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Selective Hydrogen Atom Abstraction by H Atoms in Radiolysis and Photolysis at 77 K: Decane-d_{22}, Tetramethylsilane, and Xenon Matrices

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The selective formation of HD and solute radicals in the radiolysis of n-$C_{10}D_{22}$ doped with n-$C_{10}H_{22}$ at 77 K is explained quantitatively by the mechanism of a selective hydrogen-atom-abstraction reaction by D atoms. The selective hydrogen-atom abstraction by H atoms is found also in tetramethylsilane and xenon matrices as well as in the alkane matrix. The rate constants of the abstraction reaction by H atoms are compared with the bond energies of the solvent and solute molecules. The bond energy of the solvent molecule is always higher than that of the solute molecule. Even if the difference in the bond energy between the solvent and the solute is very small, the k(solute)/k(solvent) ratio is quite large. The k(solute)/k(*neo*-C_5H_{12}) ratios for different solutes in a neopentane matrix are not influenced by the differences in the bond energy among the solutes. Since an isotope effect on the selective hydrogen-atom abstraction reaction is small, the effect may diminish the possibility of the quantum mechanical tunneling abstraction by thermal H atoms. The energy loss of hot H atoms in a Xe matrix is discussed.

Since hydrogen and alkyl radicals are the predominant products in the radiolysis of alkanes in the solid phases, C–H bond rupture, with the resultant formation of the H atom, is one of the most important processes in the radiolysis of solid hydrocarbons. H atoms may play also an important role in the radiation effect of polymers[1)] and biological solid substances.[2)]

Recently Miyazaki *et al.* have found a quite interesting phenomenon concerning a hydrogen-atom abstraction reaction by H atoms in solid alkane mixtures at 77 K.[3)] When H atoms are produced at 77 K by the UV-photolysis of hydrogen halide or by the radiolysis of solvent neopentane, the H atoms react selectively with the solute alkane, resulting in the formation of solute radicals. The experimental basis for the reaction of the H atoms has been described fully in previous papers.[3a,b,e)] This phenomenon has also been found in several alkane matrices, such as neopentane,[3a,b)] isobutane,[3a,c)] 2,2,3,3-tetramethylbutane,[3c)] cyclopropane,[3c)] cyclohexane,[3d)] pentane,[3d)] and 3-methylpentane-d_{14}.[4)]

Though a number of studies of the reaction of H atoms have been undertaken previously in gas and liquid phases at temperatures higher than room temperature, the studies in the solid phase at low temperatures have been limited to a few examples. The selective hydrogen-atom-abstraction reaction by H atoms in the solid phase at 77 K has raised new problems concerning its reaction kinetics. If hot H atoms are involved in the reaction, they must migrate a long distance through the alkane matrix 77 K without losing their kinetic energies. If thermal H atoms are involved, the activation energy for hydrogen-atom abstraction must be nearly zero in the alkane matrix at 77 K, though the value amounts to 7—10 kcal/mol in the gas phase.[5)] Therefore, the study of the behavior of H atoms in the solid phase is important in solid-reaction kinetics as well as in solid-radiation chemistry.

The research described herein was undertaken in order to obtain further information about the reaction of the H atoms at 77 K. Answers to the following three questions have been sought: (1) Lund *et al.*[6)] have reported that when n-$C_{10}D_{22}$ doped with a small amount of n-$C_{10}H_{22}$ is γ-irradiated at 77 K, solute $C_{10}H_{21}$ radicals are formed in a much higher yield than would be expected from the concentration. They ascribed this result to the excitation transfer from deuterated to protiated molecules. The results, however, can be explained also by a selective hydrogen-atom-abstraction reaction by D atoms. Recently it has been reported independently by two groups[7,8)] that HD is formed selectively in the radiolysis of n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures at 77 K. The results were interpreted qualitatively by quite different mechanisms: a mechanism of excitation transfer[7)] and one of selective hydrogen-atom abstraction by the D atom.[8)] In order to discriminate the two mechanisms, the estimation of the yield of hydrogen *via* the molecular detachment process in the radiolysis of pure n-$C_{10}D_{22}$ and n-$C_{10}H_{22}$ at 77 K is important. In this study, the yield of hydrogen *via* the molecular detachment will be reported first. Then, we will give an answer to a question of which of the two mechanisms can best explain the absolute yields of the isotopic composition of the hydrogen gas. (2) The selective hydrogen-atom abstraction by H atoms has been found previously in alkane matrices at 77 K. Does the selective reaction take place also in matrices other than alkanes? Here we have examined tetramethylsilane (TMS) and xenon matrices at 77 K. (3) Selective hydrogen-atom abstraction reactions by H atoms have been found in several alkane matrices at 77 K. What are the rate constants of these reactions? Is there any relationship between the rate constants and the C–H bond energies?

Experimental

The D content of decane-d_{22}, supplied by Merck Sharp and Dohm, Canada, Ltd., is 99%. Tetramethylsilane (TMS), supplied by the Merck Co., is more than 99.7 mol%. Xenon, supplied by the Takachiho Shoji Co., is more than 99.9 mol%. The other reagents used in this study are the same as those used before.[3c)]

UV illumination was provided by Toshiba medium-pressure

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mercury lamps. γ-Irradiation was done by Co-60 at a dose rate of 2.3×10^{19} eV/g h.

The hydrogen was analyzed by means of a gas buret connected to a Toepler pump and mass spectrometer (RMS-4 Hitachi mass spectrometer). The yields are the averages of two runs. The free radicals were measured at 77 K with a JES-3BX ESR spectrometer. The microwave power levels used did not result in the saturation of the signal of the alkyl radicals.

Results and Discussion

Selective Hydrogen-atom-abstraction Reaction in Decane-d_{22}. In order to discuss the mechanisms for the formation of hydrogen in the radiolysis of n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures, the yields of the hydrogen gas formed in an unimolecular reaction must first be estimated, though this process has been tentatively neglected in a recent paper.[7] The formation of H_2 from decane at 77 K can be represented as follows:

$$\mathrm{RH}\ \left[\begin{array}{l}\rightsquigarrow \mathrm{R}\cdot + \mathrm{H} \qquad (1)\\ \rightsquigarrow \text{Olefin} + \mathrm{H_2} \qquad (2)\end{array}\right.$$

$$2\mathrm{H} \longrightarrow \mathrm{H_2} \qquad (3)$$

$$\mathrm{H} + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{H_2} \qquad (4)$$

Here, RH and R· represent the decane and the alkyl radicals respectively. Since the alkyl radicals produced by the radiolysis of decane at 77 K are isolated radicals,[6b,9] it is assumed here that all of the alkyl radicals are trapped at 77 K. The formation of one hydrogen molecule by an H atom produces two alkyl radicals. Therefore, a half of $G(\mathrm{R}\cdot)$ corresponds to the amount of H_2 formation by an H-atom process. The G-value for the formation of a $C_{10}H_{21}$ radical in the radiolysis of pure n-$C_{10}H_{22}$ at 77 K has been reported as 5.4,[6b] 3.1,[9] and 6.0,[10] the mean value being 4.8. Therefore, $G(H_2)$ from the H-atom process is $4.8/2=2.4$. $G(C_{10}D_{21})$ in the radiolysis of n-$C_{10}D_{22}$ at 77 K has been reported as 4.1[6b] and 3.1,[9] the mean value being 3.6. $G(H_2)$ and $G(D_2)$ in the radiolysis of pure n-$C_{10}H_{22}$ and n-$C_{10}D_{22}$ at 77 K were measured here as 4.3 and 2.9 respectively at a dose of 3.4×10^{19} eV/g. Therefore, the molecular yields are (4.3—2.4) for n-$C_{10}H_{22}$ and (2.9—1.8) for n-$C_{10}D_{22}$. The ratios of G(hydrogen) by the molecular process to G(hydrogen) by the atomic process are 0.79 for n-$C_{10}H_{22}$ and 0.61 for n-$C_{10}D_{22}$. A similar high molecular yield was reported previously in the radiolysis of solid n-C_6H_{14} at 77 K.[11] The G-values of hydrogen in the radiolysis of n-$C_{10}D_{22}$-n-$C_{10}H_{22}$ mixtures at 77 K are shown in Fig. 3. The results obtained by Lund *et al.*[7] are approximately the same as those obtained by present authors. There is a possibility that hydrogen might react with alkyl radicals during the melting of the irradiated sample, as was observed in irradiated polyethylene.[12] Since the activation energy for this reaction is 13 kcal/mol, however, it takes several hours for the reaction to occur at room temperature.[12] Therefore, we can neglect the possibility that the hydrogen produced by the radiolysis of decane might react with the alkyl radicals while the irradiated decane is warmed up.

Three mechanisms explaining the hydrogen yields will be compared: energy transfer with the resultant formation of a thermal H atom, energy transfer with the resultant formation of a hot H atom, and selective hydrogen-atom abstraction by a D atom. The hydrogen yields are calculated from the yields of the alkyl radicals, which were measured by ESR spectroscopy,[6] and are compared with the hydrogen yields obtained here experimentally.

A) Energy transfer with the resultant formation of a thermal H atom.

$$\begin{array}{rcll} C_{10}D_{22} & \rightsquigarrow & C_{10}D_{22}^{*} & \qquad (1)\\ C_{10}D_{22}^{*} & \longrightarrow & C_{10}D_{21} + D \quad a & \qquad (2)\\ & \searrow & C_{10}D_{20} + D_2 \quad 0.305a & \qquad (3)\\ C_{10}D_{22}^{*} + C_{10}H_{22} & \longrightarrow & C_{10}D_{22} + C_{10}H_{22}^{*} & \qquad (4)\\ C_{10}H_{22} & \rightsquigarrow & C_{10}H_{22}^{*} & \qquad (5)\\ C_{10}H_{22}^{*} & \longrightarrow & C_{10}H_{21} + H \quad b & \qquad (6)\\ & \searrow & C_{10}H_{20} + H_2 \quad 0.395b & \qquad (7)\\ 2D & \longrightarrow & D_2 \quad a^2/[2(a+b)] & \qquad (8)\\ 2H & \longrightarrow & H_2 \quad b^2/[2(a+b)] & \qquad (9)\\ D + H & \longrightarrow & HD \quad 2ab/[2(a+b)] & \qquad (10) \end{array}$$

Here, a and b are the yields of the $C_{10}D_{21}$ and $C_{10}H_{21}$ radicals respectively, which were obtained by ESR spectroscopy.[6] The G-value of the alkyl radicals is taken as 3.6. The excited $C_{10}D_{22}$ molecule, produced by γ-irradiation, transfers its energy to the solute $C_{10}H_{22}$ (Reactions 1 and 4). It is assumed here that the decomposition of excited decane produces thermal atoms and hydrogen molecules (Reactions 2, 3, 6, and 7). The thermal atoms recombine with each other at 77 K (Reactions 8, 9, and 10). The calculated G-values of hydrogen are shown in Fig. 1. $G(H_2)$ increases remarkably with an increase in the concentration of $C_{10}H_{22}$. G(HD) increases sharply at a low concentration of $C_{10}H_{22}$ and then reaches a plateau at a higher concentration.

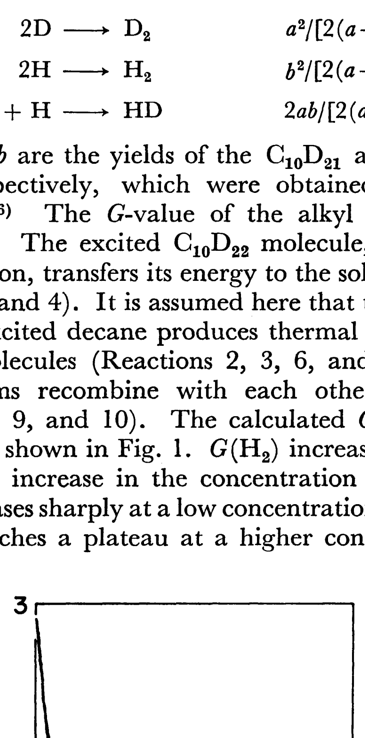

Fig. 1. Yields of hydrogen calculated by the model of energy transfer, with the resultant formation of the thermal H atom.

——, D_2; ----, HD; -·-·-, H_2; □, H_2 obtained experimentally.

The calculated G-values do not coincide at all with the experimental $G(H_2)$.

B) Energy transfer with the resultant formation of a hot H atom.

$$C_{10}D_{22} \rightsquigarrow C_{10}D_{22}^* \qquad (1)$$
$$C_{10}D_{22}^* \longrightarrow C_{10}D_{21} + D \qquad c \qquad (2)$$
$$\searrow C_{10}D_{20} + D_2 \qquad 0.61c \qquad (3)$$
$$C_{10}D_{22}^* + C_{10}H_{22} \longrightarrow C_{10}D_{22} + C_{10}H_{22}^* \qquad (4)$$
$$C_{10}H_{22} \rightsquigarrow C_{10}H_{22}^* \qquad (5)$$
$$C_{10}H_{22}^* \longrightarrow C_{10}H_{21} + H \qquad d \qquad (6)$$
$$\searrow C_{10}H_{20} + H_2 \qquad 0.79d \qquad (7)$$
$$D + C_{10}D_{22} \longrightarrow C_{10}D_{21} + D_2 \qquad c(1-x) \qquad (11)$$
$$D + C_{10}H_{22} \longrightarrow C_{10}H_{21} + HD \qquad cx \qquad (12)$$
$$H + C_{10}D_{22} \longrightarrow C_{10}D_{21} + HD \qquad d(1-x) \qquad (13)$$
$$H + C_{10}H_{22} \longrightarrow C_{10}H_{21} + H_2 \qquad dx \qquad (14)$$

Here, c and d are the yields of hot D atoms and hot H atoms respectively, which are calculated from the yields of $C_{10}D_{21}$ and $C_{10}H_{21}$ radicals.⁶⁾ x represents the mole fraction of the solute $C_{10}H_{22}$. The excited $C_{10}D_{22}$ molecule transfers its energy to the solute $C_{10}H_{22}$ (Reaction 4). It is assumed that the decomposition of excited decane produces hot H(or D) atoms and hydrogen molecules (Reactions 2, 3, 6, and 7). The hot atoms abstract H or D atoms from decane molecules (Reactions 11, 12, 13, and 14). It is assumed here that $k_{11}=k_{12}$ and $k_{13}=k_{14}$. The G-value of the alkyl radical is taken as 3.6. Though the total alkyl-radical yields in the A and B mechanisms are the same, c(or d) is different from a(or b) because of the different mechanisms of the radical formations in the two mechanisms. The calculated G-values of hydrogen are shown in in Fig. 2. $G(D_2)$ approaches zero at 10 mol% of $C_{10}H_{22}$, while G(HD) and $G(H_2)$ increase remarkably with an increase in the concentration of $C_{10}H_{22}$. The calculated G-values do not coincide at all with the experimental $G(D_2)$ and $G(H_2)$.

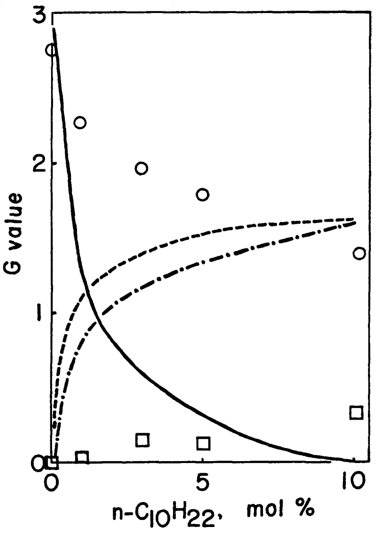

Fig. 2. Yields of hydrogen calculated by the model of energy transfer, with the resultant formation of the hot H atom.
——, D_2; ----, HD; -·-·-, H_2; ○, D_2 obtained experimentally; □, H_2 obtained experimentally.

C) Selective hydrogen atom abstraction by a D atom.

Recently it has been found that H atoms, produced by the radiolysis of solvent alkane at 77 K, react selectively with solute alkane to produce solute alkyl radicals.³⁾ Though it has been suggested that this mechanism may play only a minor role,⁶⁾ we will discuss here the possibility.

$$C_{10}D_{22} \rightsquigarrow C_{10}D_{22}^* \qquad (1)$$
$$C_{10}D_{22}^* \longrightarrow C_{10}D_{21} + D \qquad e(1-x) \qquad (2)$$
$$\searrow C_{10}D_{20} + D_2 \qquad 0.61e(1-x) \qquad (3)$$
$$C_{10}H_{22} \rightsquigarrow C_{10}H_{22}^* \qquad (5)$$
$$C_{10}H_{22}^* \longrightarrow C_{10}H_{21} + H \qquad 1.33ex \qquad (6)$$
$$\searrow C_{10}H_{20} + H_2 \qquad 1.05ex \qquad (7)$$
$$D + C_{10}D_{22} \longrightarrow C_{10}D_{21} + D_2 \qquad e(1-x)^2/[Kx+1-x] \qquad (11)$$
$$D + C_{10}H_{22} \longrightarrow C_{10}H_{21} + HD \qquad ex(1-x)K/[Kx+1-x] \qquad (12)$$
$$H + C_{10}D_{22} \longrightarrow C_{10}D_{21} + HD \qquad 1.33ex(1-x)/[Kx+1-x] \qquad (13)$$
$$H + C_{10}H_{22} \longrightarrow C_{10}H_{21} + H_2 \qquad 1.33ex^2K/[Kx+1-x] \qquad (14)$$

Here, e is a half of the yield of $C_{10}D_{21}$ radicals in the radiolysis of pure n-$C_{10}D_{22}$ and is taken as 1.8 G-unit. [The amounts of Reactions 2 and 3 at $x=0$]/[the amounts of Reactions 6 and 7 at $x=1$] is equal to [$G(D_2)$ in pure n-$C_{10}D_{22}$]/[$G(H_2)$ in pure n-$C_{10}H_{22}$], that is, 0.67. The D atoms produced by the radiolysis of n-$C_{10}D_{22}$ react selectively with the solute $C_{10}H_{22}$ to form $C_{10}H_{21}$ radicals. It is assumed that $k_{12}/k_{11}=k_{14}/k_{13}$, which is denoted by K. K is estimated to be 61 by using the yields⁶⁾ of the $C_{10}H_{21}$ and $C_{10}D_{21}$ radicals. The calculated yields for D_2, HD, and H_2 are shown in Fig. 3. The coincidence of the calculated curves with the experimental yields may be good, if we take into consideration of the fact that the calculation for the final products has been based upon independent results, that is to say, the yields of free radicals as measured by ESR spectroscopy. If K is taken tentatively as 27, the coincidence becomes much better, as is shown in Fig. 3.

Therefore, we can conclude that the selective formation of the solute $C_{10}H_{21}$ radical and HD in the radiolysis of the n-$C_{10}D_{22}$-n-$C_{10}H_{22}$ mixture at 77 K is not due to the energy transfer from the solvent to the solute, but to the selective hydrogen-atom abstraction from the solute by the D atom. The reaction-rate constant (k_{12}) of the D atom with n-$C_{10}H_{22}$ is 27 times greater than that (k_{11}) with n-$C_{10}D_{22}$.

Though the experimental results obtained here are approximately the same as those reported by Lund *et al.*,⁷⁾ the conclusion of this work is quite different from that of Ref. 7. This difference is caused by the following two factors. First, Lund *et al.* neglected tentatively the formation of hydrogen by a molecular detachment process. On the contrary, the yield of the molecular detachment process is estimated experimental-

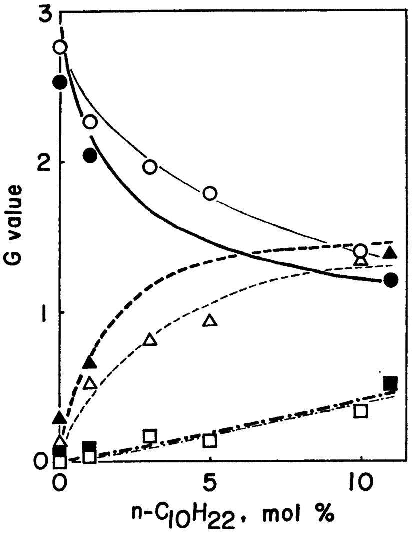

Fig. 3. Comparison of experimental hydrogen yields with the yields calculated by the model of selective hydrogen-atom abstraction by the D atom. Since the results by Lund *et al.* are relative yields, the *G*-values by Lund *et al.* are calculated by using the total *G*-value of hydrogen in this work.

○: D_2 obtained experimentally in this work, ●: D_2 obtained experimentally by Lund *et al.*, △: HD obtained experimentally in this work, ▲: HD obtained experimentally by Lund *et al.*, □: H_2 obtained experimentally in this work, ■: H_2 obtained experimentally by Lund *et al.*, ——: D_2 calculated by taking K as 61, ------: HD calculated by taking K as 61, -·-·-: H_2 calculated by taking K as 61, ——: D_2 calculated by taking K as 27, ------: HD calculated by taking K as 27, -·-·-: H_2 calculated by taking K as 27.

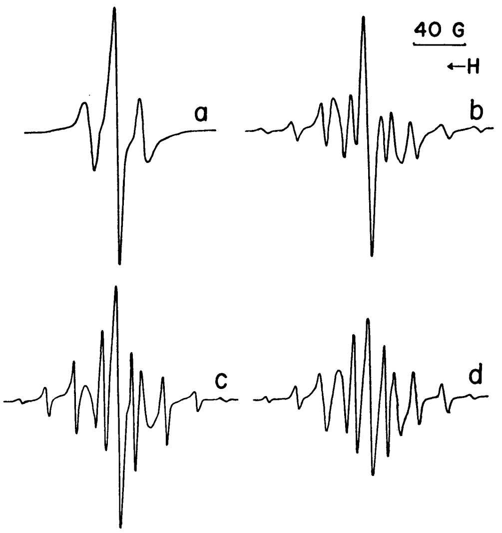

Fig. 4. ESR spectra of irradiated tetramethylsilane(TMS) at 77 K. The unit of the solute concentration is mol/100 mol of TMS.
a: γ-Irradiated TMS, b: γ-irradiated TMS-*i*-C_4H_{10}-(0.46), c: γ-irradiated TMS-*i*-C_4H_8(0.1), d: UV-irradiated TMS-*i*-C_4H_{10}(0.75)-HI(0.2).

ly in this paper and the process is taken into consideration in the discussion. Second, since it has been found that H atoms react quite selectively with the solute alkane in alkane mixtures at 77 K,3) the possibility of a high selectivity for the H atom abstraction reaction by D atoms has been considered in this paper. Lund *et al.*, however, neglected the possibility of the high selective reaction of D atoms at 77 K.

Selective Hydrogen-atom-abstraction Reaction in Tetramethylsilane (TMS). Figure 4a shows the ESR spectra of γ-irradiated pure TMS at 77 K. The spectrum of the three broad lines with a separation of 20.8 G is attributable to the $(CH_3)_3Si\dot{C}H_2$ (TMS·) radical. Figures 4a and c show the ESR spectra of γ-irradiated TMS containing *i*-C_4H_{10} and *i*-C_4H_8 respectively. The spectra consist of three broad lines, which are attributable to the TMS· radical, and eight narrow lines with a separation of 22.8 G, which are attributable to the *t*-C_4H_9 radical. Figure 4d shows the ESR spectra of UV-illuminated TMS containing *i*-C_4H_{10} and HI. The spectra consist of three broad lines, ascribed to the TMS· radicals, and eight narrow lines, ascribed to the *t*-C_4H_9 radical.

The yields of the radicals in Fig. 4b can be estimated by the integration of the spectrum. From the decomposition of the integrated spectrum into *t*-C_4H_9 and TMS· radicals, the amount of the *t*-C_4H_9 radical is estimated to be 13% of the total radical yield. Since an electron fraction of *i*-C_4H_{10} in the TMS-*i*-C_4H_{10} (0.46 mol/100 mol of TMS) mixture is 0.0031, the formation of the *t*-C_4H_9 radical is sensitized 42-fold. Therefore, some activation, produced by the γ-irradiation of TMS, is transfrred to the *i*-C_4H_{10} solute.

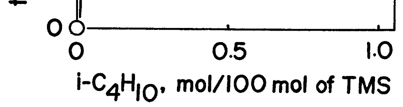

Fig. 5. Yields of the *t*-C_4H_9 radical against the concentration of *i*-C_4H_{10} in the radiolysis of TMS-*i*-C_4H_{10} mixtures at 77 K.

The yields of the *t*-C_4H_9 radicals are shown in Fig. 5 as a function of the *i*-C_4H_{10} concentration. The yields do not increase linearly with an increase in the *i*-C_4H_{10} concentration; at low concentrations they rise steeply, and then approach a plateau value at higher concentrations. This nonlinear increase in the yields indicates also that the formation of the *t*-C_4H_9 radical does not result from the direct absorption of the ionizing radiation by *i*-C_4H_{10}, but from the activation transfer from TMS to *i*-C_4H_{10}.

It is suggested by the following two reasons that the mechanism of the activation transfer may be due to a selective hydrogen-atom-abstraction reaction from *i*-

C_4H_{10} by H atoms, as is observed in the radiolysis of alkane mixtures:[3] (1) When isobutane is added to TMS, the t-C_4H_9 radical is formed by the addition of the H atom to the olefin (Fig. 4c). (2) When H atoms are produced by the photolysis of hydrogen iodide in TMS containing a small amount of i-C_4H_{10}, the H atoms react selectively with the i-C_4H_{10} solute to form t-C_4H_9 radicals (Fig. 4d).

A maximum yield of t-C_4H_9 radicals in the radiolysis of TMS-i-C_4H_{10} mixture amounts to 15% of the total radical yield. 50% of the total radical yields corresponds to the yields of TMS· radicals which are produced by the decomposition of TMS molecules (*cf.* Reactions 15 and 16). Therefore, 30% of the H atoms produced by the radiolysis of TMS migrate to the i-C_4H_{10} solute. The rest react promptly with TMS molecules (Reaction 17).

$$\mathrm{TMS} \rightsquigarrow \mathrm{TMS}\cdot + H_{ab} \qquad (15)$$

$$\mathrm{TMS} \rightsquigarrow \mathrm{TMS}\cdot + H_{mig} \qquad (16)$$

$$H_{ab} + \mathrm{TMS} \longrightarrow \mathrm{TMS}\cdot + H_2 \qquad (17)$$

$$H_{mig} + i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9 + H_2 \qquad (18)$$

$$H_{mig} + \mathrm{TMS} \longrightarrow \mathrm{TMS}\cdot + H_2 \qquad (19)$$

H_{ab} represents an H atom which reacts promptly with TMS and does not migrate through the matrix. H_{mig} represents an H atom which can migrate through the matrix and reacts with i-C_4H_{10} or TMS during its excursion. It is uncertain at present whether the difference between H_{ab} and H_{mig} atoms is due to the difference in their kinetic energies or to that in the initial direction of their translational motions, the possibility of which was suggested in a recent paper.[13] Therefore, the notation of H_{ab} and H_{mig} is a phenomenological discrimination of the two kinds of hydrogen atoms; one reacts promptly with the solvent, while the other migrates through the solvent to react with a solute alkane. The presence of two kinds of H atoms is observed also in other alkane matrices. The results are summarized in Table 1. The relative yields of H_{mig} decrease in the following order: neopentane, 2,2,3,3-tetramethylbutane, and tetramethylsilane. The yields might be influenced by a crystalline structure, the rigidness of the solid, and so on.

Table 1. H atoms produced in the radiolysis and photolysis in the alkane matrix at 77 K[a)]

Matrix	Method of production of H atom	Fractions of two kinds of H atoms	
		H_{ab}, %	H_{mig}, %
neo-C_5H_{12}	radiolysis of *neo*-C_5H_{12}	54[b)]—36[c)]	46[b)]—64[c)]
neo-C_5H_{12}	photolysis of HI[d)]	<10	>90
TMB[e)]	radiolysis of TMB[f)]	60	40
TMB[e)]	photolysis of HI[g)]	60	40
TMS[h)]	radiolysis of TMS[i)]	70	30
TMS[h)]	photolysis of TMS[j)]	70	30

a) The unit of the solute concentration in the footnotes is mol/100 mol of the solvent molecule. The concentrations of solute alkanes in this work are sufficient to capture almost all the H_{mig} atoms. b) The value is obtained in the radiolysis of *neo*-C_5H_{12}-i-C_4H_{10}(2). c) The value is quoted from the results by Iwasaki *et al.* in the radiolysis of *neo*-C_5H_{12}-c-C_6H_{12}(2) (*cf.* M. Iwasaki, K. Toriyama, K. Nunome, M. Fukaya, and H. Muto, *J. Phys. Chem.*, **81**, 1410 (1977)). d) The value is obtained in the photolysis of *neo*-C_5H_{12}-i-C_4H_{10}(2)-HI(0.5). e) TMB is 2,2,3,3-tetramethylbutane. f) The value is obtained in the radiolysis of TMB-C_3H_8 (4.9). g) The value is obtained in the photolysis of TMB-C_3H_8 (3.6)-HI(0.5). h) TMS is tetramethylsilane. i) The value is obtained in the radiolysis of TMS-i-C_4H_{10}(1.0). j) The value is obtained in the photolysis of TMS-i-C_4H_{10}(0.8)-HI(0.2).

Selective Hydrogen-atom-abstraction Reaction in Xenon. When xenon containing a small amount of i-C_4H_{10} and HI is illuminated at 77 K by ultraviolet light, t-C_4H_9 radicals are clearly observed by ESR spectroscopy. The ESM spectra were reported in a previous paper.[14] The efficiency of the formation of butyl radicals is approximately the same as that in the photolysis of the *neo*-C_5H_{12}-i-C_4H_{10}-HI system at 77 K. H atoms, produced by the photolysis of HI, migrate through a xenon matrix and react with the i-C_4H_{10} solute (Reactions 20 and 21):

$$\mathrm{HI} \xrightarrow{h\nu} \mathrm{H} + \mathrm{I} \qquad (20)$$

$$\mathrm{H} + i\text{-}C_4H_{10} \longrightarrow H_2 + t\text{-}C_4H_9 \qquad (21)$$

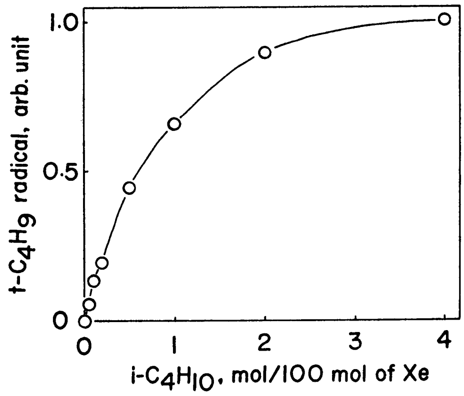

Fig. 6. Yields of the t-C_4H_9 radical against the concentration of i-C_4H_{10} in the UV-photolysis of Xe-i-C_4H_{10}-HI(0.15 mol/100 mol of Xe) at 77 K.

The yields of the t-C_4H_9 radicals are shown in Fig. 6 as a function of the i-C_4H_{10} concentration. A crude estimation of the average distance that the H atoms must be able to travel is available from the yields in Fig. 6. The simplest approach is to use a "target" model in which an H atom travels through a certain volume of the matrix where n atoms of xenon exit. When one molecule of i-C_4H_{10} exists in this volume, the H atom reacts with the i-C_4H_{10} solute. The ratio of the yield (I) of a t-C_4H_9 radical at the i-C_4H_{10} concentration (c mol/mol of Xe) to that (I_∞) at an infinite i-C_4H_{10} concentration is expected to be of the form

$$I/I_\infty = 1 - \exp(-nc). \qquad \text{(a)}$$

It is assumed that I_∞ is approximately the same as the yield of a t-C_4H_9 radical at 4 mol/100 mol of Xe. Equation a can be expressed as

$$-\log\{1-(I/I_\infty)\} = nc\log e. \qquad \text{(b)}$$

A good linear relationship between $-\log\ \{1-(I/I_\infty)\}$ and i-C_4H_{10} concentration is obtained. The actual value found for n is 114. It is concluded that the H atoms produced by the photolysis of HI migrate through 114 atoms of xenon at 77 K.

Correlation between the Rate Constant for H-atom Abstraction and the C–H Bond Energy. A selective hydrogen-atom-abstraction reaction by H atoms has been found previously in several matrices, such as n-$C_{10}D_{22}$, TMS, and Xe matrices. It is interesting to summarize the selectivities of the reactions in these matrices. H atoms which can migrate through the matrix are formed by

$$\mathrm{RH} \rightsquigarrow \mathrm{H_{mig}} + \mathrm{R}\cdot \tag{22}$$

$$(\mathrm{HI} \xrightarrow{h\nu} \mathrm{H_{mig}} + \mathrm{I}) \tag{23}$$

$$\mathrm{H_{mig}} + \mathrm{SH} \xrightarrow{k(\text{solute})} \mathrm{H_2} + \mathrm{S}\cdot \tag{24}$$

$$\mathrm{H_{mig}} + \mathrm{RH} \xrightarrow{k(\text{solvent})} \mathrm{H_2} + \mathrm{R}\cdot \tag{25}$$

the radiolysis of solvent molecules (RH) or by the photolysis of hydrogen iodide (Reactions 22 or 23). They react selectively with solute molecules (SH). It is assumed here that the H atoms may react also with solvent molecules, competing with Reaction 24. If the rate of the formation of H_{mig} is expressed as I, the following relationship is obtained by a steady-state treatment:

$$\frac{1}{r(\mathrm{S}\cdot)} = \frac{1}{I} + \frac{k(\text{solvent})[\mathrm{RH}]}{Ik(\text{solute})\,[\mathrm{SH}]}, \tag{c}$$

where $r(\mathrm{S}\cdot)$ is the rate of the formation of the solute radical and where k is the rate constant. The yields of the solute radical per unit of time ($r(\mathrm{S}\cdot)$) have been measured here and in previous studies[3e] as a function of the solute concentration ([SH]). Linear relationships between $1/r(\mathrm{S}\cdot)$ and [RH]/[SH] are obtained in many systems. The slope-to-intercept ratios give k(solvent)/k(solute), shown in Table 2.

The values of k(solute)/k(solvent) ranged from 5200 in TMS to 27 in n-$C_{10}D_{22}$. The bond-dissociation energy for the C–H bond and the difference in the bond energy between a solvent and a solute are shown in the fifth and sixth columns in Table 2 respectively. Two conclusions can be drawn from these results. First, the bond energy of the solvent molecule is always higher than that of the solute molecule. Even if the difference in the bond energy between the solvent molecule and the solute molecule is very small, the k(solute)/k(solvent) ratio is quite large. Second, the k(solute)/k(neo-C_5H_{12}) ratios for different solutes in a neopentane matrix are of the same order of magnitude, though the difference in the C–H bond energy between the solutes amounts to 7 kcal/mol.

The first conclusion may suggest that the selective abstraction reaction is not caused by hot H atoms with extremely high energies. In order to verify the second conclusion, the competitive reaction of H atoms with C_2H_6 and c-C_6H_{12} has been studied in the neopentane matrix at 77 K.[15] The experimental value for k(c-C_6H_{12})/k(C_2H_6) is 3.7, though the difference in bond energy between C_2H_6 and c-C_6H_{12} is 4 kcal/mol. If the selective hydrogen-atom-abstraction reaction is caused by a thermal H atom, a small difference in a bond energy causes a large k(solute)/k(solvent) because of a reaction at a very low temperature, such as 77 K. For example, k(C_2H_6)/k(neo-C_5H_{12}) amounts to 400—500, though the difference in the bond energy between C_2H_6 and neo-C_5H_{12} is only 1.3 kcal/mol. The hypothesis of the thermal H atom expects that k(c-C_6H_{12})/k(C_2H_6) will also be very large because of the large difference of bond energies (4 kcal/mol) betweeen c-C_6H_{12} and C_2H_6. Therefore, the experimental value of k(c-C_6H_{12})/

Table 2. Rate constant for H-atom-abstraction reaction by H(or D) atom at 77 K

Solvent	Solute	Source of H (or D) atom[a]	k(solute)/k(solvent)	C–H bond energy[b] kcal/mol Solv.	C–H bond energy[b] kcal/mol Solu.	Difference[c] kcal/mol
TMS[d]	i-C_4H_{10}	rad of TMS	5200	99.3[e]	91.0	8.3
neo-C_5H_{12}	c-C_6H_{12}	rad of C_5H_{12}	810[f]	99.3	94.0	5.3
	i-C_4H_{10}	photo of DBr	780[f]		91.0	8.3
	i-C_4H_{10}	photo of HI	700[f]		91.0	8.3
	C_2H_6	photo of HI	490[g]		98.0	1.3
	C_2H_6	rad of C_5H_{12}	380[h]		98.0	1.3
c-C_3H_6	C_2H_6	rad of C_3H_6	630[f]	101.0	98.0	3.0
TMB[i]	C_3H_8	rad of TMB	100[f]	99.3[e]	94.5	4.8
	C_3H_8	photo of HI	50[f]		94.5	4.8
i-C_4H_{10}	C_3H_8	photo of HI	39[f]	98[j]	94.5	3.5
	C_3H_8	rad of C_4H_{10}	11[f]		94.5	3.5
n-$C_{10}D_{22}$	n-$C_{10}H_{22}$	rad of $C_{10}D_{22}$	27			1.2[k]

a) Rad and photo represent radiolysis and photolysis respectively. b) The value is quoted from the paper by J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). Solv. and solu. represent solvent and solute molecules respectively. c) Difference in C–H bond energy between solvent and solute. d) TMS is tetramethylsilane. e) It is assumed that the C–H bond energies of TMS and TMB are approximately the same as that of neo-C_5H_{12}. f) The value is calculated from the results in Ref. 3e. g) The value is calculated from the results by T. Wakayama, T. Miyazaki, and Z. Kuri. h) The value is calculated from the results by T. Miyazaki. i) TMB is 2,2,3,3-tetramethylbutane. j) The value is the energy of the primary C–H bond. k) The value is the difference in zero-point energy between C–H and C–D bonds.

Table 3. Isotope effect on selective hydrogen-atom-abstraction reaction by H(or D) atoms at 77 K

Method of production of H(or D) atoms	Reaction	k(H)/k(D)
Selective H-atom-abstraction reaction by H atom at 77 K		
Radiolysis of solvent *neo*-C_5H_{12} at 77 K[a]	$H+i\text{-}C_4H_{10} \longrightarrow H_2+t\text{-}C_4H_9$ $(i\text{-}C_4H_9D)$ (HD)	1.1
Photolysis of HI in *neo*-C_5H_{12} at 77 K[a,b]	$H+i\text{-}C_4H_{10} \longrightarrow H_2+t\text{-}C_4H_9$ $(i\text{-}C_4H_9D)$ (HD)	1.7—2.5
Photolysis of HI in Xe at 77 K[c]	$H+i\text{-}C_4H_{10} \longrightarrow H_2+t\text{-}C_4H_9$ $(i\text{-}C_4H_9D)$ (HD)	4—5
Radiolysis of solvent *n*-$C_{10}D_{22}$ at 77K[c]	$D+C_{10}H_{22} \longrightarrow HD+C_{10}H_{21}$ $(C_{10}D_{22})$ (D_2) $(C_{10}D_{21})$	27
Hot-atom reaction		
Photolysis of HBr in gas phase at about 300 K[d]	$H+CH_3CD_3 \longrightarrow H_2$ or HD	2.4—3.1
Photolysis of HI in gas phase at 313 K[e]	$H+C_2H_5D \longrightarrow H_2$ or HD (CH_3CD_3)	4.8—8.5
Recoil T atom in gas phase[f]	$T+C_2H_4 \longrightarrow HT$ (C_2D_4) (DT)	1.27
Thermal abstraction reaction at 77 K		
Electron attachment to CH_3Cl at 77 K[g]	$CH_3+CH_3OD \longrightarrow CH_4+CH_2OD$ (CD_3OD)	>1000
Radiolysis of CH_3CN at 77 K[h]	$CH_3+CH_3CN \longrightarrow CH_4+CH_2CN$ (CD_3CN)	>28000

a) Ref. 3b. b) Ref. 3a. c) This work. d) Hot H atoms have energies of 1.1—2.9 eV; G. D. Beverly and R. M. Martin, *J. Phys. Chem.*, **81**, 2063 (1976). e) Hot H atoms have an energy of 1.8 eV; K. Hong and G.J. Mains, *J. Phys. Chem.*, **76**, 3337 (1972). f) J. W. Root, W. Breckenridge, and F.S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965). g) Ref. 19b. h) Ref. 19c.

$k(C_2H_6)=3.7$ cannot be explained by the hypothesis of a thermal H atom. It is interesting to note that $k(c\text{-}C_6H_{12})/k(C_2H_6)$ is 3.5 for a hot tritium atom reaction[16] and about 6 for a hot CH_3 radical reaction in the photolysis of CH_3I.[17] The experimental value obtained in the neopentane matrix is approximately of the same order of magnitude as that in the hot-atom reaction.

Isotope Effects on the H-atom Abstraction Reaction at 77 K. The isotope effects on the hydrogen-atom-abstraction reaction are summarized in Table 3. k(H) and k(D) represent the rate constants of the H-abstraction and D-abstraction reactions respectively. The values in the *neo*-C_5H_{12} and Xe matrices were estimated from the yields of $t\text{-}C_4H_9$ radicals produced by the radiolysis or photolysis in *neo*-C_5H_{12} (or Xe) containing 2 mol% of $i\text{-}C_4H_{10}$ or $i\text{-}C_4H_9D$ at 77 K. The isotope effects in the neopentane matrix ranged from 1.1 to 2.5.[18] In order to confirm the isotope effect in the *neo*-C_5H_{12} matrix, a competitive reaction of H atoms with C_2H_6 and $c\text{-}C_6H_{12}$ (or $c\text{-}C_6D_{12}$) has been studied at 77 K. The experimental value for k(H)/k(D) of cyclohexane in the neopentane matrix is 7.3.[15] Recently it has been reported that a thermal CH_3 radical abstracts a hydrogen atom at 77 K by mean of quantum mechanical tunneling.[19] The most important characteristic of this mechanism is a quite large isotope effect (*cf.* Table 3). The value for k(H)/k(D) in the neopentane matrix is quite different from the value for quantum mechanical tunneling. On the contrary, the value in the neopentane matrix is approximately the same as the value for hot-atom reactions in the gas phase.

Energy Loss of Reactive H Atoms in the Solid Phase. Since the energy of the first excited state of alkane (7—8 eV)[20] is much larger than the bond energy of the C–H bond (4 eV),[21] and since the energy of ultraviolet light (4.9 eV) is much larger than the bond energy of HI (3.1 eV),[21] the H atom produced by the radiolysis of alkane or by the photolysis of HI must have, initially, an excess energy of 2—3 eV. Recently it has been reported that the H atoms produced in the gas phase by electron impact on hydrocarbons have kinetic energies of 1.8—3.8 eV.[22] Now, we will discuss the problem of whether or not the H atoms with the excess energy lose their energy completely during their excursion in the crystal at 77 K.

The photolysis of the Xe–$i\text{-}C_4H_{10}$–HI mixture is the simplest way to discuss the energy loss of hot H atoms. When the photolysis of HI is caused by a 2537 Å light, the initial kinetic energy of an H atom 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.[23] The experimental results in Fig. 6 indicate that the H atoms produced in the photolysis of HI migrate through 114 atoms of Xe at 77 K. In order to estimate the number of H atoms colliding with Xe atoms during the excursion, three cases are considered here. First, if the collision efficiency of an H atom with solute $i\text{-}C_4H_{10}$ is the same as that of Xe, the number of collisions of the H atom with Xe is 114 until the H atom reacts with $i\text{-}C_4H_{10}$. Second, since the crystalline structure of Xe is face-centered cubic,[24] a channeling wall[25] consists of four Xe atoms. If the $i\text{-}C_4H_{10}$ solute exists as a defect in the channeling zone, it may be assumed that the collision efficiency of an H atom with i-C_4H_{10} is four times as large as that with Xe. In this case, the collision number of the H atom with Xe is 114/4(=28.5). Third, an i-C_4H_{10} molecule may exist in a lattice of crystalline Xe. It may be assumed that H atoms react with i-C_4H_{10} whenever they approach nearest neighboring Xe atoms around i-C_4H_{10}. The collision efficiency of H atoms with i-C_4H_{10} is 12 times as large as that with Xe. In this case, the collision number of an H atom with Xe is 114/12(=9.5).

The reactive H atom loses its energy by elastic collisions with Xe molecules. The energy loss by a single collision is expressed as

$$\frac{E_0-E'}{E_0} = \frac{2M_1M_2}{(M_1+M_2)^2}(1-\cos\theta), \qquad \text{(d)}$$

where E_0 and E' are the kinetic energies before and after a collision respectively.[26] M_1 and M_2 are the masses of the H atom and the Xe atom respectively. θ is the diffraction angle of the H atom caused by the collision. The mean value of the energy loss ($\langle E'/E_0\rangle$) is obtained by means of the following equation:

$$\left\langle\frac{E'}{E_0}\right\rangle = 1 - \int_0^{\pi/2}\frac{2M_1M_2}{(M_1+M_2)^2}(1-\cos\theta)\mathrm{d}\theta. \qquad \text{(e)}$$

When an H atom has, initially, a kinetic energy of 41 or 20 kcal/mol, the final energy of the H atom after the excursion in a xenon matrix is calculated by means of Eq. e for all three cases of the collision number. As is shown in Table 4, the final energy ranges from 11 to 39 kcal/mol, depending on the models for collisions and the initial energies of the H atoms. Since the activation energy for the hydrogen-atom-abstraction reaction of an H atom with i-C_4H_{10} is 7.4 kcal/mol,[5] the H atom has enough energy for a chemical reaction with i-C_4H_{10} after the excursion in the Xe matrix.

TABLE 4. FINAL ENERGY OF REACTIVE H ATOM IN Xe MATRIX AT 77 K

	Collision efficiency with solute		
	1	4	12
Collision number	114	28.5	9.5
Final energy of H atom with 41 kcal/mol,[a] kcal/mol	23	36	39
Final energy of H atom with 20 kcal/mol,[b] kcal/mol	11	18	19

a) The H atom has initially a kinetic energy of 41 kcal/mol. b) The H atom has initially a kinetic energy of 20 kcal/mol.

The theoretically estimated energies of 11—39 kcal/mol are high in comparison with the activation energy of 7.4 kcal/mol. Therefore, there remains the important question of why the H atoms with the energies of 11—39 kcal/mol abstract selectively the tertiary H atom of i-C_4H_{10}. We cannot give a good explanation of this problem as yet. Two possibilities are plausible. One is that the real energy of the reactive H atoms is near the threshold of the hydrogen abstraction reaction. The other is that the reaction in the solid state at low temperature shows the selectivity under the influence of the crystalline fields. For example, when isobutane is exposed to γ-irradiation[27] or hot-atom attack[14] at 77 K in a polycrystalline medium, the isobutyl radical is formed, while in a glassy state the tertiary butyl radical is formed. In the radiolysis of 2,3-dimethylbutane at 77 K, the $\cdot CH_2CH(CH_3)CH(CH_3)_2$ radical is formed in crystal-I, while the $CH_3\dot{C}(CH_3)CH(CH_3)_2$ radical is formed in crystal-II.[28] When glassy 3-methyl alkane are exposed to γ-irradiation, hot-atom attack, hot-radical attack, or photosensitization by aromatic solutes, radicals are formed predominantly by the rupture of secondary C–H bonds rather than by that of the weak tertiary or of the more abundant primary bonds.[29]

In conclusion, we cannot give a decisive answer to the question of whether the reactive H atoms in the radiolysis and the photolysis of solid mixtures at 77 K are thermal or hot. We will try, however, to give a probable hypothesis for further investigation. The remarkable selectivity for the reaction may diminish the possibility of hot H atoms with extremely high energies. The small isotope effect on the reaction may diminish the possibility of a quantum mechanical tunneling abstraction[19] by thermal H atoms, Since the rate constants and isotope effects for solute molecules in *neo*-C_5H_{12}-alkane mixtures are approximately the same as those for hot-atom reactions, H atoms with epithermal energy may be responsible for the reaction. When the H atoms produced by the radiolysis of the solvent alkane or by the photolysis of hydrogen halide are incident upon the channeling zone[25,3c] of the matrix, the H atoms may travel a long distance by a succession of glancing collisions with the channel walls of the solvent molecules and may then react with a solute alkane which may exist as a defect in the matrix.

The D atoms produced by the photolysis of DI react selectively with 3-methylpentane-h_{14} in 3-methylpentane-d_{14} glass at 77 K.[4] There is, however, no experimental information on the kinetic energy of the D atoms. The problem of whether the D atoms in 3-methylpentane-d_{14} glass are thermal or hot atoms requires further study in the future.

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References

1) A. Charlesby, Proceedings of the 1962 Tihany Symposium on Radiation Chemistry, Akademiai Kiado, Budapest, 1964, p. 175.

2) W. Flossman, E. Westhof, and A. Muller, *Int. J. Radiat. Biol.*, **28**, 105 (1975). Previous papers concerning the role of the H atom in biological substances are cited therein.

3) a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **77**, 2365 (1973); b) T. Miyazaki and T. Hirayama, *J. Phys. Chem.*, **79**, 566 (1975); c) T. Miyazaki, K. Kinugawa, M. Eguchi, and S. M. L. Guedes, *Bull. Chem. Soc. Jpn.*, **49**, 2970 (1976); d) T. Miyazaki, S. M. L. Guedes, L. G. A. Silva, and L. Fernandes, *Bull. Chem. Soc. Jpn.*, **50**, 301

(1977); e) T. Miyazaki, K. Kinugawa, and J. Kasugai, *Radiat. Phys. Chem.*, **10**, 155 (1977).

4) D. D. Wilkey and J. E. Willard, *J. Chem. Phys.*, **64**, 3976 (1976).

5) B. A. Thrush, *Prog. React. Kinet.*, **3**, 89 (1965).

6) a) T. Gillbro and A. Lund, *Chem. Phys. Lett.*, **27**, 300 (1974); b) T. Gillbro and A. Lund, *Int. J. Radiat. Phys. Chem.*, **8**, 625 (1976).

7) O. Claesson and A. Lund, *Chem. Phys. Lett.*, **47**, 155 (1977).

8) T. Miyazaki, *Radiat. Phys. Chem.*, **10**, 219 (1977).

9) M. Iwasaki, K. Toriyama, H. Muto, and K. Nunome, *J. Chem. Phys.*, **65**, 596 (1976).

10) D. D. Wilkey, H. W. Fenrick, and J. E. Willard, *J. Phys. Chem.*, **81**, 220 (1977).

11) L. Kevan and W. F. Libby, *J. Chem. Phys.*, **39**, 1288 (1963).

12) D. C. Waterman and M. Dole, *J. Phys. Chem.*, **74**, 1913 (1970).

13) K. Kinugawa, T. Miyazaki, and H. Hase, *Radiat. Phys. Chem.*, **10**, 341 (1977).

14) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, **44**, 2619 (1971).

15) Although the details will be given elsewhere, some of the results were presented by T. Miyazaki *et al.* at the 20th Japanese Conference of Radiation Chemistry, Sapporo, Japan, October, 1977.

16) E. Tachikawa and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 4767 (1968).

17) R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, **48**, 306 (1968).

18) Recent results obtained by T. Miyazaki *et al.* by the method of a competitive reaction also support this value.

19) a) R. J. LeRoy, E. D. Sprague, and F. Williams, *J. Phys. Chem.*, **76**, 546 (1972); b) A. Campion and F. Williams, *J. Am. Chem. Soc.*, **94**, 7633 (1972); c) E. D. Sprague, *J. Phys. Chem.*, **81**, 516 (1977).

20) J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

21) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," translated to English by W. C. Price, London, Edward Arnold (1966).

22) K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, *Chem. Phys.*, **21**, 203 (1977).

23) S. Adita and J. E. Willard, *J. Am. Chem. Soc.*, **88**, 229 (1966).

24) R. W. G. Wyckoff, "Crystal Structures," John Wiley & Sons (1965), p. 10.

25) T. Miyazaki, *Bull. Chem. Soc. Jpn.*, **50**, 1625 (1977).

26) A. Kanpanetz, "Theoretical Physics," translated to Japanese by T. Yamanouchi and H. Takami, Iwanami Shoten (1964), p. 48.

27) a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, **42**, 2086 (1969); b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970); c) Y. Saitake, T. Wakayama, T. Kimura. T, Miyazaki, K. Fueki, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, **44**, 301 (1971).

28) M. Fukaya, T. Wakayama, T. Miyazaki, Y. Saitake, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, **46**, 1036 (1973).

29) a) D. J. Henderson and J. E. Willard, *J. Am. Chem. Soc.*, **91**, 3014 (1969); b) T. Ichikawa and N. Ohta, *J. Phys. Chem.*, **81**, 560 (1977).