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Selectivity and enormous H/D isotope effects on H atom abstraction by CH₃ radicals in solid methylsilane at 3.0 K–115 K

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An EPR study was carried out to elucidate the hydrogen atom abstraction from methylsilane (CH₃SiH₃) by a methyl radical, CH₃SiH₃ + [•]CH₃ \rightarrow CH₃SiH₂[•] + CH₄, in a solid solution of CH₃SiH₃ containing 1 mol% CH₃I at the low temperatures of 3 K–115 K. The EPR spectra observed after UV-photolysis of the CH₃I at 77 K were attributed to a mixture of the CH₃SiH₂[•] radical and the [•]CH₃ radical. In the CH₃SiH₃ system, the CH₃SiH₂[•] radical was the major product immediately after the photolysis, while the [•]CH₃ radical was the major one in the CH₃SiD₃ system. The [•]CH₃ radicals decayed following first order kinetics in the dark in both systems. The decay rate constants for the reaction were experimentally determined to be $k_{(Si-H)} = 3.6 \times 10^{-2} \text{ s}^{-1}$ and $k_{(Si-D)} = 6.9 \times 10^{-6} \text{ s}^{-1} (k_{(Si-H)}/k_{(Si-D)} = 5.2 \times 10^3)$ at 77 K; the associated apparent activation energies were $E_{a(Si-H)} = 0.85 \text{ kJmol}^{-1}$ and $E_{a(Si-D)} = 8.9 \text{ kJmol}^{-1} (E_{a(Si-H)}/E_{a(Si-D)} = 1/10)$ above 20 K. A non-linear Arrhenius plot was obtained for the rate constant, $k_{(Si-H)}$, and the rate became almost independent of the temperature below 20 K. These results suggest that the quantum mechanical tunneling effect contributes significantly to the H atom abstraction from the –SiH₃ group.

1. Introduction

The quantum mechanical tunneling effect on elementary reactions is fundamentally important in low temperature chemistry. The chemical reaction via the tunneling effect is characterized by a non-linear Arrhenius plot, a large isotope H/D effect on the rate constant, and high selectivity of the reaction.^{1,2} Four decades ago a remarkable ²D effect was reported for the decay rate of radicals produced in protiated and perdeuterated organic compounds at 77 K by Sullivan and Koski.³ Since then a number of studies have been reported on tunneling reactions in low temperature solids.⁴⁻⁹ For example, in 1971, Williams and collaborators reported the H atom abstraction from CH₃CN by the CH₃ radical with a low activation energy of 1.4 kcal mol⁻¹ and a large "primary" kinetic isotope effect, $k_{(H)}/k_{(D)} > 140$, between 77 K and 87 K.⁵ One of the authors (M.S.) has clearly demonstrated a non-linear Arrhenius plot for the reaction, $CH_3OH + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}CH_2OH +$ CH₄, in solid CH₃OH at the low temperatures of 10 K-90 K.⁹

Recently, Hiraoka and his collaborators reported that amorphous silicon thin films are formed by successive H atom abstraction from the silane (SiH₄) molecule by H atoms at the low temperature of 10 K.¹⁰ They developed a methodology to generate H atoms in the ground state and sprinkled them on the silane molecular layers deposited on a silicon substrate cooled at 10 K. They proposed a reaction mechanism *via* quantum mechanical tunneling for the formation of the amorphous silicon. However, there is no direct experimental evidence of paramagnetic species as reaction intermediates, because the reaction was monitored by *in situ* IR spectroscopy, not by EPR. Furthermore, no kinetic studies have ever been reported for the H atom abstraction reaction of low temperature solid silicon compounds.

Methylsilane (CH₃SiH₃) is the simplest alkylsilane, composed of a CH₃ group and a SiH₃ group. The Si-H bond length of Si with sp³ hybridization is *ca.* 0.149 nm, which is ca. 36% longer than the corresponding C-H bond (ca. 0.110 nm);¹¹ the difference mainly comes from that in the covalent bond radii of Si and C atoms, i.e., 0.117 and 0.0771 nm, respectively.¹² In addition, the dissociation energy of the Si-H bond is more than 40 kJ mol⁻¹ smaller than the C-H bond.^{13,14} These facts may significantly contribute to either the classical or non-classical (i.e., tunnel) reaction kinetics, or both; the reaction proceeds by passing over the potential barrier in the former, but through the barrier in the latter. Hence, methylsilane was chosen as a suitable molecule for studying the hydrogen abstraction reaction because the molecule has two groups of CH₃ and SiH₃ with remarkably different reactivity expected for each.

In the present report, H atom abstraction reactions from methylsilane by CH_3 radicals in the low temperature solid CH_3SiH_3 and CH_3SiD_3 systems were studied by EPR spectroscopy. It was found that the H atoms were preferentially abstracted from the SiH_3 group, not from the CH_3 group, with a remarkable H/D isotope effect on the reaction rate as well as the apparent activation energy. Here, we wish to demonstrate experimentally that the quantum mechanical tunneling effect is manifested in the H atom abstraction from the $-SiH_3$ group.

2. Experimental

Methylsilane and methylsilane-1,1,1-d₃ were synthesized from trichloromethylsilane by a conventional method.¹⁵ The purities of both methylsilanes were greater than 98 mol% based on the ¹H–, ¹³C–, ²⁹Si-NMR analyses (JEOL Model Ex-270

spectrometer). For the CH₃SiD₃, the degree of deuteration is presumably 98 atom%, which is governed by that of LiAlD₄ (Aldrich Chemical Co., Inc) used as the reducing reagent in the synthesis. CH₃I was purchased from Tokyo Kasei Kogyo Co., Ltd., and used without further purification. The samples were prepared in a Suprasil quartz tube (4 mm diameter, 20 cm length) on a vacuum line, and subjected to UV-photolysis (high-pressure mercury lamp, 400 W) at 77 K.

EPR spectra were recorded on a Bruker ESP300E X-band spectrometer at a microwave power level small enough to avoid saturation in the region of 5 μ W–0.6 mW. For the experiments to measure the time-course of the radical concentration at 77 K, a JEOL JES-RE1X spectrometer was used. The sample temperature was controlled within ±0.1 K using a cryostat (Oxford ESR 900) with liquid helium as the coolant.

3. Results and discussion

3.1. EPR spectra

Fig. 1 shows the EPR spectra of a solid solution of CH_3SiH_3 containing 1 mol% of CH_3I irradiated by UV-light at 77 K. The spectrum consists of two components. One is a multiplet with a total hf-coupling constant of *ca*. 5 mT at the central part. The other is a quartet due to the ${}^{\bullet}CH_3$ radical as marked by the asterisk, which is generated by the photolysis of CH_3I , but is weak in intensity. The multiplet was well reproduced by assuming a triplet of quartets with isotropic ¹H hyperfine coupling constants (hfcc) of 1.2 mT (2 H) and 0.8 mT (3 H). These EPR parameters correspond well to those reported for $CH_3SiH_2^{\bullet}$ radicals.^{16,17} The concentration of $CH_3SiH_2^{\bullet}$ radicals at 77 K. The CH_3 radical concentration,



Fig. 1 EPR spectra observed for CH₃SiH₃ containing 1 mol% of CH₃I immediately (a) and 9 min (b) after UV-photolysis for 1 min at 77 K, and a simulated spectrum (c) using the following EPR parameters, $a_{\rm Si}({\rm H}) = 1.2$ mT (2 H), $a_{\rm C}({\rm H}) = 0.8$ mT (3 H), and line width of 0.35 mT. The spectra were measured at 77 K in the dark. The peaks due to the 'CH₃ radicals are denoted by an asterisk. The singlet indicated by the arrow in (a) and (b) is attributable to the paramagnetic impurities generated in the quartz sample tube by UV-light illumination.

however, was almost independent of the illumination time, and disappeared within a few minutes in the dark at 77 K after the illumination.

In contrast to the results obtained for the CH₃SiH₃ system, the decay rate of the CH₃ radical was found to be much slower in the CH₃SiD₃ system where hydrogen atoms of the SiH₃ group are fully deuterated. Fig. 2 shows the EPR spectra observed for the CH₃SiD₃ samples containing 1 mol% of CH₃I. Upon exposing the sample to UV-light at 77 K, the quartet spectrum of the CH₃ radical was clearly observed with a 2.3 mT hfcc. Furthermore, it became experimentally clear that the decaying CH₃[•] radical was accompanied by the simultaneous growth of another quartet with the smaller hfcc of 0.8 mT at the central position. The latter quartet was attributed to the ¹H hfcc of the CH₃SiD₂ radical. We repeat that the CH₃[•] radicals decayed in both systems, but the decay rate was much slower in CH₃SiD₃ than in CH₃SiH₃. The EPR results suggest that the CH₃ radical preferentially abstracts a hydrogen atom from the SiH₃ group of CH₃SiH₃ with an anomalously large H/D isotope effect on the reaction kinetics.

3.2. Rate-determining reaction

The initial and final radicals, i.e., CH₃ and CH₃SiH₂, were observed by the present EPR study. Now we shall consider the reaction mechanism for the radical conversion. There are three possible reactions (Scheme 1) for the CH₃SiH₂[•] radical formation. One is reaction (2) where the CH₃ radical abstracts the H (or D) atom directly from the silyl group (SiH₃). The other two reactions are abstraction of the H atom from the CH₃ group, reaction (3), followed by either an inter- or intra-molecular H atom transfer from the carbon to the silicon, reaction (4) or (5) (Scheme 1), respectively. As mentioned above, a large isotope effect was observed for the deuteration of the SiH₃ group, therefore, the abstraction of the H atom from the SiH₃ group either by reaction (2) or reactions (4) and (5) is expected to be the rate-determining step. If the latter reactions were the case, the decay of the 'CH2SiH3 (or •CH₂SiD₃) radical should be observable, accompanied by an



Fig. 2 EPR spectra observed for the CH_3SiD_3 systems containing 1 mol% of CH_3I immediately (a), 77 h (b), and 143 h (c) after UV-photolysis for 1 min at 77 K. The spectra were measured at 77 K in the dark. The peaks due to the CH_3 radicals are denoted by an asterisk.

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$$CH_{3}I \xrightarrow{UV} CH_{3} + I$$
(1)

$$\begin{array}{c} \mathsf{CH}_{3}\mathsf{S}\mathsf{i}\mathsf{H}_{3} + {}^{\bullet}\mathsf{C}\mathsf{H}_{3} & \frac{k_{(\mathrm{S}:\mathrm{H})}}{k_{(\mathrm{S}:\mathrm{D})}} \to \mathsf{CH}_{3}\dot{\mathsf{S}}\mathsf{i}\mathsf{H}_{2} + \mathsf{C}\mathsf{H}_{4} & (2) \\ (\mathsf{CH}_{3}\mathsf{S}\mathsf{i}\mathsf{D}_{3} + {}^{\bullet}\mathsf{C}\mathsf{H}_{3} & \frac{k_{(\mathrm{S}:\mathrm{D})}}{k_{(\mathrm{S}:\mathrm{D})}} \to \mathsf{C}\mathsf{H}_{3}\dot{\mathsf{S}}\mathsf{i}\mathsf{D}_{2} + \mathsf{C}\mathsf{H}_{3}\mathsf{D}) \end{array}$$

$$\begin{array}{c} \mathsf{CH}_{3}\mathsf{SiH}_{3} + {}^{\bullet}\mathsf{CH}_{3} & \underbrace{\mathbf{k}_{(\mathbb{C}-\mathbb{H})}}_{(\mathbb{C}-\mathbb{H})} \bullet {}^{\bullet}\mathsf{CH}_{2}\mathsf{SiH}_{3} + \mathsf{CH}_{4} \\ (\mathsf{CH}_{3}\mathsf{SiD}_{3} + {}^{\bullet}\mathsf{CH}_{3} & \underbrace{\mathbf{k}_{(\mathbb{C}-\mathbb{D})}}_{(\mathbb{C}-\mathbb{D})} \bullet {}^{\bullet}\mathsf{CH}_{2}\mathsf{SiD}_{3} + \mathsf{CH}_{4}) \end{array}$$
(3)

$$CH_{3}SiH_{3} + {}^{\bullet}CH_{2}SiH_{3} \qquad \xrightarrow{k_{(H)inter}} CH_{3}\dot{S}iH_{2} + CH_{3}SiH_{3} \qquad (4)$$

$$(CH_{3}SiD_{3} + {}^{\bullet}CH_{2}SiD_{3} \qquad \xrightarrow{k_{(D)inter}} CH_{3}\dot{S}iD_{2} + CH_{2}DSiD_{3})$$

$$^{\circ}CH_{2}SiH_{3} \xrightarrow{k_{(H)intra}} CH_{3}\dot{S}iH_{2}$$
(5)
$$(^{\circ}CH_{2}SiD_{3} \xrightarrow{k_{(D)intra}} CH_{2}D\dot{S}iD_{2})$$

Scheme 1

increase in the $CH_3SiH_2^{\bullet}$ ($CH_3SiD_2^{\bullet}$), or $CH_2DSiD_2^{\bullet}$ radical. In the present systems, however, no EPR spectra attributable to the ${}^{\bullet}CH_2SiH_3$ (or ${}^{\bullet}CH_2SiD_3$) and $CH_2DSiD_2^{\bullet}$ radicals were detected after the photolysis, even at the low temperature of 4 K. Thus, reactions (4) and (5) can be ruled out, and we conclude that the $CH_3SiH_2^{\bullet}$ radicals were preferentially generated by reaction (2).

3.3. Rate constant and activation energy

We can now take only reaction (2) into account in the following kinetic analysis. The relative number of 'CH₃ radicals was evaluated from the peak heights of the outer two lines $(m_{\rm I} = \pm 3/2)$, and the total number of radicals was obtained from the double integration of the first-derivative spectra. Fig. 3 shows the time-courses of the relative number of the [•]CH₃ radical and the whole radical in the CH₃SiD₃ system at 77 K. The 'CH₃ radicals decayed exponentially as shown in Fig. 3(a), while the relative number of whole radicals remained almost constant except for the initial several hours. The result is consistent with the assumption of reaction (2) where the •CH₃ radical decreases with corresponding increase in the CH₃SiH₂ radical. The initial decrease in the 'CH₃ radical may be caused by recombination reactions of the 'CH₃ radicals, and/or of the 'CH₃ radical with an iodine atom generated in the near vicinity. Assuming the reaction proceeds by a first order process, the natural logarithm of the 'CH₃ concentration, $\ln[{}^{\bullet}CH_3]$, was plotted vs. the reaction time, t. The plot was linear, as shown in Fig. 3(b). The CH₃ radicals decayed with a half-life of $\tau_{1/2} = 19.3$ s and 28 h for the CH₃SiH₃ and CH₃SiD₃ systems, respectively, at 77 K. The half-life of the 'CH₃ radicals in the CH₃SiH₃ system is very short, less than one-thirtieth of those reported for organic compounds such as CH_3CN ,⁵ CH_3NC ,¹⁸ and 3-methylpentane^{6,19} with $\tau_{1/2} = 28$ min, 210 min, and 11–25 min, respectively.

Based on eqn. (6) of the zero point energy (zpe) difference, one can estimate the maximum H/D isotope effect for the reaction rate constants *via* a classical mechanism, where *h* is Planck's constant, ν is the zero point vibrational frequency, and $k_{\rm B}$ is Boltzman's constant.¹⁸

$$k^{\rm H}/k^{\rm D} = 2^{1/2} \exp((h\nu^{\rm H} - h\nu^{\rm D})/2k_{\rm B}T)$$
 (6)



Fig. 3 (a) Time-courses of the number of ${}^{\bullet}CH_3$ radicals (\blacktriangle) and the whole radical (\bullet) in solid CH₃SiD₃ molecules containing 1 mol% of CH₃I at 77 K in the dark after UV-photolysis for 1 min at the same temperature. (b) First-order plot of the ${}^{\bullet}CH_3$ radical decay in the CH₃SiH₃ (\blacksquare) and CH₃SiD₃ (\bigstar) systems at 77 K in the dark.

Substituting 2148 cm⁻¹ and 1552 cm⁻¹, the frequencies for the fundamental vibrations of the Si–H and Si–D stretching modes observed for the polycrystalline methylsilanes at 77 K,²⁰ for the values of $\nu^{\rm H}$ and $\nu^{\rm D}$ in eqn. (6) yields the classical isotope effect of *ca*. 340 at most. In fact, a large H/D isotope effect of 5.2 × 10³ was experimentally evaluated for the hydrogen atom abstraction from the SiH₃ group; the value is a factor of *ca*. 15 times greater than the maximum isotope effect due to the classical mechanism at 77 K. Here, we note that the classical isotope effect on the methyl hydrogens can be several times greater than on the silyl hydrogens because of the larger difference between the zpe of the C–H and C–D bonds than between the Si–H and Si–D bonds.

Fig. 4 shows an Arrhenius plot of the first-order rate constant, k, for the CH₃ radical decay. The plot shows a nonlinear relationship. In k decreases with decreasing temperature, and becomes almost temperature independent below 20 K. If a linear relation above 20 K is assumed, one can evaluate the apparent activation energies of 0.85 kJ mol⁻¹ for CH₃SiH₃ and 8.9 kJ mol⁻¹ for CH₃SiD₃; the H/D isotope effect on the apparent activation energy is about ten.

Theoretical calculations were performed to evaluate the energy diagrams for both reactions (2) and (3), at a level of MP2/6-311G(d,p) + Δ ZPE(MP2/6-31G*) as shown in Fig. 5.^{21,22} For reaction (2), the transition state was calculated to be 12.5 kJ mol⁻¹ lower than that for reaction (3). This result is consistent with the previous experimental data showing that the activation energy for the reaction, SiH₃SiH₃ + [•]CH₃ \rightarrow SiH₃SiH₂[•] + CH₄, is 39 kJ mol⁻¹ lower than the reaction, CH₃CH₃ + [•]CH₃ \rightarrow CH₃CH₂[•] + CH₄, in the gas phase at



Fig. 4 Arrhenius plots of the rate constants, $k_{(Si-H)}$ (•) and $k_{(Si-D)}$ (**△**), for reaction (2) in the temperature region between 3.0 K and 115 K.

ca. 400 K.^{23,24} In the present low temperature solid, this lower potential barrier can be one reason why the tunneling H atom abstraction proceeds more effectively for the SiH₃ group than for the CH₃ group. In addition, preliminary calculations were performed to evaluate the dependence of the activation energy on the direction which the CH₃ radical approaches to abstract the hydrogen from the methylsilane molecule. At the transition states, TS-I and TS-II (Fig. 5), where the p_z -orbital of the CH₃ radical is collinear ($\varphi = 0$) with the Si–H (or C–H) bond of the methysilane, the activation energy is a minimum. When the atomic distance was fixed as the same as those of the transition state, $r(H \cdots CH_3) = 0.1532$ nm and $r(Si \cdots H) = 0.1642$ nm for reaction (2), $r(H \cdot \cdot \cdot CH_3) = 0.1348$ nm and $r(C \cdot \cdot \cdot H) = 0.1319$ nm for reaction (3), the activation energy was gradually increased with the departure from linearity as shown in Fig. 6. At the angles between 0° and 20° calculated here, the change in the activation energy for the Si-H bond is relatively smaller than for the C-H bond. These theoretical results are consistent with the experimental ones. Consequently, the H atom abstraction with a higher selectivity and a larger rate constant is attained at the SiH₃ group, in particular via the tunneling mechanism.

Recently, Ichikawa *et al.*²⁵ and Kumagai *et al.*²⁶ independently pointed out that a certain relaxation of the local geometrical constraints of a reactant molecule plays an important



Fig. 5 Energy diagrams for reactions (2) and (3) theoretically evaluated at the MP2/6-311G(d,p) + $\Delta ZPE(MP2/6-31G^*)$ level. The zero point energy is included here.



Fig. 6 The relationship between the activation energy for reactions (2) and (3), and the angle φ which the p_z-orbital of the CH₃ radical forms with the Si–H (or C–H) bond of the methylsilane. The energy was theoretically evaluated at the MP2/6-311G(d,p) level. The zero point energy is not included here. The atomic distance was fixed as the same as those of the transition state, $r(\text{H} \cdots \text{CH}_3) = 0.1532$ nm and $r(\text{Si} \cdots \text{H}) = 0.1642$ nm for reaction (2), $r(\text{H} \cdots \text{CH}_3) = 0.1348$ nm and $r(\text{C} \cdots \text{H}) = 0.1319$ nm for reaction (3).

role in the rate of the H atom tunneling reaction in low temperature solids. However, in the present reaction, such geometrical relaxation could not be that significant, because the H atom abstractions take place at the terminal sp^3 silicon. Rather than the geometrical relaxation of the reactant molecule, the extent to which the H atom orbital can overlap with the unpaired electron orbital of the 'CH₃ radical may play a crucial role in the tunneling reaction.

We also examined the reaction by H-atoms, which were generated by the photolysis of HI in the solid methylsilane. It was proved experimentally that the reaction was again highly selective, so that only the CH₃SiH₂[•] radical was observed, *i.e.*, the result is similar to that of the reaction initiated by the 'CH₃ radical. The reaction proceeded too rapidly to follow the H-atom decay by cw-EPR spectroscopy, even at 4 K. In addition, the CH₃SiH₂ radical was also preferentially generated by γ-ray radiolysis of pure CH₃SiH₃ at 77 K. When CH₃SiD₃ was used instead of CH₃SiH₃, only the CH₃SiD₂ radical was observed, i.e., no H/D isotope effect was detected for the site of the hydrogen abstraction both for the UV-photolysis of HI and γ -ray radiolysis. Furthermore, the H-atom abstraction by the 'CD₃ radical in the CH₃SiH₃ was also examined. No significant H/D isotope effect of the deuteration of the ${}^{\circ}CH_{3}$ radical on its decay rate was observed at 77 K, with the result that the CH₃SiH₂ radicals were preferentially generated immediately after the photolysis of CD₃I.

4. Conclusions

The EPR study revealed that the [•]CH₃ radical preferentially abstracts the H atom from the SiH₃ group of CH₃SiH₃ to form CH₃SiH₂ [•] radicals at temperatures from 3 K to 115 K. The [•]CH₃ radical decayed exponentially in the dark in this temperature range. Based on the first-order decay of the [•]CH₃ radical, the rate constants and apparent activation energies for reaction (2) were evaluated to be $k_{(Si-H)} = 3.6 \times 10^{-2} \text{ s}^{-1}$ and $k_{(Si-D)} = 6.9 \times 10^{-6} \text{ s}^{-1} (k_{(Si-H)/k(Si-D)} = 5200)$ at 77 K, $E_{a(Si-H)} = 0.85 \text{ kJmol}^{-1}$ and $E_{a(Si-D)} = 8.9 \text{ kJmol}^{-1} (E_{a(Si-H)/k}, were almost independent of the temperature below 20 K. This, together with the observed anomalously large isotope effect on the reaction, revealed that the tunneling effect contributes significantly to the H atom abstraction by$

 ${}^{\circ}CH_3$ radicals from the $-SiH_3$ group, especially at temperatures below 20 K. Further experimental and theoretical studies are being carried out on the H atom abstraction reaction for a series of alkylsilanes in order to explore the reactivity of the silyl hydrogen *via* tunneling.

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