Temperature Effect on Selective Tunneling Abstraction Reaction by H Atoms in Neopentane−Alkane Mixtures at 4−100 K

Jun Kamagai,[†] Takayuki Kumada,[†] Naoki Kitagawa,[‡] Norio Morishita,[§] and Tetsuo Miyazaki*[,†,‡]

Advanced Science Research Center, Japan Atomic Energy Research Institute (Tokai), Tokai-mura, Naka-gun, Ibaraki 319-11, Japan, Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan, and Japan Atomic Energy Research Institute (Takasaki), 1233 Watanuki, Takasaki, Gunma, 370-12, Japan

Received: November 6, 1997; In Final Form: February 4, 1998

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 suppressed below 30 K. The reactions have been studied by electron spin resonance and electron spin echo measurements at 4−100 K. The drastic temperature effect on the reaction by H atoms suggests that the H atoms concerned are not hot atoms, but thermal atoms. The thermal H atoms react with the solute alkane by quantum tunneling at low temperature. Temperature effects on the ESR spectra and the spin−lattice relaxation times of the solvent neo-C_5H_{11} radicals and the solute t-C_4H_9 radicals 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. It is concluded 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.

Introduction

A nuclear tunneling effect on a chemical reaction has been one of the important problems in chemical kinetics especially at low temperature. Recent results on the tunneling reactions have been reviewed.[1] Tunneling reactions of H atoms with hydrogen molecules have been studied in detail in solid hydrogen at very low temperature.[2,3] A tunneling reaction of H atoms with ethane was studied in a rare-gas matrix at 50 K.[4]

When H atoms are produced by the photolysis of HI or the radiolysis of neopentane in neopentane−alkane mixtures at 77 K, H atoms react several hundreds times more selectively with the solute alkane than the solvent neopentane, resulting in the selective formation of solute alkyl radicals.[2,5] Though H atoms in the radiolysis of neopentane cannot be observed by ESR at 4 K, the detailed studies by Miyazaki et al. have concluded that H atoms produced by radiolysis react with the solute alkane by a hydrogen-atom-abstraction reaction at low temperature.[2] Although the selective reaction of H atoms in the radiolysis of neopentane−alkane mixtures takes place at 77 K, it is suppressed at 4 K.[6,7]

Recently, it has been observed that the rate constant for the tunneling reaction $HD + D \rightarrow H + D_2$ in solid hydrogen increases significantly with increasing temperature above 5 K.[8] The result indicates that the tunneling reaction of hydrogen atoms in the solid phase is accelerated by a small increase of energy. 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 of the solute alkane. Here, we have undertaken to elucidate the selective reaction of H atoms in relation to the local motion of the solute alkane by use of ESR and ESE (electron spin echo) measurements in the temperature range 4−100 K.

Experimental Section

The purities of neopentane (neo-C_5H_{12}), isobutane (i-C_4H_{10}), and cyclopentane (c-C_5H_{10}) are more than 99.9, 99.7, and 99 mol %, respectively. An aqueous solution of HI was vaporized and passed through P_2O_5 to prepare hydrogen iodide. Then, the hydrogen iodide was subjected to trap-to-trap sublimation on the vacuum line several times. The mixtures of neo-C_5H_{12} containing i-C_4H_{10} (or c-C_5H_{10}) at 2 mol % were sealed into a quartz tube. Helium gas at 260 mmHg was also sealed into the tube in order to cool the sample quickly at low temperature. In the experiment of the photolysis, HI at 0.5 mol % was added to the neopentane−isobutane mixtures.

The sample was irradiated by white light X-rays (60 kV, 45 mA) or ultraviolet light at 254 nm. The 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 mainly at 100 or 77 K by a 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 use of an HP 9000 model 382 workstation with ESPRIT software connected to the spectrometer. The errors in the radical yields are about 20%. The yields were obtained by averaging the results of two or

---

* Correspondence should be addressed to T. Miyazaki (Nagoya University).

[†] Japan Atomic Energy Research Institute (Tokai).

[‡] Nagoya University.

[§] Japan Atomic Energy Research Institute (Takasaki).

S1089-5639(98)00102-9 CCC: $15.00

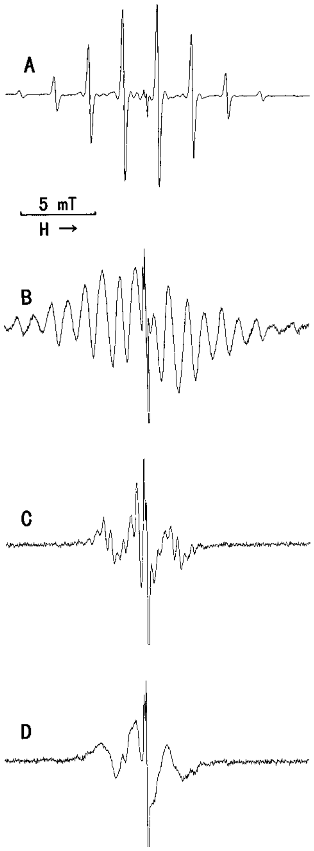

Figure 1. ESR spectra of neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures after UV irradiation. Relative ESR gain settings of spectra A, B, C, and D are 1.0, 12.5, 10, and 12.5, respectively. The narrow lines at the center of each spectrum are due to a color center produced in the irradiated quartz tube. (A) Measured at 100 K after irradiation at 100 K. (B) Measured at 30 K after irradiation at 100 K. (C) Measured at 100 K after irradiation at 4 K. (D) Measured at 70 K after irradiation at 4 K.

three runs. The electron spin echo (ESE) signals were measured with a JEOL JES-PX1050 pulse-ESR spectrometer at temperature range 4−50 K. The spin−lattice and spin−spin relaxation times were obtained by analysis of the ESE signals.

Results

Figure 1 shows the ESR spectra of the neo-C_5H_{12}−i-C_4H_{10}-(2 mol %)−HI(0.5 mol %) mixtures after the irradiation of UV light for 5 min. Figure 1A shows the spectra at 100 K after irradiation at 100 K. The spectra consist of eight clear lines in 10 lines of t-C_4H_9 radicals, in which CH_3 groups in the radical rotate freely. Figure 1B shows the spectra at 30 K after irradiation at 100 K. Although the spectra are due to t-C_4H_9 radicals, the free rotation of CH_3 groups in the radical is suppressed and the complex spectra are probably caused by a tunneling rotation of the CH_3 groups. Figure 1C shows the spectra at 100 K after irradiation at 4 K. The spectra are due to neo-C_5H_{11} radicals, where the hyperfine splitting in the spectra is caused by γ-proton interaction in the radical. The rotations around C−C bonds are partially restricted, and one of the CH_3 groups takes a preferred conformation against the unpaired electron orbital axis.[9,10] Figure 1D shows the spectra at 70 K after irradiation at 4 K. The absence of the hyperfine splitting by γ-protons indicates that even a slight motion in a neo-C_5H_{11} radical is completely suppressed below 70 K.

Figure 2 shows the effect of irradiation temperature on the yields of radicals produced by the UV irradiation of the neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures. Since the well-resolved ESR spectra were obtained at 100 K, the yields were measured at 100 K after irradiation at different temperatures. The yields of the solute radicals (t-C_4H_9) denoted by circles increase gradually with increasing temperature above 40 K. The yields of the solvent radicals (neo-C_5H_{11}) denoted by squares, however, decrease with increasing temperature above 40 K. Thus, the total yields of neo-C_5H_{11} and t-C_4H_9 radicals denoted by triangles are approximately constant in the entire temperature range.

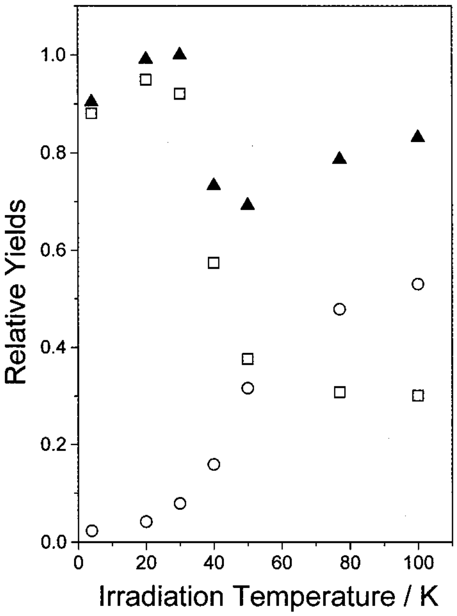

Figure 2. Effect of irradiation temperature on yields of radicals produced by UV irradiation of neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures. The yields were measured at 100 K. (▲) Sum of neo-C_5H_{11} and t-C_4H_9. (□) neo-C_5H_{11}. (○) t-C_4H_9.

Figure 3 shows the effect of irradiation temperature on the yields of radicals produced by the X-ray irradiation of the neo-C_5H_{12}−i-C_4H_{10}(2 mol %) mixtures. Since the well-resolved ESR spectra were obtained also at 77 K, the yields of radicals were measured at 77 K after irradiation at different temperatures. The yields of t-C_4H_9 radicals denoted by circles increase gradually with increasing temperature above 40 K, whereas those of neo-C_5H_{11} radicals denoted by squares decrease with increasing temperature. Thus, total yields of t-C_4H_9 and neo-C_5H_{11} radicals denoted by triangles are independent of the irradiation temperature. Figure 3 shows also the effect of irradiation temperature on the yields of cyclopentyl radicals produced by the X-ray irradiation of the neo-C_5H_{12}−c-C_5H_{10}(2 mol %) mixtures. The yields of cyclopentyl radicals denoted by diamonds increase gradually with increasing temperature above 40 K.

Figure 4 shows the temperature dependence of the spin−lattice (T_1^{-1}) and spin−spin (T_2^{-1}) relaxation rates for radicals produced by the UV irradiation of the neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures. t-C_4H_9 and neo-C_5H_{11} radicals were produced by irradiation at 4 and 100 K, respectively. The relaxation times were directly obtained by the electron spin echo method with a three-pulse sequence ($\pi/2-\pi/2-\pi$) for the spin−lattice relaxation time (T_1) and a two-pulse sequence ($\pi/2-\pi$) for the spin−spin relaxation time (T_2), as described in ref 11. Figure 4 shows also the temperature dependence of the line width of ESR spectra of t-C_4H_9 radicals, since the line width gives qualitative information on the spin−spin relaxation rates. The spin−lattice relaxation times of

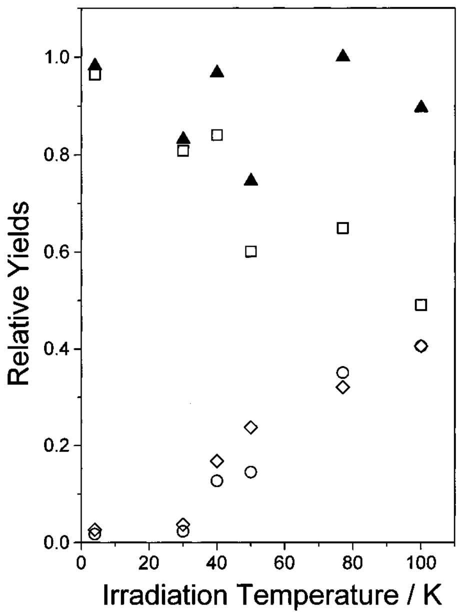

Figure 3. Effect of irradiation temperature on yields of radicals produced by X-ray irradiation of neopentane−alkane mixtures. The yields were measured at 77 K. (▲) Sum of neo-C_5H_{11} and t-C_4H_9 in neo-C_5H_{12}−i-C_4H_{10}(2 mol %) mixtures. (□) neo-C_5H_{11} in neo-C_5H_{12}−i-C_4H_{10}(2 mol %) mixtures. (○) t-C_4H_9 in neo-C_5H_{12}−i-C_4H_{10}(2 mol %) mixtures. (◇) c-C_5H_9 in neo-C_5H_{12}−c-C_5H_{10}(2 mol %) mixtures. The relative yield of c-C_5H_9 at 100 K is normalized to the value of t-C_4H_9 at 100 K.

t-C_4H_9 radicals could not be measured above 30 K because of the very short relaxation time, while those of neo-C_5H_{11} radicals could be measured up to 46 K.

Discussions

Selective Abstraction Reaction of H Atoms. Figure 1A shows clearly that H atoms produced by the photolysis of HI react selectively with the solute isobutane in the neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures to form t-C_4H_9 radicals at 100 K.

$$\mathrm{HI} \xrightarrow{h\nu} \mathrm{H} + \mathrm{I} \tag{1}$$

$$\mathrm{H} + \text{i-}\mathrm{C_4H_{10}} \rightarrow \mathrm{H_2} + \text{t-}\mathrm{C_4H_9} \tag{2}$$

$$\mathrm{H} + \text{neo-}\mathrm{C_5H_{12}} \rightarrow \mathrm{H_2} + \text{neo-}\mathrm{C_5H_{11}} \tag{3}$$

Sixty-three percent of the amount of H atoms produced in reaction 1 react with i-C_4H_{10} at 2 mol %, while the rest of them react with the solvent neo-C_5H_{12} (cf. Figure 2). There is the possibility that HI and the solute i-C_4H_{10} form a complex, and thus H atoms produced react promptly with i-C_4H_{10}. To check this possibility, H atoms are produced by X-ray radiolysis of neo-C_5H_{12} in neo-C_5H_{12}−i-C_4H_{10}(2 mol %) mixtures at 100 K in the absence of HI (cf. Figure 3).

$$\text{neo-}\mathrm{C_5H_{12}} \rightsquigarrow \text{neo-}\mathrm{C_5H_{11}} + \mathrm{H} \tag{4}$$

H atoms produced by the radiolysis of neo-C_5H_{12} in reaction 4 react selectively with the solute i-C_4H_{10} to produce t-C_4H_9 radicals significantly. Other mechanisms may be considered for the selective formation of t-C_4H_9 radicals in the radiolysis of neo-C_5H_{12}−i-C_4H_{10} mixtures. Detailed studies, reported previously,[2] concluded that the solute t-C_4H_9 radicals are neither formed by an energy transfer from irradiated neopentane to the solute nor formed by a radical site migration of solvent neopentyl radicals to the solute. Therefore, the solute radicals are formed by a selective reaction of H atoms with the solute alkane.[2]

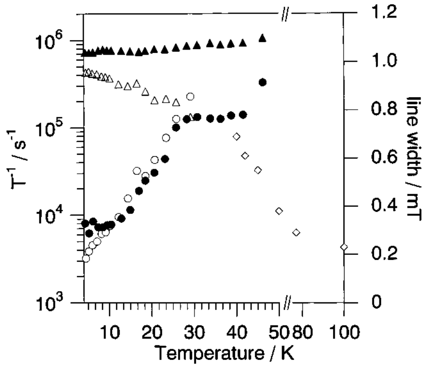

Figure 4. Temperature dependence of the spin−lattice and spin−spin relaxation rates of t-C_4H_9 and neo-C_5H_{11} radicals produced by UV irradiation of neo-C_5H_{12}−i-C_4H_{10}(2 mol %)−HI(0.5 mol %) mixtures. The relaxation rate is represented by a reciprocal of the relaxation time denoted by *T*. After t-C_4H_9 and neo-C_5H_{11} radicals were produced by the irradiation at 100 and 4 K, respectively, their relaxation times were measured at each temperature from 4.2 to 46 K. (●) Spin−lattice relaxation rate of neo-C_5H_{11}. (○) Spin−lattice relaxation rate of t-C_4H_9. (▲) Spin−spin relaxation rate of neo-C_5H_{11}. (△) Spin−spin relaxation rate of t-C_4H_9. (◇) ESR line width of t-C_4H_9.

When H atoms are produced by the photolysis of HI or the radiolysis of neo-C_5H_{12}, they react selectively with i-C_4H_{10} at 100 K to form t-C_4H_9 radicals in both cases. The selective formation of t-C_4H_9 radicals by H atoms is suppressed gradually with decreasing temperature below 100 K, while the yields of neo-C_5H_{11} radicals increase with decreasing temperature (cf. Figures 2 and 3). The remarkable temperature effect on the reaction of H atoms indicates that the H atoms are not hot atoms, but probably thermal atoms. Since the barrier height for reaction 2 is 6.4 kcal mol^{-1},[12] the abstraction reaction by the H atoms takes place at low temperature by a tunneling effect.[13] The mechanism of the selective tunneling abstraction by thermal H atoms at 77 K is also supported by the following previous results. The selective hydrogen atom abstraction by H atoms in the neopentane−alkane mixtures at 77 K occurs more effectively with the decrease in the initial energy of the H atoms.[14] H atoms trapped in the rare-gas matrix react with ethane at 50 K.[4]

The selective tunneling reaction of H atoms with the solute i-C_4H_{10} is suppressed below 30 K (cf. Figures 2 and 3). There is the possibility that the suppression of the selective reaction below 30 K may be due to the characteristic property of i-C_4H_{10}. Thus, the temperature effect on the selective reaction of H atoms with the solute has been studied in the X-ray radiolysis of the neopentane containing cyclopentane(2 mol %) as a solute. In Figure 3 the selective formation of cyclopentyl radicals decreases gradually with decreasing temperature below 100 K and is finally suppressed at 30 K, at which the selective reaction of H atoms with the solute isobutane is also stopped. Therefore, the selective abstraction reaction by H atoms in the neopentane−alkane mixtures takes place above 40 K and is suppressed below 30 K. Since the thermodynamic properties of crystalline neopentane do not show any phase transition in the temperature range between 4 and 100 K,[15] we will discuss the selective tunneling reaction in relation to local motion of the solute molecules.

Selective Reaction of H Atoms and Local Motion of Solute Molecules. Information on the local motions of the solute i-C_4H_{10} molecules and the solvent neo-C_5H_{12} molecules will be obtained approximately from the motions of the solute t-C_4H_9 radicals and the solvent neo-C_5H_{11} radicals. When CH_3 groups in t-C_4H_9 radicals rotate freely, 10 equally separated ten lines of ESR spectra are expected. In Figure 1A eight lines of them can be observed clearly. Since the eight lines were observed above 40 K, the CH_3 groups in a t-C_4H_9 radical rotate freely above this temperature. The drastic change of the spectra of t-C_4H_9 radicals below 30 K (cf. Figure 1B) indicates the suppression of the free rotation of the CH_3 groups. In contrast to the free rotation around C−C bonds in the solute t-C_4H_9 radical above 40 K, the rotation around the $(CH_3)_3C-CH_2^{\bullet}$ bond in a neo-C_5H_{11} radical is completely restricted even at 100 K.[9] The ESR spectra in Figure 1C show that a CH_3 group in the neo-C_5H_{11} radical can take one preferable orientation and the CH_3 group rotates at 100 K. Since the hyperfine structures disappear below 70 K (cf. Figure 1D), even the slight local motion of the CH_3 group that takes the preferable orientation is suppressed below this temperature. Thus, the local motion of solvent neopentane molecules is severely restricted. The appearance of the local motion of the solute isobutane molecules at 40 K may be related to the onset of the selective reaction of H atoms above 40 K. Since the ESR spectra of cyclopentyl radicals produced by X-ray radiolysis of the neo-C_5H_{12}−c-C_5H_{10}(2 mol %) mixtures consist of eight broad lines, we could not obtain clear information on the local motion of the cyclopentyl radicals from the broad ESR spectra.

The differences in the local motions between the solvent neo-C_5H_{11} radicals and the solute t-C_4H_9 radicals were observed from the difference of their spin-lattice relaxation rates, which were measured directly from the ESE recovery method. Gillbro and Lund[16] reported that the alkyl radical formed at 77 K by γ-ray irradiation of n-$C_{16}H_{34}$ has much faster spin−lattice relaxation rates when the radical is located next to the terminal methyl group than when it was located between methylene groups. They suggested that the higher mobility of the end of the alkane chain which causes a modulation of hyperfine interaction contributes to the rapid relaxation of the radicals located in the terminal methyl group.[16] Although the mechanism of the spin−lattice relaxation is complex, the relaxation time gives qualitative information on the local motion of the radicals. As shown in Figure 4, the spin−lattice relaxation rate (T_1^{-1}) of the solute t-C_4H_9 radicals above 30 K becomes quite fast and exceeds the limit of the measurement, whereas those of the solvent neo-C_5H_{11} radicals could be measured up to 46 K. The fast relaxation rate of the t-C_4H_9 radicals above 30 K suggests that the local motion of the solute radicals becomes significant above this temperature. The spin−spin relaxation rate (T_2^{-1}) of the solvent neo-C_5H_{11} radicals is approximately constant in the temperature range 4−46 K, while the rates of the solute t-C_4H_9 radicals decrease gradually with increasing temperature in the same temperature range. The decrease of the spin−spin relaxation rate is due to the enhancement of superhyperfine fluctuation, which is caused by the increase of the local motion of the solute radicals with increasing temperature.[17]

H atoms may become mobile above 40 K in the neopentane matrix and react selectively with the solute isobutane. Since the CH_3 groups in a solute i-C_4H_{10} molecule rotate in the neopentane matrix, the isobutane molecule can take an orientation more favorable for the hydrogen abstraction reaction by H atoms than rigid neopentane molecules, resulting in the selective reaction with H atoms. The difference in the bond energy between a tertiary C−H bond of i-C_4H_{10} and a primary C−H bond of neo-C_5H_{12}, which corresponds to the difference in the barrier height for the reaction, may also be another factor in the selective abstraction reaction in the neo-C_5H_{12}−i-C_4H_{10} mixtures, as pointed out previously.[2]

When H atoms are produced in the neo-C_5H_{12}−C_2H_6 mixtures at 77 K, they react 490 times more selectively with the solute C_2H_6 than the solvent neo-C_5H_{12}.[2] Since both neo-C_5H_{12} and C_2H_6 consist of primary C−H bonds, the difference in the barrier height for the abstraction reaction by H atoms is quite small. In fact, the barrier heights for reactions 5 and 3 were measured as 9.4 and 9.6 kcal mol^{-1}, respectively.[12]

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \tag{5}$$

If the above reactions take place by a quantum tunneling at 77 K, the rate constants (k) for the reactions can be estimated by the model that the potential energy curve for the reaction is approximated by an Eckart barrier,[18] where the barrier height for the reverse reaction is taken as 12.7 kcal mol^{-1}.[12] The ratio (k_5/k_3) of the rate constants for reactions 5 and 3 is less than 2.2, which is much smaller than the experimental ratio of 490. Thus, the large experimental value of k_5/k_3 for reactions 5 and 3 in the neo-C_5H_{12}−C_2H_6 mixtures cannot be explained by the small difference in the barrier height between reactions 5 and 3. C_2H_5 radicals, produced by γ-ray radiolysis of the neo-C_5H_{12}−C_2H_6(4.8 mol %) mixtures at 77 K, show well-resolved ESR spectra,[19] which indicate a free rotation of the CH_3 group in the C_2H_5 radical. The local motion of the solute C_2H_6 molecules causes a selective tunneling abstraction by H atoms, resulting in the selective formation of C_2H_5 radicals. The barrier height for the hydrogen abstraction reaction by H atoms from alkane becomes minimum when H atoms approach the alkane from the extension of the C−H axis.[20] If the local motion of solvent neopentane molecules is restricted in the solid phase, the neopentane molecules cannot take the orientation favorable for the reaction, resulting in an increase of the barrier height for the reaction. Thus the rate for the tunneling reaction of H atoms with solvent neopentane molecules is probably much slower than that for the reaction with the solute ethane, which can take the orientation favorable for the reaction by the local motion.

It is concluded that the selective tunneling abstraction by H atoms in the neopentane−alkane mixtures above 40 K is caused by the local motions of the solute alkane in the rigid neopentane matrix. Tunneling reactions assisted by the local motion of the reactants in the solid phase have been observed in the following reactions: a proton transfer reaction to a $C_6H_6^-$ anion in ethanol glass and a H_2 molecule detachment from a 2,3-dimethylbutane cation in solid alkane.[21]

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture.

References and Notes

(1) Benderskii, V. A.; Makarov, D. E.; Wight, C. A. *Chemical Dynamics at Low Temperature*; John Wiley & Sons, Inc.: New York, 1994.
(2) Miyazaki, T. *Radiat. Phys. Chem.* **1991**, *37*, 635, and related papers cited therein.
(3) Miyazaki, T.; Kitamura, S.; Morikita, H.; Fueki, K. *J. Phys. Chem.* **1992**, *96*, 10331.
(4) Muto, H.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1980**, *84*, 3402.
(5) Wakayama, T.; Miyazaki, T.; Fueki, K.; Kuri, Z. *J. Phys. Chem.* **1973**, *77*, 2365.
(6) Kinugawa, K.; Miyazaki, T.; Hase, H. *Radiat. Phys. Chem.* **1977**, *10*, 341.
(7) Iwasaki, M.; Muto, H.; Toriyama, K.; Fukaya, M.; Nunome, K. *J. Phys. Chem.* **1979**, *83*, 1590.
(8) Kumada, T.; Komaguchi, K.; Aratono, Y.; Miyazaki, T. *Chem. Phys. Lett.* **1996**, *261*, 463.

(9) Lin, J.; Williams, F. *J. Phys. Chem.* **1968**, *72*, 3707.

(10) Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 616.

(11) Poole, C. P.; Farach, H. A. *Relaxation in Magnetic Resonance*; Academic Press: New York and London, 1971.

(12) Kerr, J. A., Moss, S. J., Eds. *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press, Inc.: Boca Raton, FL, 1981.

(13) Miyazaki, T.; Hirayama, T. *J. Phys. Chem.* **1975**, *79*, 566.

(14) Miyazaki, T.; Guedes, S.; Fueki, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1813.

(15) Enokido, H.; Shinoda, T.; Mashiko, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 84.

(16) Gillbro, T.; Lund, A. *Chem. Phys.* **1974**, *5*, 283.

(17) Ichikawa, T.; Yoshida, H. *J. Phys. Chem.* **1988**, *92*, 5684.

(18) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1981.

(19) Miyazaki, T.; Wakayama, T.; Fukaya, M.; Saitake, Y.; Kuri, Z. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1030.

(20) Morokuma, K.; Davis, R. E. *J. Am. Chem. Soc.* **1972**, *94*, 1060.

(21) Miyazaki, T.; Kumada, T.; Komaguchi, K.; Aratono, Y. *Radiat. Phys. Chem.* **1997**, *50*, 523.