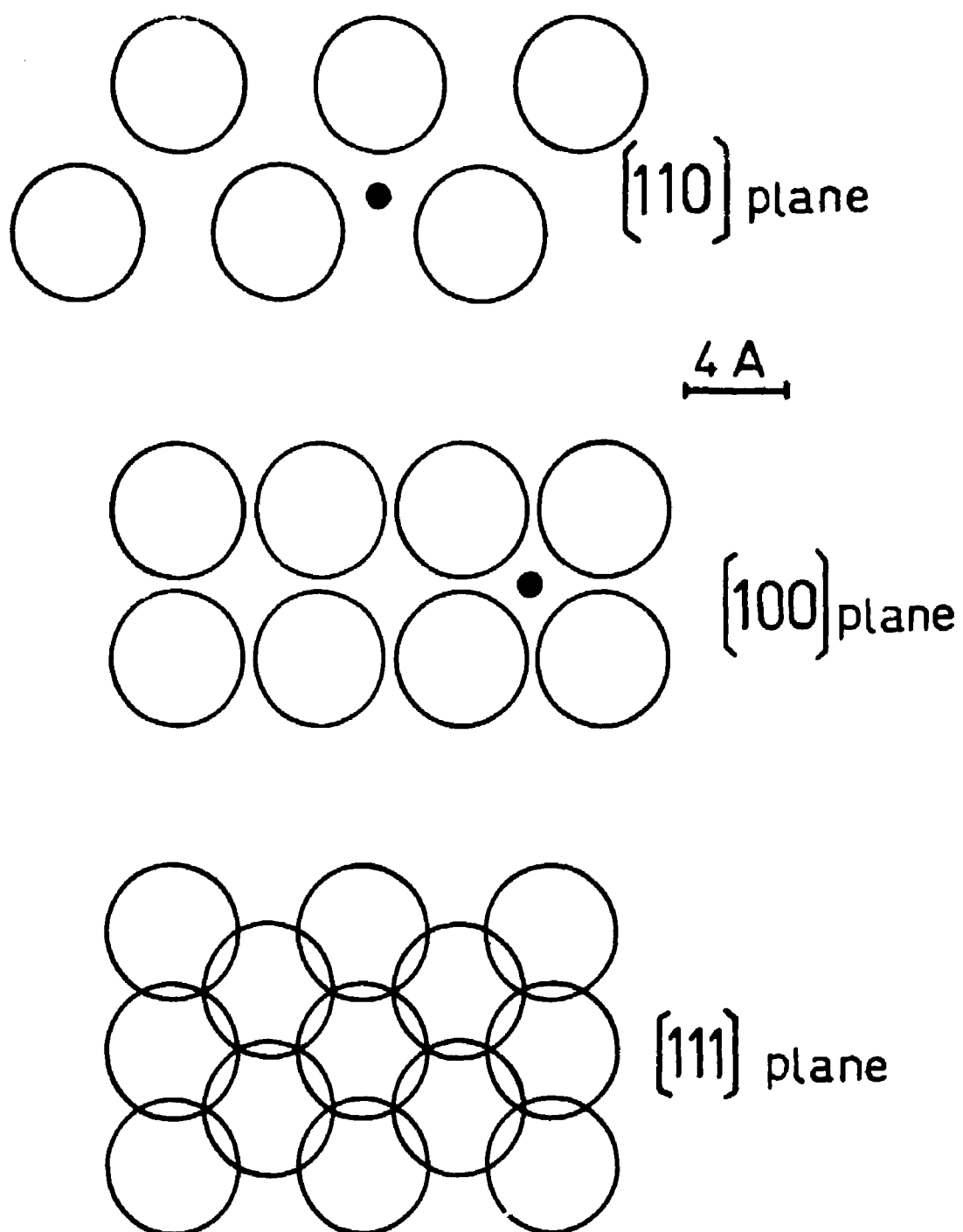


Figure 6 – Molecular arrangement of the three principal planes of the f.c.c. lattice of crystalline neopentane at 77 K

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