



MATRIX EFFECT ON HYDROGEN-ATOM TUNNELING OF ORGANIC MOLECULES IN CRYOGENIC SOLIDS

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1. INTRODUCTION

Although the tunneling of atoms through potential energy barriers separating the reactant and reaction systems is not paid much attention in organic reactions, this plays an important role in reactions including the transfer of light atoms. Atomic tunneling is especially important for chemical reactions at low temperatures, since the thermal activation of reactant systems is very slow process in comparison with the tunneling.

One of the typical reactions of atomic tunneling is hydrogen-atom abstraction from alkanes in cryogenic solids exposed to high-energy radiation. Irradiation of alkane molecules causes the homolytic cleavage of C-H bonds, which results in the pairwise formation of free hydrogen atoms and organic free radicals. Since the activation energies for the abstraction of hydrogen atoms from alkane molecules by free hydrogen atoms are higher than 5 kcal/mol, the lifetime of free hydrogen atoms at 77 K is estimated from the Arrhenius equation of $k = \nu \exp(-E_a/RT)$ to be longer than 10 hrs. However, except for solid methane, free hydrogen atoms immediately convert to alkyl radicals even at 4.2 K by hydrogen-atom tunneling from alkane molecules to the free hydrogen atoms.

The rate of hydrogen atom tunneling does not necessary increase with decreasing activation energy or the peak height of the potential energy barrier preventing the tunneling. Although the activation energy is the lowest at the tertiary carbon of alkanes, hydrogen atom tunneling from branched alkanes with tertiary carbon at the antepenultimate position of the carbon skeleton is the fastest at the secondary penultimate carbon.

Based on our experimental results, we have proposed that the peculiarity of the hydrogen-atom abstraction in cryogenic solids comes from the steric hindrance by matrix molecules to the deformation of alkane molecules from the initial sp^3 to the final sp^2 configurations. The steric hindrance causes the increase of the height of the potential energy barrier for the tunneling of hydrogen atoms. Since the tunneling rate depends not on the peak height of the potential barrier but on the area of the barrier, the restriction of molecular motion by rigid matrices causes the retardation of the hydrogen-atom tunneling. The steric hindrance increases with increasing number and length of alkyl chains attached to a carbon atom to be hydrogen-abstracted. The Penultimate secondary carbon therefore shows the highest reaction rate.

To study the matrix effect on hydrogen-atom tunneling is interesting not only from the theoretical point of view but also from the practical point of view, since it suggests a new possibility of controlling chemical reactions by changing the viscosity of a solvent.

In this article, we have summarized our recent studies on the effect of matrices on the rates of hydrogen atom tunneling from alkyl and allylic carbon of alkanes and linear alkenes, and to vinyl carbon of linear alkenes in organic solids at 77 K [ref. 1].

2. EXPERIMENTAL

Deuterated alcohols and alkanes were used as matrices for studying hydrogen-atom abstraction by free deuterium atoms from solute alkanes and hydrogen-atom addition to the vinyl carbon of solute alkenes. The concentrations of solute molecules were less than 2 vol.%.

One of the advantages of using deuterated matrices is to see only the tunneling reaction by eliminating hot-atom reactions. Although hydrogen or deuterium atoms are quite hot just after the formation, they were thermalized before encountering dilute solute molecules. The cold atoms thus generated preferentially generate solute radicals, since the tunneling of hydrogen atoms is much faster than that of deuterium atoms. Another advantage was that the ESR spectra of deuterated matrix radicals are so narrow that the ESR identification of solute radicals is possible to be carried out without spectral separation.

Free deuterium atoms were generated at 77 K by homolytic cleavage of the C-D bonds of matrix molecules MD by γ -irradiation with ^{60}Co , as $\text{MD} + \gamma \rightarrow \text{M} + \text{D}$.

Free hydrogen atoms were generated at 77 K by photoionization of triphenylamine in CD_3OH matrices with UV light of $\lambda > 300$ nm followed by the attachment of the photoejected electrons to protons, as $(\text{C}_6\text{H}_5)_3\text{N} + 2h\nu \rightarrow (\text{C}_6\text{H}_5)_3\text{N}^+ + e^-$, $e^- + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$.

The concentrations of triphenylamine and hydrogen chloride were about 10 mmol/dm³ and 0.1 mol/dm³, respectively.

All the samples were degassed before irradiation by repeated freezing-pumping-warming cycles. The semi-quantitative analyses of solute radicals were carried out by analyzing the X-band ESR spectra of the solute radicals recorded mostly at 77 K.

3. RESULTS AND DISCUSSION

Shown in Table 1 are the relative yields of solute radicals generated by hydrogen-atom abstraction of free deuterium atoms from solute alkanes. It can be concluded that the yield and therefore the rate of hydrogen-atom abstraction in glassy matrices depends not only on the activation energy or the peak 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. This is because 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. This explanation seems quite plausible since the hydrogen-atom abstraction from 3-methylpentane in a perdeuterated adamantane matrix, in which guest molecules can move rather freely in their trapping sites, takes place at the tertiary carbon.

Hydrogen-atom addition to the vinyl carbon of alkenes is the symmetrical reaction to the hydrogen-atom abstraction from alkanes. The addition causes the deformation of the attacked vinyl carbon from the initial sp^2 to the final sp^3 configurations. The steric hindrance to the deformation increases with increasing length of alkyl chains attached to the vinyl carbon, so that major alkyl radicals generated by hydrogen-atom tunneling to the vinyl carbon of 2-hexene, $CH_3CH=CH(CH_2)_2CH_3$, is expected to be not $CH_3\dot{C}H-CH_2(CH_2)_2CH_3$ but $CH_3CH_2\dot{C}H(CH_2)_2CH_3$. However, as shown in Table 2, the ESR spectrum of the resultant alkyl radicals in the glassy matrix of CD_3OH accords well with the 1:1 mixture of $CH_3\dot{C}H-CH_2(CH_2)_2CH_3$ and $CH_3CH_2-\dot{C}H(CH_2)_2CH_3$. The reactivity of vinyl carbon toward the hydrogen-atom addition does not depend on the chain length of a substituted alkyl group.

The rate of hydrogen-atom tunneling from alkyl carbon depends on the length of alkyl chains attached to the reacting carbon, whereas the tunneling rate to the vinyl carbon does not. This difference

Table 1. Relative yield of alkyl radicals generated at 77 K by hydrogen-atom tunneling from solute alkane to free deuterium atoms in perdeuterated matrices. ^a

Alkane	Alkyl radicals ^{b,c}
$CH_3(CH_2)_3CH_3$	$CH_3\dot{C}H(CH_2)_2CH_3 > CH_3CH_2\dot{C}HCH_2CH_3$
$CH_3(CH_2)_4CH_3$	$CH_3\dot{C}H(CH_2)_3CH_3 > CH_3CH_2\dot{C}H(CH_2)_2CH_3$
$CH_3(CH_2)_5CH_3$	$CH_3\dot{C}H(CH_2)_4CH_3 > CH_3CH_2\dot{C}H(CH_2)_3CH_3 > CH_3(CH_2)_2\dot{C}H(CH_2)_2CH_3$
$CH_3(CH_2)_6CH_3$	$CH_3\dot{C}H(CH_2)_5CH_3 > CH_3CH_2\dot{C}H(CH_2)_4CH_3 > CH_3(CH_2)_2\dot{C}H(CH_2)_3CH_3$
$(CH_3)_2CHCH_2CH_3$	$(CH_3)_2\dot{C}HCH_2CH_3 \gg (CH_3)_2CH_2\dot{C}HCH_3$
$(CH_3)_2CH(CH_2)_2CH_3$	$(CH_3)_2CHCH_2\dot{C}HCH_3 > (CH_3)_2\dot{C}HCH_2CH_2CH_3 > (CH_3)_2CH\dot{C}HCH_2CH_3$
$(CH_3CH_2)_2CH(CH_3)$	$CH_3\dot{C}HCH(CH_3)CH_2CH_3 \gg CH_3CH_2\dot{C}H(CH_3)CH_2CH_3$ $CH_3CH_2\dot{C}H(CH_3)CH_2CH_3 \gg CH_3\dot{C}HCH(CH_3)CH_2CH_3$ in adamantane

a) Unless otherwise stated, matrices used are glassy matrices of perdeuterated alcohols or branched alkanes.

b) The location of hydrogen-abstracted carbon atom is shown with *.

c) $A \approx B$, $A > B$ and $A \gg B$ mean that the yield of B with respect to A are about 1~0.5, 0.5~0.2 and $\ll 0.2$ (undetectable by ESR), respectively.

Table 2. The observed yields and the peak heights of potential energy barriers for the formation of alkyl radicals from linear alkenes.

Reactant	Product	Relative yield	Peak height/kcal/mol ^a (Activation energy ^b)
CH ₂ =CH(CH ₂) ₃ CH ₃ + H	CH ₃ C [*] H(CH ₂) ₃ CH ₃	1	3.2 (1.5)
	C [*] H ₂ CH ₂ (CH ₂) ₃ CH ₃	0	4.6 (2.8)
CH ₃ CH ₂ CH=CHCH ₂ CH ₃ + H	CH ₃ CH ₂ C [*] H(CH ₂) ₂ CH ₃	1	
CH ₃ CH=CH(CH ₂) ₂ CH ₃ + H	CH ₃ CH ₂ C [*] H(CH ₂) ₂ CH ₃	0.5	4.7 (2.1)
	CH ₃ C [*] HCH ₂ (CH ₂) ₂ CH ₃	0.5	4.6 (2.1)

a) MP2/3-21G ab initio calculation.

b) Experimental value.

can be explained by taking the structural change of the reaction systems during the tunneling into consideration. The rate constant k for the tunneling of a particle with effective mass μ depends not on the peak height of the potential energy barrier $U(r)$ but on the square-root area of the barrier above the energy of the initial state E_i , as

$$k \approx \exp\left(-2\sqrt{2\mu/\hbar^2} \int_a^b \sqrt{U(r) - E_i} dr\right)$$

so that the tunneling rate is very sensitive to the change of the barrier area. The atomic configuration of the reaction system other than the tunneling particle also changes during the tunneling process from that of the initial reactant state to the final product one. The steric hindrance to the deformation of the reaction system to the product state generally causes the retardation of the tunneling. However, the steric hindrance does not cause the retardation if the atomic configuration at the exit of the optimal tunneling channel is the same as that at the entrance and therefore the atomic configuration is unchanged during the tunneling. This explanation was proved to be valid by comparing the shape of the potential energy surfaces for the hydrogen-atom abstraction and the addition as calculated with MP2/3-21G under two different reaction conditions: no restriction on the motion of atoms, and the fixed C-C-C bond angles of initial reactant states. The area of the tunneling barrier for hydrogen-atom addition was not changed by the restriction posed to the C-C-C bond angle, since the bond angle was scarcely changed during the tunneling. On the other hand, the area of the barrier for hydrogen-atom abstraction was increased by the restriction, since the bond angle at the exit of the tunneling channel was close to that of the final sp² state.

REFERENCES

[ref. 1] T. Ichikawa, K. Kagei, H. Tachikawa, Y. Ishitani, J. Phys. Chem.A, 103, 6288-6294 (1999), and references cited therein.