The Moderation and Tunneling Reaction of Recoil T Atoms in Solid Xenon-Hydrogen Mixtures at 77 K

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Recoil T atom reactions were studied in Xe-H_2-D_2 mixtures at 77 K. The isotope effect on the T-atom reaction with H_2 and D_2 ($k(T+H_2 \rightarrow HT+H)/k(T+D_2 \rightarrow DT+D)$) was measured on the basis of the HT and DT yields. The isotope effect ($k(T+H_2)/k(T+D_2)$) is 1.1 in the range of hydrogen concentrations of 0.1—1.0 mol%. Since the small isotope effect (1.1) is similar to the isotope effect (1.0) for a hot T-atom reaction in the gas phase, recoil T atoms are not thermalized at these concentrations in solid xenon and form HT and DT by means of hot-atom reactions. At concentrations of hydrogen of less than 0.1 mol%, the recoil T atoms are thermalized before they encounter the solute hydrogen. The isotope effect increases with a decrease in the hydrogen concentration and amounts to 3.1 at a hydrogen concentration of 0.01 mol%. Since a large isotope effect is expected for the tunneling reaction of T atoms, the large isotope effect (3.1) at 0.01 mol% hydrogen was interpreted in terms of the tunneling reaction of thermalized T atoms. The present results in the solid xenon-hydrogen mixtures were compared with those in the gaseous xenon-hydrogen mixtures reported previously. It was concluded that hot T atoms in the solid xenon at 77 K are deactivated much less effectively than in the gas phase and that they migrate long distances with excess kinetic energies.

The moderation and reaction of hot hydrogen atoms in the solid phase are interesting problems, related as they are to chemical kinetics in the solid phase, hot-atom chemistry, radiation chemistry, and the behavior of high-energy hydrogen in nuclear-fusion materials. There have, however, been few studies of hot hydrogen atoms in the solid phase.

The selective hydrogen-atom abstraction by H atoms in the photolysis of neopentane-ethane mixtures was studied at 77 K by the use of hot atoms with different kinetic energies. It was found that the selectivity of a reaction depends upon the kinetic energy of the H atoms, suggesting that H atoms with small excess energies migrate through the neopentane matrix.[1] Miyazaki proposed a long distance migration of hot H atoms through crystals.[2]

Though a number of studies have been made of the behavior of recoil T atoms in the gas phase of rare gases,[3] studies of recoil T atoms in the solid phase of rare gases have been limited to that of a xenon-ethane system at 77 K[4] and at ultralow temperatures.[5] The reactions of T atoms with ethane are too complex for us to elucidate the elementary processes of hot T atoms in the solid phase. Thus, it is desirable to study such a simple reaction as the reaction of T atoms with hydrogen in a rare-gas matrix. Since the reaction of recoil T atoms with hydrogen in rare gas has previously been studied in the gas phase[3,6,7] the results in the solid phase can be compared with those in the gas phase.

The role of quantum mechanical tunneling in $H_2(D_2)$+H(D) reactions has been an important problem in the theory of chemical reaction. Recently direct evidence for the tunneling reaction of H(D) atoms with hydrogen molecules has been obtained at ultralow temperatures.[8] Thus, it is interesting to study the tunneling reaction of thermal T atoms produced by the moderation of hot T atoms in the rare-gas matrix.

To elucide the moderation process of hot T atoms in the solid phase and the tunneling reaction of thermalized T atoms at low temperatures, the reaction of recoil T atoms in a xenon matrix containing hydrogen has here been studied at 77 K. A large isotope effect on T-atom reactions with H_2 and D_2, that is, a large value for $k(T+H_2 \rightarrow HT+H)/k(T+D_2 \rightarrow DT+D)$, can be expected for the tunneling reactions of thermal T atoms, while no isotope effect is expected for the hot T atom reaction. The isotope effect on the T-atom reaction with hydrogen is one of the most important values for the discrimination of tunneling reactions of thermal atoms from hot-atom reactions; thus, the isotope effect has been measured in this study.

Experimental

^{6}Li-enriched ^{6}LiF, prepared from metal ^{6}Li, has a ^{6}Li/(^{7}Li+^{6}Li) ratio of 0.95. The purity of Xe gas is greater than 99.995 mol%. The purities of the H_2, D_2, and HD gases are greater than 99.999, 99.5, and 98 mol% respectively. The xenon-hydrogen mixtures ($(4—12)\times10^{-4}$ mol) and ^{6}LiF (0.0015 g) were sealed into quartz cells for neutron irradiation.

The neutron irradiation at 77 K was done in the JRR-4 reactor of the Japan Atomic Energy Research Institute. The thermal neutron flux and the dose rate of γ-rays at the irradiation port were 3×10^{17} nm^{-2}s^{-1} and 2×10^{6} Gy h^{-1} respectively. The irradiation time was 15 s. The details of the irradiation procedure were described in a previous paper.[9]

After neutron irradiation at 77 K, the samples were warmed to room temperature for the analysis of HT and DT. The tritiated products were analyzed by means of

radiogas chromatography (5-m iron(III) oxide/γ-alumina column at 77 K).

Results

Figure 1 shows the ratios of the HT yields to the DT yields against the H_2/D_2 ratios in the tritium reaction in the xenon-hydrogen (H_2 and D_2) mixtures at 77 K, where the total hydrogen concentrations (H_2+D_2) are varied from 0.01 to 1.0 mol%. The results for a Xe-HD (0.03 mol%) mixture are also depicted in the closed square. The HT/DT ratio increases linearly with an increase in the H_2/D_2 ratio. However, it does not show zero at a zero concentration of H_2. A part of the HT may be produced by wall reactions or reactions with some impurities in xenon. Thus, the isotope effect on the tritium reaction was estimated from the slope of the linear relationship between the HT/DT and H_2/D_2 ratios.

Since hydrogen gas itself is not solidified at 77 K, there are two possibilities for the formation of HT and DT. One is that the T atoms react with the hydrogen dissolved in solid xenon. The other is that the T atoms react with hydrogen which is not dissolved in the xenon matrix but which exists in the gas phase in a sample cell. The following results support the former possibility. First, the hydrogen yields (HT+DT) in Xe-hydrogen-^{6}LiF mixtures are 5—6 times as large as those in hydrogen-^{6}LiF mixtures without xenon. Thus, recoil T atoms injected into solid xenon react effectively with solute hydrogen.

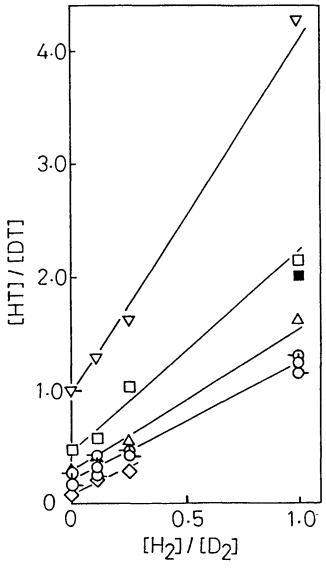

Fig. 1. Yield ratio of HT/DT for recoil T atom reactions against isotope hydrogen ratio (H_2/D_2) in Xe-H_2-D_2 mixtures at 77 K. The concentrations of total hydrogen are 0.01 mol% (▽), 0.03 mol% (□), 0.06 mol% (△), 0.2 mol% (Ⓞ, Ⓞ-, -Ⓞ), and 1.0 mol% (◇). The total amounts of xenon at 0.2 mol% hydrogen are varied as 12×10^{-4} (Ⓞ), 8×10^{-4} (Ⓞ-), and 4×10^{-4} (-Ⓞ) mole/sample. A Xe-HD (0.03 mol%) mixtrure is represented by ■.

Second, the volume of solid xenon in a sample cell was varied in order to check the fraction of the solid-state reaction. The total hydrogen yields (HT+DT) in Xe-hydrogen (0.2 mol%)-^{6}LiF (0.0015 g) mixtures do not depend upon the total amounts of the solid mixtures, suggesting that almost all of the T atoms react in the xenon matrix. The HT/DT ratios in the three different amounts of solid xenon are shown in Fig. 1, where they are designated by Ⓞ (12×10^{-4} mol), Ⓞ- (8×10^{-4} mol), and -Ⓞ (4×10^{-4} mol). The same isotope effect was obtained in these mixtures independently of the amounts of the solid.

Discussion

Isotope Effect on Hydrogen-Atom Abstraction by T Atoms from Hydrogen. The main reaction scheme for the production of hydrogen in a solid xenon-hydrogen mixture at 77 K may be represented as follows:

$$^6\mathrm{Li}+\mathrm{n} \rightarrow \mathrm{T}^*+\alpha \quad (1)$$

$$\mathrm{T}^*+\mathrm{H_2(D_2)} \rightarrow \mathrm{HT(DT)}+\mathrm{H(D)} \quad (2)$$

$$\mathrm{T}^*+\mathrm{Xe} \rightarrow \mathrm{T}+\mathrm{Xe}^* \quad (3)$$

$$\mathrm{T}+\mathrm{H_2(D_2)} \rightarrow \mathrm{HT(DT)}+\mathrm{H(D)} \quad (4)$$

Hot T atoms (T*), produced by a nuclear reaction (Reaction 1), react with H_2 (or D_2) to form HT (or DT) (Reaction 2). The hot T atoms are thermalized by collisions with xenon (Reaction 3). The thermal T atoms thus produced can react with hydrogen at 77 K by means of quantum mechanical tunneling (Reaction 4), where a hydrogen atom passes through the potential energy barrier for the reaction because of its wave character.

As for the possibility of Reaction 4, it was reported recently that H and D atoms react with hydrogen at 4.2 K by means of a tunneling effect. The absolute rate constants for the tunneling reaction $H+H_2 \rightarrow H_2+H$ is 1.8×10 $cm^3 mol^{-1} s^{-1}$ at 4.2 K.[8] Takayanagi and Sato[10] have calculated the rate constants for tunneling reactions $T+H_2$ (or D_2) by the use of the variational-transition-state theory.[11] The calculated rate constant for the tunneling reaction $T+H_2 \rightarrow HT+H$ at 77 K is 300 times as large as that at 4.2 K. Thus, thermal T atoms react quickly with H_2 by means of tunneling at 77 K, resulting in the production of HT.

There is a possibility that the recombination reaction of the thermal T and H atoms (Reaction 5), produced by the radiolsis of H_2, may compete with Reaction 4:

$$\mathrm{T}+\mathrm{H} \rightarrow \mathrm{HT} \quad (5)$$

If it is assumed that Reactions 4 and 5 constitute a diffusion-controlled reaction in solid xenon at 77 K, the rates for the two reactions depend upon the concentrations of H and $H_2(D_2)$. The H atoms are not trapped in solid xenon at 77 K; thus, the steady-state concentration of H atoms during the reactor

irradiation is much lower than the concentration of H_2 molecules. Therefore, most of the HT yields can be ascribed not to Reaction 5, but to Reactions 2 and 4.

According to Reactions 2 and 4, HT and DT are formed by both hot and thermal T atoms; the process may be represented as follows:

$$T^*(T) + H_2 \xrightarrow{k(T+H_2)} HT + H \quad (6)$$

$$T^*(T) + D_2 \xrightarrow{k(T+D_2)} DT + H \quad (7)$$

where k is the relative probability of reactions and where its ratio is defined by:

$$k(T+H_2)/k(T+D_2) = [HT][D_2]/[DT][H_2] \quad (8)$$

The $k(T+H_2)/k(T+D_2)$ ratio was obtained from the slope of the [HT]/[DT] vs. $[H_2]/[D_2]$ plots in Fig. 1.

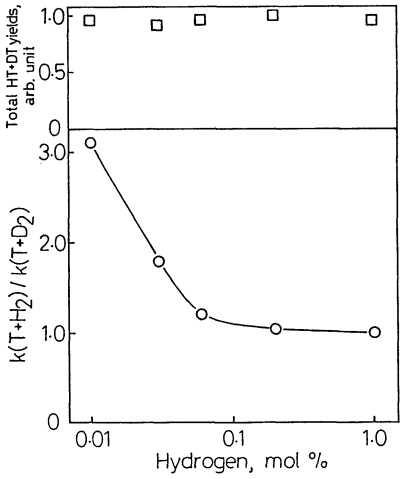

Fig. 2. Concentration dependence of the isotope effect ($k(T+H_2)/k(T+D_2)$) for recoil T atom reaction in xenon-hydrogen mixture at 77 K (○). Upper figure: total yields of HT and DT (□).

Figure 2 shows the $k(T+H_2)/k(T+D_2)$ ratios as a function of the hydrogen concentration in xenon at 77 K; the total yields (HT+DT) are also shown there. The total yields are approximately constant at all hydrogen concentrations. The $k(T+H_2)/k(T+D_2)$ ratio increases, however, with a decrease in the hydrogen concentration. The ratio is 1.1 at 0.2 mol% hydrogen, while it amounts to 3.1 at 0.01 mol% hydrogen.

Table 1 summarizes the isotope effects on the T-$H_2(D_2)$ reactions obtained here as well as on those reported previously. The $k(T+H_2)/k(T+D_2)$ ratios for recoil hot T atoms[7] and hot T atoms with 2.8 eV[12] are known to be 1.0. The $k(T+H_2)/k(T+D_2)$ ratios for thermal T atoms at low temperatures have been calculated recently.[10,13] Such a very large isotope effect as 5.6×10^6 is expected at 4.2 K, while the isotope effect decreases to 13—21 at 200 K. In fact, a very large isotope effect for the reactions of H(D) atoms was observed experimentally at 4.2 K.[8,14] For example, the ratios of the rate constants for two reactions, such as $k(H+H_2\rightarrow H_2+H)/k(D+D_2\rightarrow D_2+D)$ and $k(D+H_2\rightarrow HD+D)/k(H+D_2\rightarrow HD+D)$, are 10^4 and $>3\times10^4$ respectively.

The isotope effect (1.1) for recoil T atoms, —that is, the ratio of the reaction probabilities of the two reactions ($k(T+H_2\rightarrow HT+H)/k(T+D_2\rightarrow DT+D)$), as defined by Eq. 8, in a solid Xe-hydrogen (0.2 mol%) mixture at 77 K —is similar to the value (1.0) for hot T atoms. Thus, hot T atoms, produced by Reaction 1, migrate through solid xenon without substantial thermalization and react with solute hydrogen at 0.2 mol%. The finding that the isotope effects increase with a decrease in the hydrogen concentration indicates that some of the hot T atoms are thermalized

Table 1. Isotope Effects on T-H_2 (D_2) Reactions

Hydrogen atom	Conditions	$\frac{k(T+H_2)}{k(T+D_2)}$	Remarks
Recoil T	77 K; 0.2mol% hydrogen in solid Xe	1.1	Experimental value in this work
Recoil T	77 K; 0.01mol% hydrogen in solid Xe	3.1	Experimental value in this work
Recoil hot T	Room temp.; gas phase	1.0	Experimental value quoted from Ref. 7
Hot T with 2.8ev	Room temp.; gas phase	1.0	Experimental value quoted from Ref.12
Thermal T	4.2 K	5.6×10^6	Theoretical value for tunneling reaction quoted from Refs. 10, 11
Thermal T	77 K	1.6×10^3	Theoretical value for tunneling reaction quoted from Refs. 10, 11
Thermal T	200 K	21	Theoretical value for tunneling reaction quoted from Refs. 10, 11
Thermal T	200 K	13	Theoretical value for tunneling reaction quoted from Ref. 13
Thermal H(D)	4.2 K; solid hydrogen	10^4	Experimental value for tunneling- reaction-ratio $k(H+H_2)/k(D+D_2)$ quoted from Ref. 8
Thermal H(D)	4.2 K; solid hydrogen	$>3\times10^4$	Experimental value for tunneling-reaction-ratio $k(D+H_2)/k(H+D_2)$ quoted from Ref. 14

before they encounter the solute hydrogen at concentrations less than 0.2 mol%. The thermalized T atoms react with hydrogen by tunneling, resulting in the increase in the isotope effect. The large isotope effect at low hydrogen concentrations obtained in the present work indicates that the tunneling reactions of thermal T atoms take place at 77 K.

The isotope effect (3.1) for recoil T atoms, — that is, the ratio of the reaction probabilities of the two reactions ($k(T+H_2 \rightarrow HT+H)/k(T+D_2 \rightarrow DT+D)$), at 0.01 mol% hydrogen in the solid xenon — is much lower than the calculated value (1.6×10^3)[10,11] for thermal T atoms at 77 K. This difference may be explained as follows. First, recoil T atoms are not thermalized completely before they encounter the solute hydrogen at 0.01 mol%. A part of HT and DT may be formed by a hot T-atom reaction even at this hydrogen concentration. Second, the reaction of thermal T atoms in the solid xenon at 77 K may be partly a diffusion-controlled reaction, resulting in the low isotope effect. Third, the reaction of recoil T atoms in the solid phase may take place in a hot zone of their track the temperature of which is higher than 77 K.[15] As is shown in Table 1, the isotope effect on the thermal T-atom reaction at temperatures above 77 K is less than that at 77 K.

Since the information on the hot T atoms in the solid phase is very scanty at present, we cannot conclude which mechanism is the most plausible. In any case, the increase in the isotope effect at low concentrations of hydrogen implies the reaction of thermal T atoms by tunneling.

Moderation of Hot T Atoms in Solid Xe at 77 K. The results in the previous section show that there is no isotope effect on the reaction of hot T atoms (T*) with H_2 and D_2, while a large isotope effect can be expected for the reaction of thermal T atoms (T) at 77 K. Thus, it is reasonable to assume that $k(T^*+H_2)/k(T^*+D_2)=1$ for a hot-atom reaction and $k(T+H_2)/k(T+D_2) \gg 1$ for a thermal-atom reaction. Therefore, when equimolar H_2 and D_2 are contained in the xenon-hydrogen mixtures, the DT yields and equivalent yields of HT are due to a hot-atom reaction, while the rest of the HT yields comes from a thermal-atom reaction. Thus, the maximum yield of hot reaction is represented by Eq. 9:

$$\text{Hot reaction yields} = 2[DT]/([HT]+[DT]). \quad (9)$$

Figure 3 shows the hot-reaction yields, represented by squares, in the solid xenon at 77 K. In order to compare the deactivation of hot T atoms in the solid phase with that in the gas phase, the experimental hot-reaction yields of recoil T atoms in the gaseous xenon-hydrogen mixtures at room temperature, as studied by Hawke and Moir,[6] are shown by open circles in Fig. 3. The deactivation of hot T atoms in the gas phase can be discussed theoretically by the use of the average logarithmic energy loss on collision,

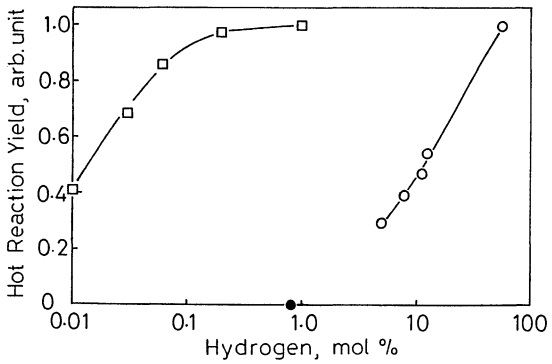

Fig. 3. Concentration dependence of hot reaction yields. (□) xenon-hydrogen mixtures in the solid phase at 77 K. (○) xenon-hydrogen mixtures in the gas phase at room temperature quoted from Ref. 6. (●) Theoretical concentration of hydrogen in gaseous xenon-hydrogen mixtures at which hot T atoms are thermalized completely (see text).

α(Xe), defined as:

$$\alpha(\text{Xe}) = -\ln(E/E_0) \quad (10)$$

where E_0 and E are the kinetic energies of the hot T atom before and after a collision respectively. For hard-sphere elastic collisions, α(Xe) is given by:

$$\alpha(\text{Xe}) = 1-[(M-m)^2/2Mm]\ln[(M+m)/(M-m)] \quad (11)$$

where M and m are the masses of Xe and T atoms respectively.[16] α(Xe) is estimated as 0.0449 from the masses of the Xe and T atoms.[17] Recoil T atoms with an initial kinetic energy of 2.7 MeV lose their energy by collisions and enter the energy range ($\leq$250 eV)[18] of chemical reactions. The hot T atoms with about 250 eV are deactivated further by collisions with xenon molecules. The threshold energy for the $T+H_2$ (or D_2) reaction, i.e., the minimum energy for a hot atom reaction, is 0.43 eV. The number (n) of collisions necessary for the energy degradation of the hot T atoms from 250 eV to 0.43 eV can be estimated by the use of Eq. 12:

$$(E/E_0)^n = 0.43/250 \quad (12)$$

Since E/E_0 is 0.956 for α(Xe)=0.0449 (cf. Eq. 10), the collision number (n) for the deactivation is estimated as 142. The cross section for T-Xe collisions is 1.3 times as large as that for $T-H_2$ (or D_2) collisions.[19,20] The concentration of the solute, at which hot T atoms are thermalized before they encounter the solute, is obtained roughly as $(1/n)\times1.3=(1/142)\times1.3\approx0.009$ mole fraction (i.e., 0.9 mol%). This value is denoted by a closed circle in Fig. 3; the circle coincides approximately with the concentration obtained by the extrapolation of the experimental hot-reaction yields to zero (cf. open circles).

Now, it is very interesting to compare the hot-reaction yields in the solid xenon-hydrogen mixtures at 77 K with those in the gaseous xenon-hydrogen mixtures. In the solid phase, the deactivation of hot

T atoms becomes appreciable at hydrogen concentrations of less than 0.1 mol%, whereas hot T atoms in the gas phase are deactivated at high concentrations such as about 10 mol%. The results mean that, in the solid xenon at 77 K, the hot T atoms are not deactivated; thus, they migrate long distances with excess kinetic energies until they encounter solute hydrogen at a low concentration. In the gaseous xenon, however, the hot T atoms effectively lose their energy by collisions with xenon before they encounter solute hydrogen at a high concentration.

If the concentration of the solute at which hot T atoms are completely thermalized in the solid xenon is taken as 0.01 mol%, the effective mass of xenon for the deactivation in the solid phase can be estimated by the use of Eqs. 10, 11, and 12, where M is considered as the effective mass. The effective mass obtained is 13000, about 100 times larger than the mass of a xenon atom. The ineffective moderation of hot T atoms in the solid xenon may be related to a characteristic of crystals, namely, their interatomic coupled interactions.

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