ESR, ENDOR, and ESEEM Spectroscopy Study on the Local Structure and Motion of Reactants: Highly Selective Tunneling Radical Abstraction in a Neopentane−Ethane Mixture

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Local structures and motions of radical reactants in highly selective tunneling abstraction reaction in neopentane−ethane mixture are investigated with CW-ESR, ENDOR, and ESEEM spectroscopy at different temperatures. H atoms produced by the radiolysis of neo-C_5H_{12} in the neo-C_5H_{12}−C_2H_6 (2 mol %) mixtures above 40 K react selectively with the solute C_2H_6 to give ethyl radicals. The selective reaction is suppressed below 30 K. The local structures of neopentane matrix around neopentyl and ethyl radicals are approximately the same in the temperature range from 4.4 to 45 K. Although neopentyl radicals are rigidly trapped below 100 K, ethyl radicals in neopentane matrix begin to librate even at 6 K and increase the degree of motion up to 30 K. Finally, the librating motion of the ethyl radicals in neopentane matrix is vigorous above 40 K. The ethane molecule can take more favorable orientation for the hydrogen abstraction reaction by H atoms than rigid neopentane molecules by the vigorous libration motion, resulting in the selective reaction with H atoms.

1. Introduction

The tunneling reaction that occurs by passing through the energy barrier for the reaction by a quantum-mechanical tunneling effect is a new type of chemical reactions. Nearly 30 years ago Miyazaki et al. found that H atoms react several hundreds times faster with the solute alkane than the solvent neopentane to form solute alkyl radicals when H atoms are produced by the radiolysis of neopentane in neopentane−alkane mixtures at 77 K.[1] The selective reaction is, however, suppressed at 4 K.[2,3] Although H atoms have never been observed by ESR in irradiated neat neopentane−alkane mixtures even at 4 K, the detailed studies by Miyazaki et al. have concluded that H atoms produced by radiolysis react with solute alkane by a hydrogen atom abstraction reaction due to atomic tunneling.[4] Let us consider the following reactions 1 and 2:

$$\text{neo-}C_5H_{12} + H \xrightarrow{k_1} \text{neo-}C_5H_{11} + H_2 \quad (1)$$

$$C_2H_6 + H \xrightarrow{k_2} C_2H_5 + H_2 \quad (2)$$

Since both neopentane (neo-C_5H_{12}) and ethane (C_2H_6) molecules are composed of primary C−H bonds, the difference in the energy barrier height for the abstraction reactions between 1 and 2 is very small. In fact, the barrier heights for the reactions 1 and 2 in the gas phase has been measured as 9.6 and 9.4 kcal mol^{-1}, respectively.[5] If the above reactions take place by quantum tunneling, the rate constants (k) for the reactions can be estimated by the model where the potential energy curve for the reaction is approximated by an Eckart barrier.[6] The model predicts that the ratio (k_2/k_1) of the rate constants for reactions 1 and 2 is less than 2.2,[7] which is much smaller than the experimental ratio of 380.[4] Thus, the large experimental value of k_2/k_1 for reactions 1 and 2 in the neo-C_5H_{12}−C_2H_6 mixtures cannot be explained by the small difference in the barrier height between reactions 1 and 2. Thus, the large experimental value of k_2/k_1 for reactions 1 and 2 in the neo-C_5H_{12}−C_2H_6 mixtures cannot be explained by the small difference in the barrier height between reactions 1 and 2.

Recently, it has been observed that the rate constant for the tunneling reaction HD + D → H + D_2 in solid hydrogen increases significantly with increasing temperature in the range 5−6.5 K.[8] The activation energy, observed from the increase of the rate constant with increasing temperature, is 90 K, which is approximately equal to the vacancy formation energy in solid hydrogen.[9,10] The result indicates that the tunneling reaction of hydrogen atoms in the solid phase is accelerated by a small increase of energy accompanying the vacancy formation, which causes local motions of reactants. If the selective reaction of H atoms in the neopentane−alkane mixtures is a tunneling reaction, the selectivity in the tunneling reaction may be related to local motions or local environment of the solute alkane. Very recently, we have investigated the selective reaction in neopentane−isobutane (i-C_4H_{10}) mixture with HI.[7] When H atoms are produced by the photolysis of HI or the radiolysis of neo-C_5H_{12} in the neo-C_5H_{12}−i-C_4H_{10} (2 mol %) mixtures above 40 K, the H atoms react selectively with the solute i-C_4H_{10}. The selective reaction is also suppressed below 30 K. The selectivity was investigated by measuring the temperature dependence of

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continuous wave (CW) ESR signals of the solvent neo-C_5H_{11} radicals and the solute t-C_4H_9 radicals. The results indicate that local motions of the solute i-C_4H_{10} molecules take place above 40 K, while motions of the solvent neo-C_5H_{12} molecules are severely restricted, even at 100 K. Thus, we have speculated that the local motions of the solute i-C_4H_{10} assist the tunneling abstraction reaction by H atoms, resulting in the selective reaction with the solute above 40 K. In the previous study, however, we have not managed to clarify the structure and the local motion of neopentane and solute molecules.

ENDOR (electron nuclear double resonance) and ESEEM (electron spin−echo envelope modulation) spectroscopy are employed in this study in order to analyze the temperature dependence of the selective reactions in the neopentane−ethane mixture. ENDOR spectroscopy has a potential to clarify not only intramolecular hyperfine coupling constants of the radical but also dipole−dipole interactions between the radical and protons in matrix molecules. The former information is very important for the intramolecular structure of the radical, and the latter one, the so-called matrix ENDOR, will determine the distances between the radical and matrix protons.[11] ESEEM spectroscopy also detects magnetic dipole−dipole interactions between the radical and matrix protons or deuterons.[12−14] Since the ESEEM signals include both information about distances between the radical and matrix protons or deuterons and numbers of the matrix protons or deuterons, the number of matrix protons or deuterons from the radical at the same distance can be strictly determined by combining the results of matrix ENDOR. The purpose of this study is to elucidate the highly selective tunneling reaction in the solid neopentane−ethane mixtures in relation to the local structures around reactants and their local motion. The first question is whether the local structure around a solute ethane is the same as that around a solvent neopentane. The second question is whether the local motion of solute ethane is the same as that of solvent neopentane.

2. Experimental Section

The purities of neopentane-h_{12} (neo-C_5H_{12}), neopentane-d_{12} (neo-C_5D_{12}), and ethane (C_2H_6) are more than 99.9, 98.0, and 99.9 mol %, respectively. The mixtures of neo-C_5H_{12} (or neo-C_5D_{12}) containing 2 mol % C_2H_6 were sealed in a quartz tube. Helium gas at 260 mmHg was also sealed into the tube in order to facilitate rapid cooling of the sample at low temperature. The sample was irradiated by white light X-rays (50 kV, 48 mA for CW-ESR and ESEEM, 70 kV, 20 mA for ENDOR, respectively). The irradiation temperatures were exactly controlled by a model 9650 cryogenic temperature indicator/controller (Scientific Instruments Inc.) combined with a cryostat using liquid helium as a coolant within an error of ±0.05 K.

After the irradiation at different temperatures, ESR spectra of radicals were measured at 77 K by a X-band JEOL JES-TE200 spectrometer at a microwave power level at which microwave power saturation of the signals did not occur. The yields of radicals were obtained by double integration of the signals by ESPRIT software developed by JEOL.

The electron nuclear double resonance (ENDOR) signals of neo-C_5H_{12}(98%)−C_2H_6(2%) or neo-C_5D_{12}(98%)−C_2H_6(2%) mixtures X-ray-irradiated at 77 K were measured with a X-band Bruker ELEXSYS E580 spectrometer in Linköping University at the temperature range 4−50 K.

The electron spin−echo (ESE) signals of neo-C_5D_{12}(98%)−C_2H_6(2%) mixture X-ray-irradiated at 4 or 77 K were measured with a X-band JEOL JES-PX1050 pulse-ESR spectrometer in Advanced Science Research Center of Japan Atomic Energy Research Institute at the temperature range 4−50 K. The ESE signals were observed by the $\pi/2-\pi$ two-pulse sequences.[12−14]

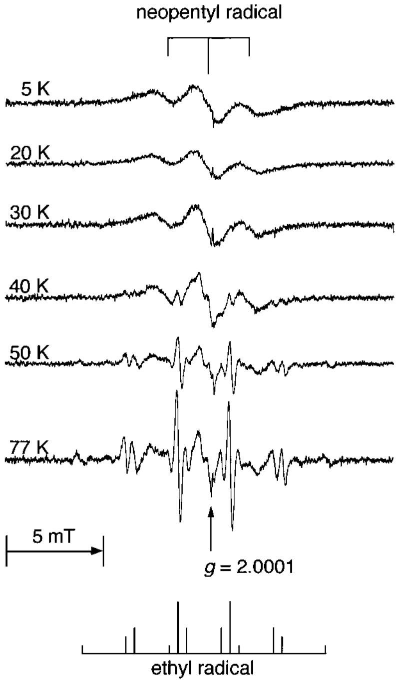

Figure 1. ESR spectra at 77 K of a neopentane-h_{12} (98%)−ethane (2%) mixture X-irradiated at 5−77 K. Microwave frequency is 8.987 GHz.

3. Results

Figure 1 shows the ESR spectra at 77 K of a neo-C_5H_{12} (98%)−C_2H_6 (2%) mixture X-ray irradiated at different temperatures between 5 and 77 K. When the sample is X-irradiated at 5−30 K, the observed signals are composed of broad triplet lines assigned to the neopentyl radical. Two α-protons, which have hyperfine coupling constants (HFCC) of 2.1 mT, give rise to the triplet lines.[15] When the sample is X-irradiated at 40−77 K, well-resolved signals due to ethyl radicals are overlapped on the signal of neopentyl radicals. The isotropic hyperfine coupling constants of the ethyl radical are reported as 2.239 mT for two α-protons and 2.687 mT for three β-protons, respectively.[16] The intensity of the signal due to ethyl radicals is increased with increasing temperature from 40 to 77 K. The ratio of the yields of neopentyl and ethyl radicals and the total yields of both radicals in the mixture are plotted in Figure 2 against X-ray-irradiation temperature. When the temperature increased from 30 to 77 K, the ratio of the relative yields of ethyl radicals is increased to 18%. There is appreciable scatter in the total amounts of both radicals. Within the uncertainly of the determination, the total yield of the radicals seems to be independent of the temperature.

The detailed studies by Miyazaki et al. have concluded that H atoms produced by radiolysis react with solute alkane by a hydrogen atom abstraction reaction due to atomic tunneling.[4] The average distance the H atoms might travel in the neopentane matrix has not been clarified yet; however, the rate of diffusion probably becomes significant above 30 K, because the selective reactions in the matrix take place above 30 K, even if solutes in the matrix are other molecules such as isobutane and cyclopentane.[7]

Figure 3 shows the ESR spectra at 5−50 K of neopentane (98%)−ethane (2%) mixture irradiated by γ-rays at 77 K. Since

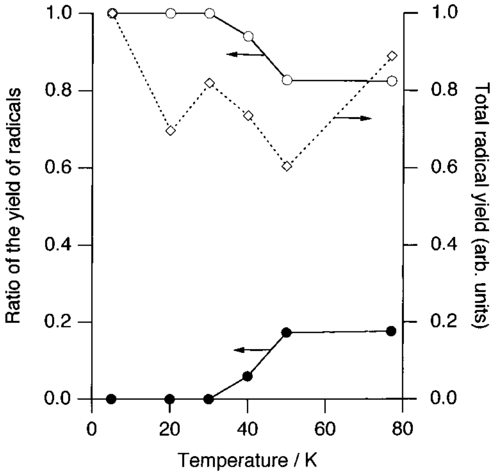

Figure 2. Dependence of the ratio of the yields of neopentyl (open circle) and ethyl (solid circle) radicals and total yields of the radicals (open diamond) in the irradiated neopentane-h_{12} (98%)−ethane (2%) mixture on the X-ray irradiation temperature.

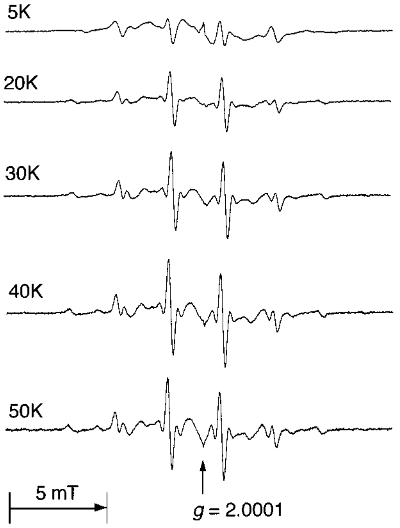

Figure 3. ESR spectra at 5−50 K of neopentane (98%)−ethane (2%) mixture irradiated by γ-rays at 77 K.

the signals due to ethyl radicals are approximately isotropic at the whole range of temperatures, the CH_3 group seems to rotate classically even at 20 K in the neopentane matrix. Thus, the local motion of ethyl radicals is not strongly restricted, even at 20 K. This is opposite to the case of *tert*-butyl radicals in the neopentane matrix, where classical rotation of CH_3 groups is restricted below 30 K.[7]

Figure 4 shows the matrix ENDOR spectra of neopentyl (left) and ethyl (right) radicals at 4.2, 20, and 45 K, respectively. The ENDOR spectra were observed by scanning the radio frequency, simultaneously resonating on the ESR absorption lines of neopentyl and ethyl radicals, indicated by thick arrows in the ESR spectra at 20 K above each ENDOR spectrum. Magnetic fields for the ENDOR measurements are chosen at 339.15 and 337.04 mT for the neopentyl and ethyl radicals, respectively, and corresponding proton NMR frequencies (υ_0) are determined as 14.44 and 14.35 MHz, respectively. The microwave frequency is 9.500 GHz for all measurements of the ENDOR spectra. Micro- and radiowave powers are 20.07 mW and 2 dB, respectively, and FM modulation of the radiowave is 50 kHz.

All ENDOR spectra of neopentyl radicals are composed of five sets of peaks indicated by lines above the spectrum at 4.2 K. Two peaks at 12.22 and 16.66 MHz, indicated by solid lines, are attributable to the hyperfine coupling constant (A) of weakly coupled protons in the neopentyl radical, appearing at $\upsilon_0 \pm A/2$. The hyperfine coupling constant A of 4.22 MHz, which corresponds to 0.15 mT in field units, is assigned as γ-protons of methyl groups in the molecule of neopentyl radical. The other sets of peaks at 13.64 and 15.24 MHz (indicated by dotted lines), at 13.98 and 14.90 MHz (broken lines), at 14.13 and 14.75 MHz (chain lines), and at 14.37 and 14.51 MHz (double chain lines) correspond to interactions of the unpaired electron in the neopentyl radicals with the protons of neopentane matrix molecules. Although the heights of the peaks changed with the temperature, probably due to variation of the rates of spin−lattice relaxation of the neopentyl radical, frequency positions of the peaks are constant at all temperatures. Since these frequency positions of the peaks reflect local structures around the neopentyl radicals, the structures around the neopentyl radicals remain unchanged between 4.2 and 45 K. The intensities of the ENDOR signals above 50 K were decreased drastically, probably due to the rapid increase of the rate of spin−lattice relaxation of the neopentyl radical. The very sharp signal at 12.50 MHz, indicated by an asterisk in the figure, is a ghost one, which also appeared on offset ESR resonance condition at 4.2 K.

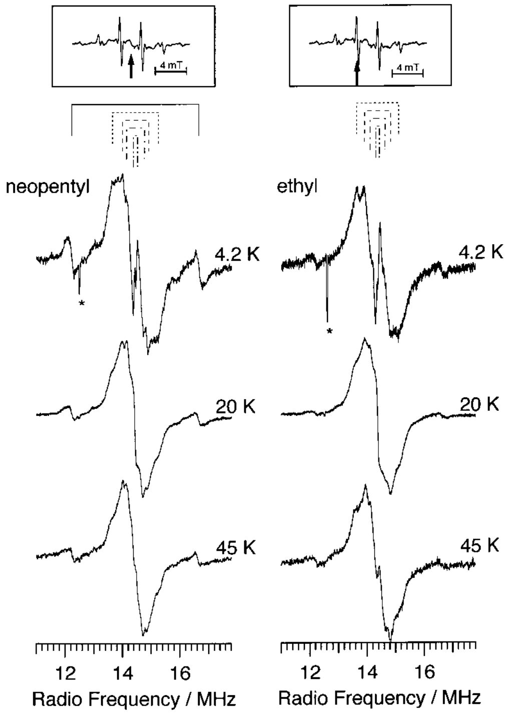

Figure 4. The matrix ENDOR spectra of neopentyl (left) and ethyl (right) radicals in neopentane-h_1(98%)−ethane (2%) mixture at 4.2, 20, and 45 K, respectively. The ENDOR spectra were observed by scanning the radio frequency, simultaneously resonating on the ESR absorption lines of neopentyl and ethyl radicals, as indicated by thick arrows in the ESR spectra at 20 K above each ENDOR spectrum. Magnetic fields for the ENDOR measurements are chosen at 339.15 and 337.04 mT for the neopentyl and ethyl radicals, respectively, and the corresponding proton NMR frequencies (υ_0) are determined as 14.44 and 14.35 MHz, respectively. The microwave frequency is 9.500 GHz for all measurements of the ENDOR spectra. Micro- and radiowave powers are 20.07 mW and 2 dB, respectively, and FM modulation of the radiowave is 50 kHz.

All ENDOR spectra of the ethyl radicals are composed of four sets of peaks indicated by lines above the spectrum at 4.2 K. Four sets of peaks at 13.62 and 15.08 MHz (indicated by dotted lines), at 13.89 and 14.81 MHz (broken lines), at 14.09 and 14.61 MHz (chain lines), and at 14.29 and 14.41 MHz

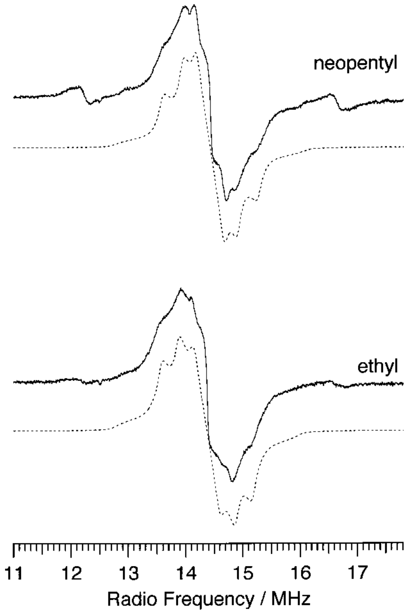

Figure 5. Matrix ENDOR spectra at 20 K of neopentyl (upper) and ethyl (lower) radicals. The spectra shown in solid and broken lines are observed and simulated ones, respectively. Only magnetic dipole−dipole interactions between an unpaired electron and surrounding matrix protons from first to third positions are taken into account in the simulation. The parameters for the simulation are summarized in Table 1.

TABLE 1: Simulation Parameters for the Matrix ENDOR Spectra of Neopentyl and Ethyl Radicals in Neopentane Matrix

	distance/nm	
*i*th nearest position	neopentyl[a]	ethyl[a]
first	0.360	0.365
second	0.430	0.425
third	0.530	0.540

[a] The number (*N*) of protons which locate at the *i*th nearest positions from the radicals on the simulation were taken as 3 (first), 6 (second), and 10 (third) for neopentyl radicals, and 2 (first), 3 (second), and 4 (third) for ethyl radicals. Since the amplitude of ENDOR signals depends on the spin−lattice relaxation, *N* values have no physical importance except for satisfying the spectral shapes of the observed spectra. The real number of matrix protons around the radicals observed by the ESEEM spectroscopy is shown in the Table 2.

(double chain lines) correspond to matrix protons. Although the heights of the peaks changed with the temperature in the same way as for the neopentyl radicals, the frequency positions of the peaks are constant at all temperatures. Thus, it is indicated that the structure around the ethyl radicals remains unchanged between 4.2 and 45 K. The intensities of the ENDOR signals above 50 K decreased drastically. The very sharp signal at 12.60 MHz, indicated by an asterisk in the figure, is a ghost one, which also appeared on offset ESR resonance condition at 4.2 K.

Figure 5 shows the matrix ENDOR spectra at 20 K of neopentyl (upper) and ethyl (lower) radicals. The spectra shown in solid and broken lines are observed and simulated ones, respectively. Only magnetic dipole−dipole interactions between the unpaired electron and surrounding matrix protons from first to third nearest positions are taken into account in the simulations. Details of the method of simulation are described elsewhere,[11,17] and the parameters for the simulation are summarized in Table 1. The simulations for the matrix ENDOR spectra give the distances between the neopentyl or ethyl radicals and matrix protons explicitly. As shown in Table 1, the distances to matrix protons are almost the same for neopentyl and ethyl radicals.

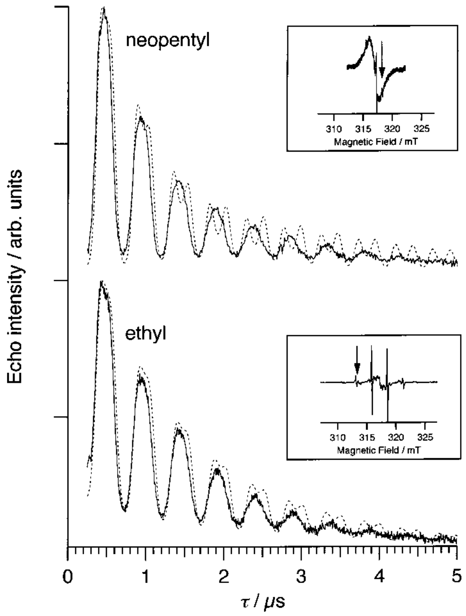

Figure 6. The ESE spectra at 20 K of neopentyl and ethyl radicals in neopentane-d_{12} matrix. The spectra, shown in solid and broken lines, are observed and simulated ones, respectively. The ESE signals were measured by using $\pi/2-\pi$ two-pulse sequences. The parameters for the simulation are summarized in Table 2.

TABLE 2: Simulation Parameters for the ESEEM Spectra of Neopentyl and Ethyl Radicals in Neopentane(d_{12}) Matrix

*i*th nearest position	neopentyl		ethyl	
	N[a]	distance/nm	*N*[a]	distance/nm
first[b]	15 (9 + 6)[b]	0.360	6	0.365
second	18−21	0.430	18−21	0.425
third	27−33	0.530	27−33	0.540

[a] *N* is the number of deuterium atoms located at *i*th nearest positions from the radicals. Isotropic hyperfine coupling constants of 0.15 and 0.10 MHz for neopentyl and ethyl radicals are introduced for the simulation of ESEEM spectra at the first positions. [b] The unpaired electron of a perdeuterated neopentyl radical interacts with nine γ-deuterons in the radical itself and six deuterons of neopentane molecules at the first positions.

Figure 6 shows the ESE spectra at 20 K of neopentyl and ethyl radicals in a neopentane-d_{12} matrix. The spectra, shown in solid and broken lines, are observed and simulated ones, respectively. The ESE signals were measured by using $\pi/2-\pi$ two-pulse sequences.[12−14] The periodic modulation on the envelope signals, ESEEM, arises from magnetic interactions between the unpaired electron of the neopentyl or ethyl radicals and the deuterons of perdeuterated matrix neopentane molecules. Large magnetic interactions such as hyperfine couplings of α- or β-protons in ethyl or neopentyl radicals are not detectable in ESEEM spectra.[12,13] Simulations of the ESEEM spectra were done by the second-order perturbation theory described elsewhere.[12−14] The parameters for the simulation are summarized in Table 2. The periodic modulation on the envelope signals can be expressed as a function of the distances between the unpaired electron and surrounding matrix deuterons and the number of matrix deuterons. The simulation of the ESE signals is done by changing the number of matrix deuteron atoms at each nearest position by using the observed distances by matrix ENDOR. As shown in Figure 6, the simulated spectra coincide very well with the observed ones. The number of surrounding matrix deuterons is not the same for the neopentyl and ethyl

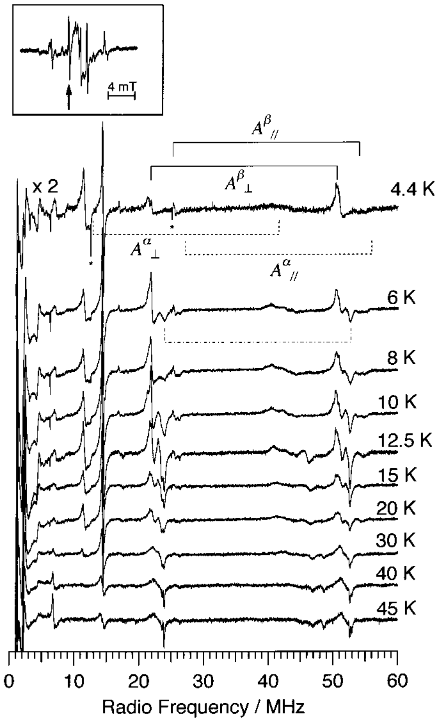

Figure 7. Temperature dependence of the ENDOR spectra of neopentane-d_{12} (98%)−ethane (2%) X-ray irradiated at 77 K. The ENDOR spectra were observed by scanning radio frequency, simultaneously resonating on the ESR absorption lines of ethyl radical, indicated by thick arrow in the ESR spectrum at 4.4 K at the left upper of the figure. Magnetic field for the ENDOR measurements is chosen at 338.05 mT when the microwave frequency is 9.501 GHz. Micro- and radiowave powers are 20.07 mW and 2 dB, respectively, and FM modulation of the radiowave is 100 kHz. The proton NMR frequency (υ_0) is determined as 14.39 MHz in the applied magnetic field. The largest signal at 14.39 MHz is probably due to protons present as impurities in the neopentane-d_{12} molecules.

radicals, especially not in the nearest position. Since the neopentyl radical has nine γ-deuterons in the radical itself, the unpaired electron of the radical in the matrix presumably interacts with the magnetic moments of these nine deuterons and additionally with six deuterons in neopentane matrix molecules. On the other hand, the unpaired electron of the ethyl radical interacts only with the magnetic moments of matrix deuterons in neopentane molecules. Under this assumption, the number of deuterons from the neopentane matrix in the first, second, and third nearest positions around the neopentyl and ethyl radical are approximately the same. The parameters in Table 2 for the two radicals are consistent with the observed ESE spectra at 5−45 K and agree very well between the two radicals. Therefore, the local structures of matrix neopentane around neopentyl and ethyl radicals are similar and very rigid in the temperature range from 5 to 45 K. Thus, the ethyl radicals are probably trapped in the substitutional sites of the neopentane matrix. Details on the local structures around solvent neopentane and solute ethane molecules are discussed in the Discussion section.

Figure 7 shows the temperature dependence of the ENDOR spectra at 4.4−45 K of ethyl radicals produced in X-ray-irradiated neopentane-d_{12} (98%)−ethane (2%) at 77 K. The ENDOR spectra were observed by scanning the radio frequency, simultaneously resonating on the ESR absorption lines of ethyl radical, indicated by the thick arrow in the ESR spectrum at 4.4 K at the upper left of the figure. The magnetic field for the ENDOR measurements is chosen at 338.05 mT when the microwave frequency is 9.501 GHz. Micro- and radiowave powers are 20.07 mW and 2 dB, respectively, and FM modulation of the radiowave is 100 kHz. The strong signal at 14.39 MHz in all the spectra, corresponding to the proton NMR frequency (υ_{H0}) at the applied magnetic field, is probably due to protons present as impurities in the neopentane-d_{12} molecules.

The ENDOR spectrum at 4.4 K has two signals around 22 and 52 MHz, and their shapes are rather similar to each other. Since the shapes of the signals appear to be axially symmetric, those signals are due to hyperfine coupling constants (A) of α- or β-protons of ethyl radicals which should appear at $|A/2 \pm \upsilon_{H0}|$. The ENDOR peaks at 21.77 and 50.56 MHz, corresponding to a hyperfine coupling of 2.581 mT in magnetic units, is attributable to $A_{\perp}$ of the β-protons in ethyl radical, and the peaks at 25.20 and 53.98 MHz, corresponding to 2.825 mT in magnetic units, is attributable to $A_{\|}$ of the β-protons. Those values are in good agreement with the previous ESR study of ethyl radicals observed at 4.2 K in an Ar matrix by McDowell et al.[18] Since the ENDOR spectrum due to β-protons has an axially symmetric shape, the CH_3 groups in ethyl radicals are rotating classically about the C−C bond axis, which is fixed in space. Although the ENDOR peaks due to the α-protons are expected to appear in the spectrum, as indicated by dotted lines in the figure,[18] it is difficult to identify the peaks in the observed spectrum at 4.4 K. The very sharp signals at 12.50 and 25.04 MHz, indicated by asterisks in the figure, are ghost ones, which also appeared on offset ESR resonance condition at 4.4 K.

When the temperature increases from 4.4 to 6 K, new peaks appear at 23.90 and 52.68 MHz (indicated by chain lines), and the relative intensity of the peaks to adjacent peaks at 21.77 and 50.56 MHz are increasing with increase in the temperature from 6 to 30 K. However, when temperature increased from 30 to 45 K, the signal shapes around 23 and 52 MHz are approximately constant. The frequency positions of the new peaks at 23.90 and 52.68 MHz are also different from the expected $A_{\|}$ or $A_{\perp}$ α-proton values at 4.4 K, therefore, the new peaks probably appeare by the onset of libration in space of the C−C bond axis of the ethyl radicals above 6 K, resulting in apparent changes of the A values of the β-protons. Thus, the libration becomes larger and larger by increasing the temperature from 6 to 30 K.

4. Discussion

4.1. Local Structures around Solvent Neopentane and Solute Ethane Molecules. It is assumed in this study that the local structures around neopentane or ethane molecules are approximately equal to those of neopentyl or ethyl radicals in the neopentane matrix. Thus, the local structures where the tunneling reactions occur are evaluated by analyzing the local structures around the reactant radical molecules.

There are two issues on the local structures around the solvent and solute molecules in neopentane matrix that must be considered. The first issue is whether the structure of the neopentane matrix is deformed by the presence of solute ethane molecules. The second issue is whether the local structures around solute ethane and/or solvent neopentane are changing with temperature. Distances from both solvent neopentyl radicals and solute ethyl radicals to the matrix neopentane molecules were determined with matrix ENDOR spectroscopy as shown in Figure 5. The analysis of the spectra shows that the distances from both the solute ethyl radical and the solvent neopentyl radical to the protons of matrix neopentane are approximately the same. The number of deuteron atoms from the perdeuterated neopentane matrix at the first, second, and third nearest positions around solute ethyl radicals and solvent neopentyl radicals is investigated with ESEEM spectroscopy as shown in Figure 6.

The analysis of the spectra shows that the numbers of surrounding matrix deuterons at each layer is approximately the same for the neopentyl and ethyl radicals as given in Table 2. Thus, the ethyl radicals are probably trapped in the substitutional sites of neopentane matrix. It is concluded that the local structures of matrix neopentane around neopentyl and ethyl radicals are approximately the same.

The second issue, whether the local structures around solute ethane and/or solvent neopentane change with temperature, can be partly answered by an analysis of the ENDOR spectra of both solvent neopentyl and solute ethyl radicals in neopentane matrix at 4.2−45 K as shown in Figure 4. Although the heights of the peaks changed with the temperature, frequency positions of the peaks are constant at all temperatures. Since these frequency positions of the peaks reflect local structures around a neopentyl or a ethyl radical, the structures around these radicals seem to remain unchanged between 4.2 and 45 K. In addition, the parameters in Table 2 are quite consistent with the observed ESE spectra at 5−45 K. Therefore, the structure of neopentane matrix is not deformed by the existence of solute ethane molecules in the temperature range from 5 to 45 K.

4.2. Local Motions of Solvent Neopentane and Solute Ethane Molecules. It is assumed in this study that the local motions of neopentane or ethane molecules are approximately equal to those of neopentyl or ethyl radicals in the neopentane matrix. Thus, the local motions of solvent and solute molecules are evaluated by analyzing the reactant radical molecules by ESR and ENDOR spectroscopy.

The rotation around the $(CH_3)_3C-CH_2$ bond in the neopentyl radical in neopentane matrix is restricted even at 100 K and the hyperfine structure due to γ-protons of the CH_3 group disappear below 80 K.[7,15] Even the slight local motion of the CH_3 group is suppressed below 80 K. Thus, the local motion of solvent neopentane molecules is severely restricted, even at 80 K. The CH_3 group in an ethyl radical, however, is freely rotating, even at 20 K in the neopentane matrix, as shown in the ESR spectrum in Figure 3. As shown in Figure 7, the ENDOR signals due to hyperfine coupling constants of β-protons of ethyl radicals in axial symmetric shape is only observed at 4.4 K, and the axial symmetric shape of the signal converted to complex shapes even at 6 K, probably due to increase in the libration mode of the C−C bond axis of ethyl radicals in space. It indicates that the ethyl radicals are trapped more freely than the neopentyl radicals in neopentane matrix. Neopentyl radicals are rigidly trapped in the neopentane matrix, preventing local motions even at higher temperature. On the other hand, ethyl radicals in neopentane matrix begin to librate, even at 6 K, increasing the degree of motion to 30 K, to become vigorous above 40 K. As mentioned in the previous section, the numbers of surrounding matrix deuterons at each layer is approximately the same for the neopentyl and ethyl radicals. In another words, the smaller ethane molecule has more free volume in the trapping site of the matrix, which presumably underlies its greater mobility. One might speculate that the ethane molecule can take an orientation more favorable for the hydrogen abstraction reaction by H atoms because of the its greater mobility compared to the rigid neopentane molecules. It is concluded that the selective tunneling abstraction by H atoms in the neopentane−ethane mixtures above 40 K is caused by the local motions of the solute ethane in the rigid neopentane matrix.

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