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ARTICLES

Matrix Effect on Hydrogen Atom Tunneling from Alkane to Free Deuterium Atoms in Cryogenic Solid

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ESR study on alkyl radicals generated in deuterated organic matrixes at 77 K by hydrogen atom tunneling from alkane molecules to free deuterium atoms has been carried out for elucidating control factors for the tunneling. For small alkane molecules, the tunneling rate is determined by the height of the potential energy barrier for the tunneling. For larger molecules in glassy matrixes, the rate decreases with increasing number and length of alkyl chains bonded to a carbon atom to be hydrogen abstracted. The tunneling rate from antepenultimate tertiary carbon is much slower than that from penultimate secondary carbon, even the potential energy barrier is lower. This abnormal effect is explained as being due to the steric hindrance by matrix molecules to the deformation of alkane molecules during the reaction. The alkyl chains surrounded by matrix molecules prevent the deformation of the chemical bonds of the carbon atom from the initial sp^3 to the final sp^2 configuration, which may cause the increase of the thickness of the potential energy barrier and thereby decrease of the tunneling rate. Free deuterium atoms in a crystalline adamantane matrix selectively abstract hydrogen atoms from the antepenultimate tertiary carbon, probably due to less steric hindrance to the deformation.

Introduction

Hydrogen atom abstraction from C−H carbon of organic molecules is one of the simplest chemical reactions and has been extensively studied by many researchers. The rate of abstraction is known to increase in the order of primary, secondary, and tertiary carbon atoms, since the activation energy decreases in the same order.[1] However, this rule is not applicable to the reaction at low temperature. Hydrogen atom abstraction from branched alkanes with tertiary carbon at the antepenultimate position of the carbon skeleton is the fastest at the secondary penultimate carbon. Henderson and Willard found that γ-irradiation at 77 K of singly branched alkanes with branching at the antepenultimate position of the carbon skeleton caused selective rupture of a secondary C−H bond of the $-CH_2CH_3$ group but not of a tertiary C−H bond.[2] Ichikawa and Ohta then showed that the location of the selective rupture could be changed to the tertiary C−H bond by replacing the $-CH_2CH_3$ group with $-CD_2CH_3$.[3,4] Using ESR and electron spin echo spectroscopy, we found that anomaly of the C−H bond rupture came from the conversion of primary alkyl radicals and free hydrogen atoms to penultimate secondary alkyl radicals by selective hydrogen atom tunneling from the penultimate position of the carbon skeleton.[5] We also found the selective tunneling of hydrogen atoms from the penultimate carbon of linear alkanes to free deuterium atoms.[6]

On the basis of the experimental results, we have proposed that the peculiarity of the hydrogen atom abstraction in cryogenic solids comes from the steric hindrance to the deformation of alkane molecules from the initial sp^3 to the final sp^2 configurations. The steric hindrance increases with increasing number and length of alkyl chains attached to a carbon atom to be hydrogen abstracted, since the matrix restricts the motion of the alkyl chains. Penultimate secondary carbon therefore shows the highest reaction rate. However, the reason the steric hindrance retards the reaction has not been clarified yet. Moreover, the relative rate of hydrogen atom tunneling from carbon atoms other than the penultimate secondary one has not been determined.

Knowing the relative rate of hydrogen atom tunneling from each carbon atom in a molecule necessitates the discrimination of different types of alkyl radicals from the overlapping ESR spectra. However, this is not an easy task. Hydrogen atom abstraction from linear alkanes, for example, gives two kinds of secondary alkyl radicals, CH_3CHCH_2- with five β protons and $-CH_2CHCH_2-$ with four β protons. However, both of them give eight-line spectra with the hyperfine splitting of ca. 2.2 mT. In the present study, discrimination of alkyl radicals has been carried out by the use of selectively deuterated alkane molecules. Calculations of the energy of the deformation of alkane molecules during the reaction and the potential energy barriers for the hydrogen atom transfer have also been made for understanding the effect of the steric hindrance on the hydrogen atom tunneling.

Experimental Section

Perdeuterated glassy and crystalline matrixes were used for the generation of solute alkyl radicals by tunneling hydrogen atom abstraction. Perdeuterated methanol and perdeuterated

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methylcyclohexane were used as glassy matrixes. About 3 vol % of D_2O was added to methanol for making a clear glassy matrix. The concentration of alkanes was 2 vol %. A perdeuterated adamantane matrix containing a small amount of 3-methylpentane as a substitutional-type impurity was prepared by crystallizing the adamantane in 3-methylpentane. Partially deuterated alkanes were synthesized from corresponding alcohols, ketones, or esters using $LiAlD_4$ and $LiB(C_2H_5)_3D$ as deuteration reagents. The reactions used for the deuteration were[7,8]

$$R_1R_2C{=}O + LiAlD_4 \rightarrow (+\text{dil. HCl}) \rightarrow R_1R_2CDOH$$

$$RCOOC_2H_5 + LiAlD_4 \rightarrow (+\text{dil. HCl}) \rightarrow RCD_2OH$$

$$R_1R_2R_3COH + PBr_3 \rightarrow R_1R_2R_3CBr$$

$$R_1R_2R_3CBr + LiB(C_2H_5)_3D \rightarrow R_1R_2R_3CD$$

Here R refers to an alkyl group, hydrogen atom, or deuterium atom. The reactions were carried out in dried ether at room temperature under nitrogen atmosphere. The purity and the yields of the deuterated products were more than 98% and 60%, respectively. Free deuterium atoms were generated at 77 K by two methods. One was the photoionization of triphenylamine in perdeuterated methanol matrixes followed by the attachment of the photoejected electrons to deuterons, as

$$(C_6H_5)_3N + 2h\nu \rightarrow (C_6H_5)_3N^+ + e^-$$

$$e^- + DCl \rightarrow D + Cl^-$$

The concentrations of triphenylamine and deuterium chloride were about 10 mmol/dm^3 and 0.1 mol/dm^3, respectively. The other was homolytic cleavage of the C−D bonds of matrix molecules by γ-irradiation, $MD + \gamma \rightarrow M + D$

The ESR spectra of alkyl radicals generated by hydrogen atom transfer to deuterium atoms, $RH + D \rightarrow R + HD$, did not depend on the method of D formation, as long as the UV light of $\lambda > 300$ nm was used for the photoionization. Irradiation of the UV light shorter than 300 nm caused the photoconversion of alkyl radicals.[9,10] The samples were degassed before irradiation by repeated freezing−pumping−warming cycles. In the following section, we will only show the results of γ-irradiation. The ESR spectra of alkyl radicals in the glassy matrixes were recorded at 77 K and were analyzed by using the hyperfine coupling constants (hfcc) of 2.3 mT for three methyl β protons, 2.2 and 4.4 mT for methylene β protons of secondary radicals, and the combination of 2.2 and 2.2 mT, 2.2 and 0 mT, and 0 and 2.2 mT for the two methylene β protons of tertiary alkyl radicals. The anisotropic hfcc of α protons were 1.17, 1.96, and 3.52 mT for all the alkyl radicals examined. The ESR spectrum for the irradiated adamantane matrix was measured at 77, 113, and 178 K.

Results

Hydrogen Atom Abstraction in Glassy Matrixes. The ESR spectra of γ-irradiated glassy samples were composed of a narrow intense spectrum due to perdeuterated solvent radicals and wider ones due to solute alkyl radicals. The yield of alkyl radicals was more than 20% of the total radical yield, which implies that the direct formation of alkyl radicals from solute alkanes by ionizing radiation is negligible. Most of the solute radicals are generated by tunneling transfer of hydrogen atoms from solute molecules to free deuterium atoms, $RH + D \rightarrow R + HD$. The abstractions of heavier deuterium from solvent molecules are much slower.[11−13] One of the advantages of using perdeuterated matrixes is to see only the tunneling reaction by eliminating hot-atom reactions. The thermalization distance of free deuterium atoms in cryogenic matrixes is so short that they are thermalized before reacting with dilute solute alkanes.[14] Another advantage is that the generated alkyl radicals are free from radical conversion.[5] It is possible to convert alkyl radicals to solvent radicals by abstracting hydrogen atoms from solvent molecules, which is prevented by the deuteration of solvent molecules. Intramolecular conversion of alkyl radicals is negligible unless they are photoexcited.[9,10] The location of the radical carbon of the solute alkyl radicals is therefore the same as where the hydrogen atom tunneling takes place. Primary alkyl radicals showing a characteristic sharp ESR spectrum were not observed for all the alkanes examined, probably due to too high potential energy barrier for hydrogen atom tunneling.

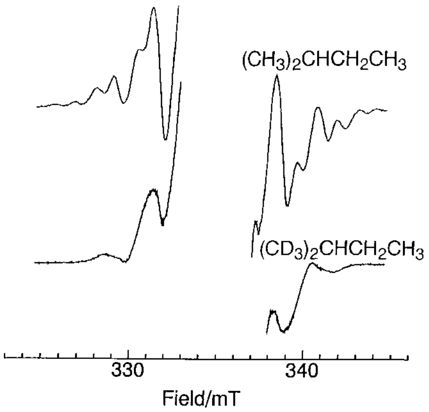


Figure 1. ESR spectra of alkyl radicals generated from ordinary and deuterated 2-methylbutane in perdeuterated methanol matrix at 77 K. The central intense signals are due to solvent radicals.

Figure 1 compares the ESR spectra of alkyl radicals generated from ordinary and partially deuterated 2-methylbutane. The ESR spectrum for ordinary 2-methylbutane shows the characteristic spectrum of $(CH_3)_2C^*CH_2CH_3$ composed of overlapping spectra of eight lines and nine lines with the intensity ratio of 2:1. Here C* denotes hydrogen atom abstracted radical carbon. Deuteration of the methyl groups of tertiary carbon narrows the entire spectral width and hides away the spectrum into that of perdeuteratd solvent radicals. The remaining spectrum after the deuteration is therefore due to $(CD_3)_2CHC^*HCH_3$. The yield ratio of $(CD_3)_2CHC^*HCH_3$ to $(CH_3)_2C^*CH_2CH_3$ obtained by the spectral simulation was 1:2 to 1:3. We concluded in the previous paper that the rate of hydrogen atom tunneling from penultimate secondary carbon is much faster than that from penultimate tertiary carbon.[5] However, the present result shows that the rate depends not only on the location of the carbon atom in a molecule but also on the molecular size. The height of the potential energy barrier seems to be a predominant control factor for smaller molecules.

Addition of one CH_2 unit to the carbon skeleton drastically changes the rate of hydrogen atom tunneling. As shown in Figure 2, the major radical generated from ordinary 2-methylpentane is not tertiary radical but secondary $(CH_3)_2CHCH_2C^*HCH_3$ showing an eight-line ESR spectrum. A weak nine-line spectrum of $(CH_3)_2C^*CH_2CH_2CH_3$ is also observed as shoulders to the eight-line spectrum. Deuteration of the methyl groups of the tertiary carbon does not cause so significant a change of the spectrum as to that of 2-methylbutane. The yield ratio of $(CD_3)_2CHCH_2C^*HCH_3$ to $(CH_3)_2C^*CH_2CH_2CH_3$ is 2:1 to 3:1.

The shift of the tertiary carbon atom to the antepenultimate position causes a very drastic effect. As shown in Figure 3, the

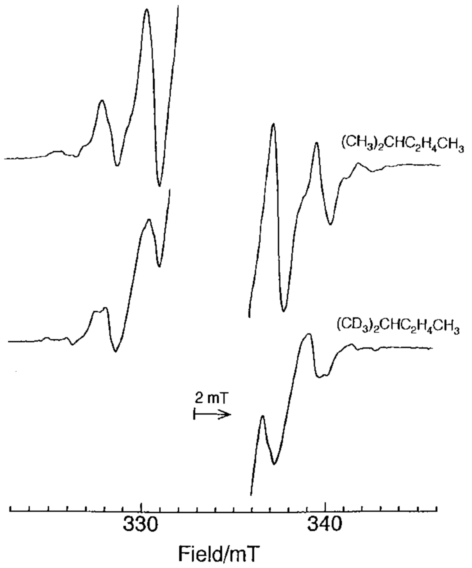


Figure 2. ESR spectra of alkyl radicals generated from ordinary and deuterated 2-methylpentane in perdeuterated methanol matrix at 77 K.

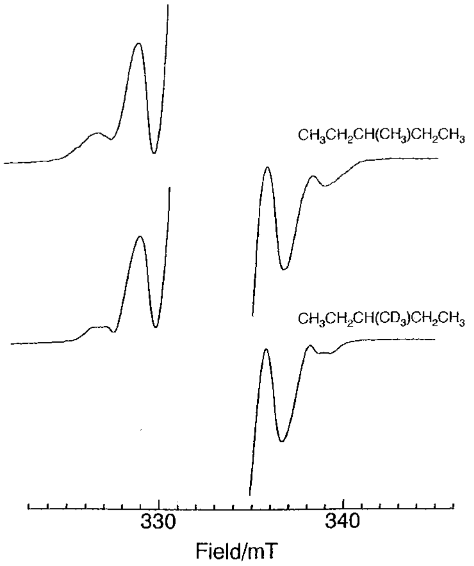


Figure 3. ESR spectra of alkyl radicals generated from ordinary and deuterated 3-methylpentane in perdeuterated methanol matrix at 77 K.

ESR spectrum of alkyl radicals generated from 3-methylpentane is not changed by the deuteration of methyl groups of the tertiary carbon. The radical species generated from 3-methylpentane is only $CH_3CH^*CH(CH_3)CH_2CH_3$. No $CH_3CH_2C^*(CH_3)CH_2CH_3$ is generated, irrespective of its lowest potential energy barrier.

The same kind of tendency was found for hydrogen atom tunneling from normal alkanes to free deuterium atoms. As mentioned earlier, two kinds of ESR-distinguishable alkyl radicals are possible to be formed from alkanes. They are $CH_3C^*HCH_2-$ showing eight-line ESR spectra with the intensity ratio of 1:5:11:15:15:11:5:1 and $-CH_2C^*HCH_2-$ showing also eight-line spectra with the intensity ratio of 1:3:5:7:7:5:3:1. The number of reaction sites giving the former radicals (the number of methylene protons adjacent to methyl groups) is four for all the linear alkanes. The number of reaction sites for the latter radicals (the number of the other methylene protons), however, increases with increasing molecular length. ESR spectrum for normal alkane may therefore change with the molecular length, if the rate of hydrogen atom tunneling is independent of the molecular length. Figure 4 compares the ESR spectra for pentane, hexane, and octane. These spectra can be overlapped with each other, which means that the yield of $-CH_2C^*HCH_2-$ with respect to $CH_3C^*HCH_2-$ is kept constant. The rate of hydrogen atom tunneling decreases with increasing length of alkyl groups bonded to a carbon atom to be hydrogen-abstracted so that the total rate of hydrogen atom tunneling from antepenultimate carbon atoms with respect to penultimate ones is kept constant. As shown in Figure 5, no spectral change does not mean the absence of $-CH_2C^*HCH_2-$. Although the spectrum is shifted to the central part by successive deuteration of the methyl groups, the outermost lines due to $-CH_2C^*HCH_2-$ still remains. The yield ratio of $-CH_2C^*$-

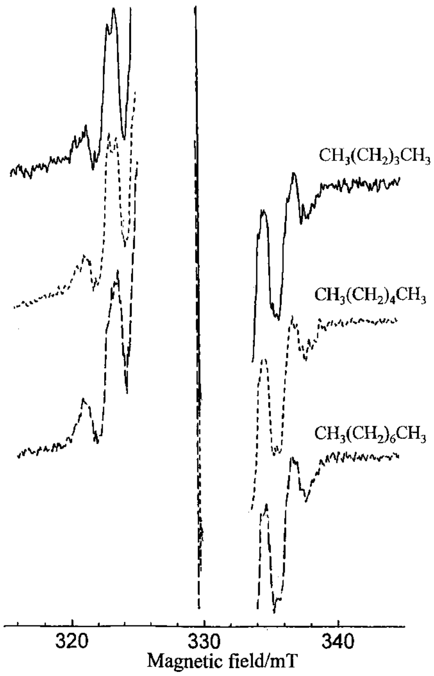


Figure 4. ESR spectra of alkyl radicals generated from normal alkanes in perdeuterated methylcyclohexane matrix at 77 K.

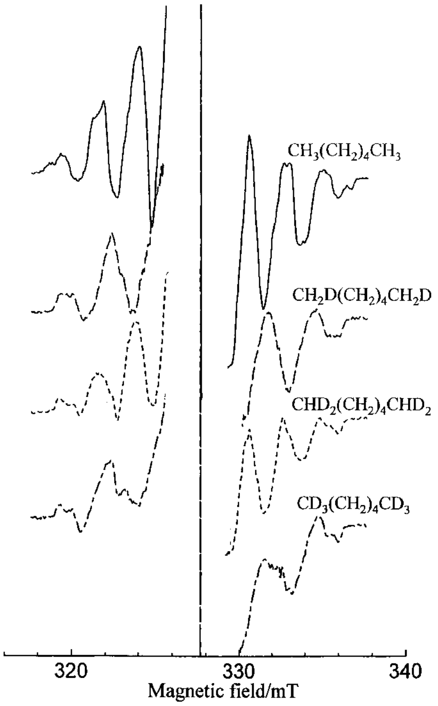
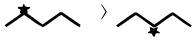
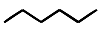
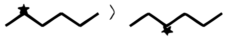
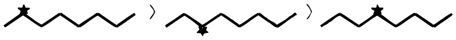
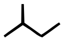
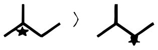
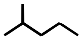
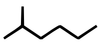
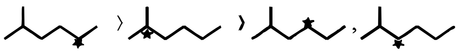
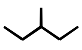
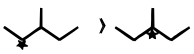
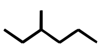
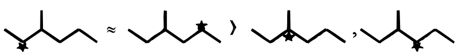
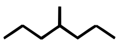
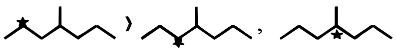


Figure 5. ESR spectra of alkyl radicals generated from ordinary and deuterated hexane in perdeuterated methanol matrix at 77 K.

TABLE 1: Relative Yield of Alkyl Radicals Generated at 77 K by Hydrogen Atom Tunneling from Solute Alkane to Free Deuterium Atoms in Perdeuterated Glassy Matrixes

Alkane	Alkyl radicals[a,b]
	
	
	
	
	
	
	
	
	

[a] The location of hydrogen-abstracted carbon atom is shown with *. [b] A ≈ B, A > B, and A ≫ B mean that the yield of B with respect to A is about 1−0.5, 0.5−0.2, and ≪0.2 (undetectable by ESR), respectively.

HCH_2- to $CH_3C^*HCH_2-$ is 1:2 to 1:3 for hexane. We concluded in the previous paper that only penultimate secondary alkyl radicals are generated from normal alkanes.[6] The present result shows that antepenultimate secondary alkyl radicals are also formed, but not as a major product.

Table 1 summarizes the relative yield of solute alkyl radicals obtained by the analysis of the ESR spectra. It can be concluded that the yield and therefore the rate of hydrogen atom abstraction depends not only on the height of the potential energy barrier but also on the number and the length of alkyl chains bonded to a carbon atom to be hydrogen abstracted. The rate of abstraction always decreases with increasing number and length of the bonded alkyl chains. A simple explanation of this effect is that the alkyl chains cover the C−H bond to be hydrogen abstracted so that the C−H bond is protected from the approach of deuterium atoms. However, this may not be useful for explaining the drastic change of the selectivity among 2-methylbutane, 2-methylpentane, and 3-methylpentane. Another explanation, which we proposed in the previous paper,[5,6] is that matrix molecules surrounding the bulky alkyl chains prevent the deformation of the C−C−C bond from the initial sp^3 of alkanes to the final sp^2 of alkyl radicals and thereby prevent the hydrogen atom abstraction. The steric hindrance to the deformation increases with increasing number and length of alkyl chains bonded to the carbon atom so that the rate of hydrogen atom abstraction decreases. The paramagnetic relaxation of alkyl radicals due to the molecular motion of alkyl chains bonded to radical carbon was found to decrease with increasing length of the chains,[5,6] which supports the validity of the above explanation.

Hydrogen Atom Abstraction in Adamantane. Adamantane is known to be an excellent matrix for obtaining well-resolved ESR spectra of free radicals at low temperature.[14,15] Crystalline adamantane offers a large space to guest molecules trapped as substitutional-type impurities so that free radicals generated from the guest molecules can be rotated fast enough for averaging out the spectral distribution, even at low temperature. The use of adamantane as a matrix for hydrogen atom abstraction is therefore suitable for reducing the steric hindrance to the deformation during the hydrogen atom abstraction.

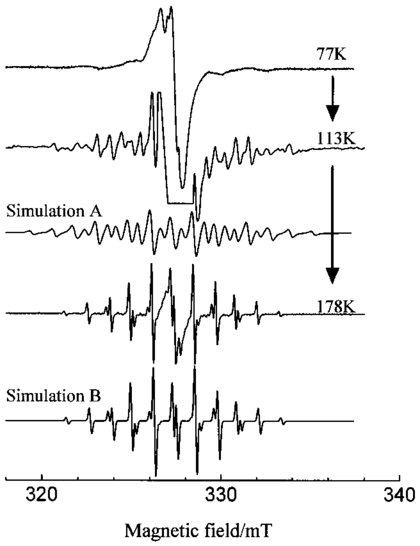


Figure 6. Effect of temperature on the ESR spectra of alkyl radicals generated by γ-irradiation at 77 K of perdeuterated adamantane matrix containing 3-methylpentane as guest molecules. Simulation A is a simulated spectrum obtained by using the hyperfine coupling constants of 2.32 mT for three methyl protons, 1.26 mT for two methylene protons, and 3.05 mT for the other two methylene protons. Simulation B is also a simulated spectrum obtained by using the hyperfine coupling constants of 2.32 mT for three methyl protons and 1.26 mT for four methylene protons.

Figure 6 shows the ESR spectra for a γ-irradiated perdeuterated adamantane matrix containing a small amount of 3-methylpentane as guest molecules. Broad ESR lines at the center of the spectra are due to free radicals from matrix molecules. Although free radicals from 3-methylpentane are not rotated at 77 K, they start to rotate at 113 K. Rotation of the free radicals suggests that the steric hindrance during the hydrogen atom abstraction is very weak in the adamantane matrix. The rotation is fast enough at 178 K to average out the spectral distribution. The spectrum is in good accordance with the simulated one that is obtained by assuming that an electron spin interacts with freely rotating three methyl protons with the hfcc of 2.32 mT and four equivalent protons with the hfcc of 1.26 mT. Since the hfcc of a β proton is approximately given by $4.8 \cos^2 \theta$ mT,[16] where θ is the dihedral angle between the 2p orbital of the unpaired electron and the C−H bond of the β carbon, the latter protons are attributable to two sets of methylene β protons with the $C_\alpha-C(H_2)-C(H_3)$ planes parallel to the 2p orbital. The free radicals observed at 178 K are therefore assigned to $CH_3CH_2C^*(CH_3)CH_2CH_3$, which is generated by hydrogen atom abstraction from the tertiary carbon atom of 3-methylpentane.

The spectrum at 113 K is also attributable to the tertiary alkyl radicals with several orientations of methylene protons with respect to the 2p orbital of the unpaired electron. As shown in Figure 6, most of the hyperfine lines observed at 113 K can be assigned to the interaction with three methyl protons with hfcc = 2.32 mT, two methylene protons with hfcc = 1.26 mT ($\theta \approx \pm 2\pi/3$), and the other two methylene protons with hfcc = 3.05 mT ($\theta \approx \pm 2\pi/3$). The latter methylene group has a conformation with the $C_\alpha-C(H_2)-C(H_3)$ plane almost perpendicular to the 2p orbital. The fitting between the observed and the simulated spectra is, however, not satisfactory due probably to the overlapping of the spectra of the tertiary radicals with different

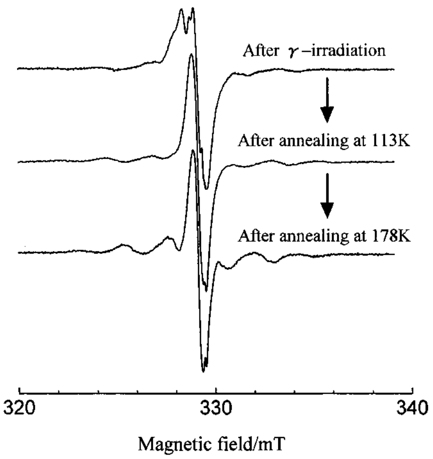


Figure 7. ESR spectra at 77 K for γ-irradiated adamantane matrix after thermal annealing.

conformations. The spectral change between 113 and 178 K was not reversible. The spectrum at 113 K of the sample annealed at 178 K was the same as that at 178 K except for the broadening of the ESR lines. The conformation with the $C_\alpha-C(H_2)-C(H_3)$ planes parallel to the 2p orbital is obviously the most stable structure for the tertiary radicals.

Figure 7 compares the spectral intensity of the sample after the thermal treatment. The double-integrated intensities of the entire and the central part of the spectrum were not changed by the thermal treatment, which certifies that the solute radicals are generated at 77 K by hydrogen atom abstraction with free deuterium atoms generated from the matrix molecules.

Discussion

The experimental results suggest that the rate of hydrogen atom tunneling from alkane molecules depends on the steric hindrance to the motion of the molecules. We propose that the anomaly of the hydrogen atom abstraction is due to the steric hindrance to the deformation of alkyl radicals from sp^3 to sp^2 configurations by matrix molecules. The relation between the chain length and the steric hindrance can be qualitatively expressed by calculating the energy for the reorientation of alkyl chains in a viscous fluid from sp^3 to sp^2 configurations. We assume that alkyl chains attached to a carbon atom to be hydrogen atom abstracted can be expressed by linear rods. Setting the initial locations of the edges of the i-th rod with length L_i to be (0, 0, 0) and (X_i,Y_i,Z_i), the location of point (x_i,y_i,z_i) on the rod at length l_i is given by

$$x_i = (l_i/L_i)X_i, \quad y_i = (l_i/L_i)Y_i, \quad z_i = (l_i/L_i)Z_i \tag{1}$$

where

$$X_i^2 + Y_i^2 + Z_i^2 - L_i^2 = 0 \tag{2}$$

The C−C−C bond angles of alkane molecules are about 112° so that

$$X_iX_j + Y_iY_j + Z_iZ_j - (\cos 112°)L_iL_j = 0 \tag{3}$$

Hydrogen atom abstraction from the carbon atom induces the movement of the edges of the rod from (0,0,0) to $(\Delta X_0,\Delta Y_0,\Delta Z_0)$ and from (X_i,Y_i,Z_i) to $(X_i + \Delta X_i, Y_i + \Delta Y_i, Z_i + \Delta Z_i)$, which causes the change of the location of point (x_i,y_i,z_i) to $(x_i + \Delta x_i, y_i + \Delta y_i, z_i + \Delta z_i)$, where

$$\begin{aligned}(x_i + \Delta x_i) &= (l_i/L_i)(X_i + \Delta X_i - \Delta X_0) + \Delta X_0\\ (y_i + \Delta y_i) &= (l_i/L_i)(Y_i + \Delta Y_i - \Delta Y_0) + \Delta Y_0\\ (z_i + \Delta z_i) &= (l_i/L_i)(Z_i + \Delta Z_i - \Delta Z_0) + \Delta Z_0\end{aligned} \tag{4}$$

$$(X_i + \Delta X_i - \Delta X_0)^2 + (Y_i + \Delta Y_i - \Delta Y_0)^2 + (Z_i + \Delta Z_i - \Delta Z_0)^2 - L_i^2 = 0 \tag{5}$$

$$(X_i + \Delta X_i - \Delta X_0)(X_j + \Delta X_j - \Delta X_0) + (Y_i + \Delta Y_i - \Delta Y_0)(Y_j + \Delta Y_j - \Delta Y_0) + (Z_i + \Delta Z_i - \Delta Z_0)(Z_j + \Delta Z_j - \Delta Z_0) - (\cos 120°)L_iL_j = 0 \tag{6}$$

The energy for moving the rod in a fluid with viscosity η is given by

$$E_i = \int_0^{L_i} \mathrm{d}l_i \int_0^{\Delta s_i} \eta \nu(l_i)\, \mathrm{d}s_i \approx \int_0^{L_i} \eta \nu(l_i) \Delta s_i\, \mathrm{d}l_i \tag{7}$$

where $\nu(l_i)$ and s_i are the velocity and the position of the track of point l_i, respectively. These are expressed by

$$\nu(l_i) \approx \Delta s_i/\Delta t \tag{8}$$

and

$$\begin{aligned}(\Delta s_i)^2 &= \Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2\\ &= [(l_i/L_i)(\Delta X_i - \Delta X_0) + \Delta X_0]^2 + [(l_i/L_i)(\Delta Y_i - \Delta Y_0) + \Delta Y_0]^2 + [(l_i/L_i)(\Delta Z_i - \Delta Z_0) + \Delta Z_0]^2\end{aligned} \tag{9}$$

where Δs_i and Δt are the length of the track and the time of reaction, respectively. The total energy for the reorientation of the rods from sp^3 to sp^2 configurations are given by

$$\begin{aligned}E_t &= \sum_{i=1}^{n} E_i\\ &= \frac{\eta}{3\Delta t}\sum_{i=1}^{n} L_i(\Delta X_i^2 + \Delta X_i\Delta X_0 + \Delta X_0^2 + \Delta Y_i^2 + \Delta Y_i\Delta Y_0 + \Delta Y_0^2 + \Delta Z_i^2 + \Delta Z_i\Delta Z_0 + \Delta Z_0^2)\end{aligned} \tag{10}$$

where n is the number of rods attached to the carbon atom. The calculus of variation with LaGrange's undetermined multipliers originated from eqs 5 and 6 gives the minimum energy of reorientation, viz.,

$$\begin{aligned}F = {}& \frac{\eta}{3\Delta t}\sum_{i=1}^{n}[L_i(\Delta X_i^2 + \Delta X_i\Delta X_0 + \Delta X_0^2 + \Delta Y_i^2 + \Delta Y_i\delta Y_0 + \Delta Y_0^2 + \Delta Z_i^2 + \Delta Z_i\Delta Z_0 + \Delta Z_0^2)] + \sum_{i=1}^{n} a_i[(X_i + \Delta X_i - \Delta X_0)^2 + (Y_i + \Delta Y_i - \Delta Y_0)^2 + (Z_i + \Delta Z_i - \Delta Z_0)^2 -\\ & L_i^2] + \sum_{i=1}^{n}\sum_{j\neq i}^{n} b_{ij}[(X_i + \Delta X_i - \Delta X_0)(X_j + \Delta X_j - \Delta X_0) + (Y_i + \Delta Y_i - \Delta Y_0)(Y_j + \Delta Y_j - \Delta Y_0) + (Z_i + \Delta Z_i - \Delta Z_0)(Z_j + \Delta Z_j - \Delta Z_0) + (\cos 120°)L_iL_j]\end{aligned} \tag{11}$$

and

$$\frac{\partial F}{\partial \Delta X_0} = \frac{\partial F}{\partial \Delta Y_0} = \frac{\partial F}{\partial \Delta Z_0} = \frac{\partial F}{\partial \Delta X_i} = \frac{\partial F}{\partial \Delta Y_i} = \frac{\partial F}{\partial \Delta Z_i} = 0 \quad (12)$$

Figure 8 shows the energy of reorientation thus calculated. (*m*, *n*, *N*) in the figure correspond to the numbers of carbon atoms in three alkyl chains bonded to a carbon atom to be hydrogen atom abstracted. Using Figure 8, we can make the rough estimation of the energy of the reorientation of alkane molecules for the hydrogen atom abstraction. The energy for a secondary penultimate carbon atom scarcely increases with increasing length of the other alkyl chain, since the reorientation of a small methyl group is enough for changing the configuration from sp^3 to sp^2. The energy of reorientation for secondary alkyl radicals increases with increasing the number of carbon atoms in the shorter chain. The energies for octane $CH_3C^*H(CH_2)_5CH_3$, $CH_3CH_2C^*H(CH_2)_4CH_3$, and $CH_3CH_2CH_2C^*H\ (CH_2)_3CH_3$ are 0.15, 0.9, and 1.8, respectively. This may give the reason the hydrogen atom abstraction is more difficult from the inner carbon atoms of normal alkanes.

The energy for the reorientation is much higher for tertiary carbon atoms, since the reorientation necessitates the reorientation of at least two alkyl chains. The energies for $CH_3C^*(CH_3)CH_2CH_3$, $CH_3C^*(CH_3)CH_2CH_2CH_3$, and $CH_3CH_2C^*(CH_3)CH_2CH_3$ are 1.2, 1.5, and 2.3, respectively. The steric hindrance to the formation of $CH_3CH_2C^*(CH_3)CH_2CH_3$ is about twice as much as that of $CH_3C^*(CH_3)CH_2CH_3$. This may also give the reason the hydrogen atom abstraction from the tertiary carbon of 3-methylpentane is much slower than that of 2-methylbutane.

We have assumed so far that the rate of hydrogen atom abstraction decreases with increasing steric hindrance to the deformation of alkyl radicals from sp^3 to sp^2 configurations by matrix molecules. However, the relation between the steric hindrance and the rate of hydrogen atom abstraction is not straightforward. The reaction would be slowed by the steric hindrance if the reaction proceeds through a thermal activation process, since the steric hindrance necessitates an additional thermal energy. However, the reaction proceeds through the atomic tunneling of C−H hydrogen without a thermal activation process. It is therefore necessary to understand how the steric hindrance affects the tunneling of hydrogen atoms.

The rate of hydrogen atom tunneling is generally expressed by the Fermi's golden rule, as

$$k = \frac{2\pi}{\hbar} \sum_{i,j} |\langle \psi_I | U(r) | \psi_{F,i} \rangle|^2 |\langle \chi_I | \chi_{F,j} \rangle| \delta(E_I - E_{i,j}) \quad (13)$$

Here ψ refers to a wave function expressing the motion of tunneling atom and $U(r)$ to an interaction potential connecting the initial alkane + D state and the final alkyl radical + HD state. Since propane + H is the simplest reaction system of hydrogen atom abstraction from secondary carbon, we adopt this system for explaining the effect of the steric hindrance with the aid of quantum chemical calculation. For hydrogen atom abstraction from the central carbon of $CH_3CH_2CH_3$, ψ corresponds to an antisymmetric $(CH_3)_2HC{-}H{-}D$ stretch motion with the initial state of $(CH_3)_2HC{-}H{\cdots}D$ and the final state of $(CH_3)_2HC{\cdots}H{-}D$. The wave functions of the other vibrational modes deformed by the reaction are given by χ. E_I and $E_{i,j}$ are the energies of the initial reactant and the final product states, and $\delta(E)$ is the term for energy conservation and is 1 or 0, depending on whether $E = 0$ or not 0, respectively. Although the deformation of χ can play a significant role in energy conservation by absorbing the heat of reaction, in hydrogen atom abstraction by deuterium atoms, the heat of reaction may be carried out as rotational and translational energies of product HD. The most important term for the hydrogen atom tunneling is therefore $\langle \psi_I | U(r) | \psi_F \rangle$ or the shape of the potential energy barrier separating the initial alkane + D and the final alkyl radical + HD states. The tunneling rate is then expressed by the well-known equation for the tunneling penetration of a particle through a one-dimensional potential barrier, as

$$k \approx |\langle \psi_I | U(r) | \psi_F \rangle|^2 \approx \exp\left(-2\sqrt{2\mu/\hbar^2} \int_a^b \sqrt{U(r) - E_I}\, dr\right) \quad (14)$$

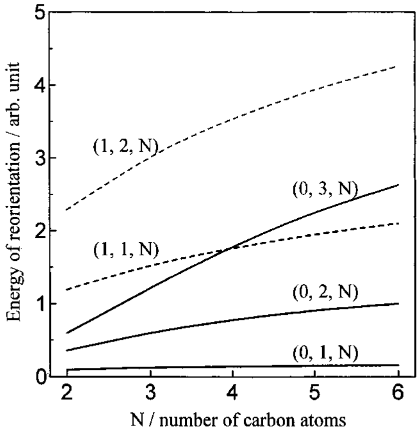


Figure 8. Relation between the energy of the reorientation of alkyl chains from sp^3 to sp^2 configurations and the length of the chains. (*m*, *n*, *N*) denote the numbers of carbon atoms of three alkyl chains bonded to a carbon atom to be hydrogen atom abstracted.

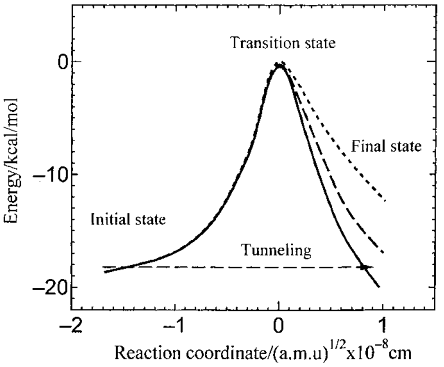


Figure 9. Potential energy surfaces for model reaction $H + CH_3CH_2CH_3 \rightarrow H_2 + CH_3CHCH_3$ under three reaction conditions: reactions under no restriction on the motion of atoms (—); under the fixed C−C−C bond angle (114°) of initial propane (- - -); under the fixed atomic configurations except for attacking H and attacked H (• • •).

Here, μ is the reduced mass of the tunneling particle and a and b are the locations where the potential energy is equal to E_I. It is evident from eq 14 that the tunneling rate considerably decreases with increasing area of the potential barrier above the initial energy.

Figure 9 shows the shape of the potential energy barriers for hydrogen atom abstraction as calculated with 3-21G* basis set[18] under three different reaction conditions: no restriction on the motion of atoms, the fixed C−C−C bond angle of initial propane, and the fixed C−C−C and C−C−H bond angles of initial propane. The first, the second, and the third conditions were selected to simulate the hydrogen atom tunneling in a vacuum, in a rigid matrix, and in a rigid matrix from an immobile tertiary carbon atom, respectively. The height of the potential energy barrier is scarcely changed by the restrictions posed to propane. This is because hydrogen atom abstraction is a typical reaction with early transition state; the transition state with minimum energy is attained without much change of the vibrational modes other than the reaction one. However, the differences gradually increase after passing the transition state. This is mainly due to the repulsion between the unpaired electron in the 2p orbital of the radical carbon and the electrons in product H_2. The 2p orbital projects toward product H_2 as long as no conformational relaxation of the propyl radical takes place. Since the rate constant k of tunneling is exponentially dependent on the square root of the cross section of the potential energy barrier above the energy of the initial state, it is evident that the tunneling rate considerably decreases with increasing steric restrictions posed to alkane molecules. The tunneling of hydrogen atoms from the tertiary carbon of 3-methylpentane is therefore much slower than that from the secondary carbon, even though the barrier is lower. It should be noted that such a matrix effect could not be expected for Arrhenius-type reactions, since the reaction rate is independent of the thickness of the potential barrier.

It should also be noted that the matrix effect depends on the nature of both the solute molecules and matrixes. The difference between the selectivity of hydrogen atom abstraction from 3-methylpentane in the methanol and the adamantane matrixes can be explained by the difference of the mobility of 3-methylpentane. As mentioned earlier, the 3-methylpentane molecules are mobile in the vacancies of the adamantane matrix, which may reduce the energy for the deformation during the hydrogen atom abstraction and cause the selective abstraction from the tertiary carbon with the lowest activation energy. The change of the matrix from methanol to adamantane may also cause a change in the collision cross sections of deuterium atoms with the methylene and methine hydrogen atoms of 3-methylpentane, which may cause a change in the selectivity of the abstraction. However, we believe that the effect of the collision cross section may not be so important, since the observed change of the selectivity is so drastic.

The present results suggest that the rate of hydrogen atom tunneling from alkane molecules in cryogenic solids is very sensitive to the steric hindrance by the solids to the deformation of the molecules during the tunneling. This may give a reason that the kind of alkyl radicals and the resultant stable products generated by γ-irradiation of organic solids depend on the physical nature of the solids.[19−24]

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