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Effect of γ-Ray Irradiation on the Recoil Tritium Reaction in Xenon-Hydrogen Mixtures at 77 and 4.2 K. Competition of the Tunneling Reaction with the Combination Reaction

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Recoil T-atom reactions have been studied in Xe–H_2–D_2 mixtures at 77 and 4.2 K. When T atom reactions were caused at 77 K by neutron irradiation at an extremely low dose rate of γ-rays, a large isotope effect ($k_{HT}/k_{DT}\approx 7$) on the formation of HT and DT was observed. When T-atom reactions were caused at 77 K by neutron irradiation at a high dose rate of γ-rays, there was no isotope effect ($k_{HT}/k_{DT}\approx 1$) on the formation of HT and DT. The production of H and D atoms by γ-irradiation of the Xe–H_2–D_2 mixtures was studied by ESR spectroscopy at 4.2 K. The significant effect of the dose rate of γ-rays on the HT and DT formation was interpreted in terms of competition between a tunneling reaction of thermal T atoms with H_2(D_2) and a combination reaction of thermal T atoms with H(D) atoms produced by γ-radiolysis.

The recoil tritium reaction is usually caused by thermal neutron irradiation from a nuclear reactor, where γ-ray irradiation takes place as well. Thus, the effect of γ-ray irradiation is one of the important problems in recoil-atom reactions.[1] The elucidation of the behavior of T atoms in solids is important regarding tritium technology relevant to nucluear fusion reactors. Since the materials of the reactors are irradiated by strong ionizing radiation, the effect of ionizing radiation on the tritium behavior in the solid phase is one of the fundamental problems needed to be solved.

Since hydrogen atom–molecule reactions can be considered to be a prototype bimolecular reaction, the role of the tunneling effect in these reactions has been one of the significant problems in the theory of chemical reaction. Clear evidence for the tunneling reaction of H(D) atoms with hydrogen molecules has been obtained at ultralow temperatures.[2] The tunneling reaction of T atoms with hydrogen is a fascinating problem, as well as that of H(D) atoms.

In order to elucidate the elementary processes of tritium reactions in the solid phase, we have studied tritium reactions in both simpliest type solids, such as hydrogen,[3] and rare gases at low temperatures.[4,5] Moderation of hot T atoms and the tunneling reaction of termalized T atom were studied in a previous study of the xenon–hydrogen system at 77 K. However, the possibility of a combination reaction of thermal T atoms with H and D atoms, produced by γ-ray irradiation of the Xe–H_2–D_2 mixtures, was neglected because of scanty information concerning the production of H and D atoms by γ-ray radiolysis, as well as the short lifetimes of H and D atoms in the xenon matrix at 77 K.

In this study we used a new neutron-irradiation port in the JRR-4 reactor at the Japan Atomic Energy Research Institute. This irradiation facility has two characteristics: (1) The dose rate of γ-rays in this facility (denoted here as a neutron-irradiation port) is 2×10^{-5} times as low as that in the previous irradiation port (denoted here as a γ/neutron-irradiation port). We can thus study the γ-ray irradiation effect on tritium reactions by comparing the results in the neutron-irradiation port with those in the γ/neutron-irradiation port. (2) Since the new facility has a large space for the irradiation, we can put a large cryostat in the irradiation field. In this work we made a special cryostat which can be cooled by either liquid helium or liquid nitrogen, for neutron irradiation at 4.2 or 77 K. H and D atoms produced by γ-ray irradiation can be trapped in a xenon matrix at 4.2 K and have long lifetimes, but they cannot be trapped stably at 77 K with very short lifetimes. If the results at 4.2 K are compared with those at 77 K, we can study the effect of H and D atoms on tritium reactions. Moreover, the formation of H and D atoms by the γ-ray irradiation of Xe–H_2–D_2 mixtures was studied here by a direct observation of the atoms by ESR spectroscopy at 4.2 K.

Experimental

^{6}Li-enriched LiF, prepared from metal ^{6}Li, has a ^{6}Li/(^{7}Li+^{6}Li) ratio of 0.95. The purities of the H_2, D_2, and Xe gases were greater than 99.999, 99.5, and 99.995 mol%, respectively. Both xenon–hydrogen mixtures (0.0012 mol) and ^{6}LiF (0.0075 g) were sealed into quartz cells for neutron irradiations.

Neutron irradiation was carried out at two irradiation ports of the JRR-4 reactor at the Japan Atomic Energy Research Institute. The thermal enutron flux and the dose rate of γ-rays at the γ/neutron-irradiation port were 3×10^{17} n m^{-2} s^{-1} and 2×10^{6} Gy h^{-1}, respectively. The irradiation time was 15 s. The thermal neutron flux and the dose rate of γ-rays at the neutron-irradiation port were 1.7×10^{13} n m^{-2} s^{-1} and 4.1×10 Gy h^{-1}, respectively. The irradiation time was 6 h. In the neutron-irradiation port samples were placed in a stainless-steel cryostat (95-cm height; 37 cm diameter), filled with liquid helium at 4.2 K or liquid nitrogen at 77 K.

After neutron irradiation at 4.2 or 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 (1.2-m-long activated alumina column containing 10 wt% manganese chloride) at 77 K. An example of a radiogas chromatogram was given in a previous paper.[3]

In order to directly observe the formation of H(D) atoms, the Xe–H_2(D_2) mixtures were irradiated at 4.2 K with γ-rays from a ^{60}Co source to a total dose of 1.2×10^3 Gy, and the H(D) atoms produced were measured at 4.2 K by a JES-FE2XG ESR spectrometer at low microwave power level (0.04 μW) that did not result in any saturation of the signals of the hydrogen atoms.

Results

When Xe–H_2–D_2 mixtures are irradiated by γ-rays at 4.2 K, the H and D atoms are produced in significant amounts. Figure 1 shows the ESR spectra of the H and D atoms after γ-irradiation of a Xe–H_2(0.5 mol%)–D_2(0.5 mol%) mixture at 4.2 K. The ESR spectrum of the H atoms comprises low- and high-field lines separated by about 500 G. Figure 1A shows the low-field component in the ESR spectrum of H atoms. The main line accompanies several satellite lines caused by a superhyperfine interaction with the magnetic nuclei of the Xe atoms around a trapped H atom.[6-8] A small peak, indicated by an arrow (⇧), is due to the H atoms produced in the irradiated quartz cell. The ESR spectrum of D atoms comprises three lines separated by about 80 G. Figure 1B shows the lowest-field component in the ESR spectrum of D atoms. The main line also accompanies several satellite lines that are similar to those of the H atoms. Although the absolute yields of the H and D atoms should be obtained by the use of the satellite lines, in addition to the main line, the relative yields of the H and D atoms can be estimated simply by double integration of the main line with a digitizer-personal computer system.

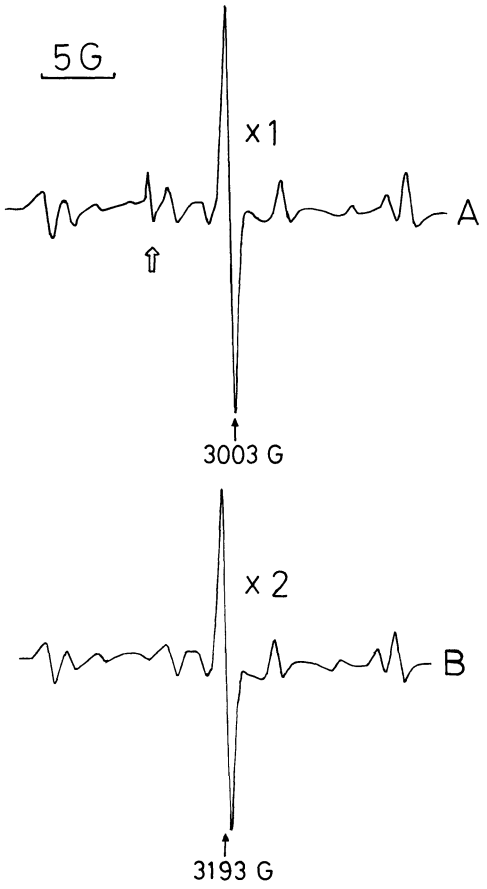

Fig. 1. ESR spectra of the γ-irradiated Xe–H_2(0.5 mol%)–D_2(0.5 mol%) mixture at 4.2 K. A, Low-field component of ESR spectra of H atoms. B, Lowest-field component of ESR spectra of D atoms. The arrow (⇧) indicates H atoms produced in the irrdiated quartz cell.

Figure 2 shows the fractions of the HT yield (depicted by ○, △ for a neutron-irradiation port at 77 K; ▽ for a neutron-irradiation port at 4.2 K; ◇, □ for a γ/neutron-irradiation port at 77 K) in total yields of HT and DT, produced by a recoil tritium reaction in solid Xe–H_2–D_2 mixtures. The fraction of H atom yields in the total yields of H and D atoms, produced by γ-ray radiolysis of Xe–H_2–D_2 mixtures at 4.2 K, are shown by closed circles. The HT yields are not zero at zero concentration of H_2.

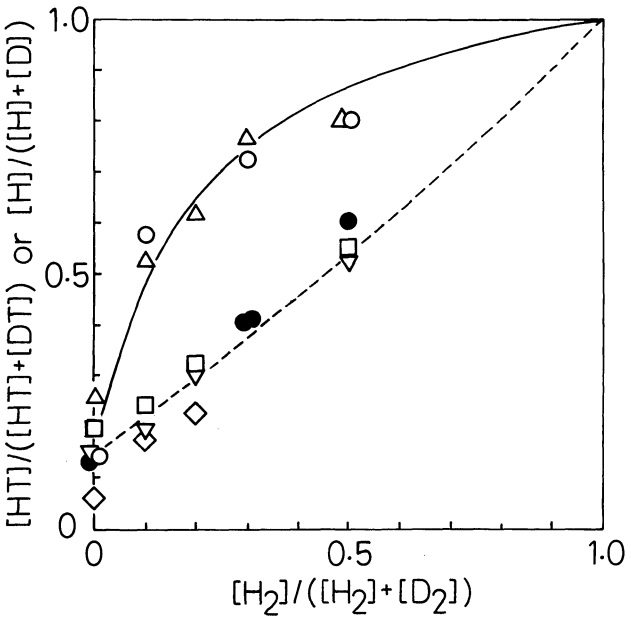

Fig. 2. Fractions of HT yields produced by recoil T atom reaction and those of H atom yields produced by γ-radiolysis in the Xe–H_2–D_2 mixtures. HT yields in neutron-irradiation port at 77 K, where total concentration of H_2 and D_2 is 1 mol% (○) and 0.2 mol% (△); (▽) HT yields in neutron-irradiation port at 4.2 K, where total concentration of H_2 and D_2 is 1 mol%; HT yields in γ/neutron-irradiation port at 77 K, where total concentration of H_2 and D_2 is 1 mol% (◇) and 0.2 mol% (□); (●) H atom yields in γ-irradiation at 4.2 K, where total concentration of H_2 and D_2 is 1 mol%. Curves are HT yields calculated by assuming isotope effect (k_H/k_D) as 7 (——) and 1 (----) (see text).

A part of HT may be produced by wall reactions or reactions with some impurities in xenon.

Discussion

γ-Irradiation Effect on HT and DT Formation in Xe-H_2-D_2 Mixtures at 77 and 4.2 K. When Xe–H_2–D_2 mixtures were irradiated in a γ-neutron-irradiation port at 77 K, the relative yields of HT ([HT]/([HT]+[DT])), denoted by ◇ and □ in Fig. 2, increased linearly with increasing mole fractions ([H_2]/([H_2]+[D_2])) of H_2, where the total concentrations of H_2 and D_2 in the mixtures are 1 mol% (◇) and 0.2 mol% (□). However, when the mixtures were irradiated in a neutron-irradiation port at 77 K, the relative yields of HT, denoted by ○ and △, increased sharply at low mole fractions of H_2, when the total concentrations of H_2 and D_2 are 1 mol% (○) and 0.2 mol% (△). An apparent kinetic isotope effect (k_H/k_D) is defined here by:

$$[HT]/[DT] = (k_H/k_D)[H_2]/[D_2] \quad (1)$$

In Fig. 2, [HT]/([HT]+[DT]) ratios for $k_H/k_D=1$ and 7 are shown by a dashed line and a solid line, respectively, where HT formation by some wall reaction or reactions with some impurities in the absence of H_2 is taken into consideration. The HT yields (depicted by ◇ and □) in the γ/neutron-irradiation port coincide with a dashed line for $k_H/k_D=1$, whereas the HT yields (depicted by ○ and △) in the neutron-irradiation port agree roughly with a solid line for $k_H/k_D=7$.

A small isotope effect ($k_H/k_D \approx 1$) for the HT yields in the γ/neutron-irradiation port was interpreted in a previous paper[4] only in terms of a hot-atom reaction. The isotope effect, however, amounts to about 7 in the neutron-irradiation port, where the dose rate of γ-rays is 1/50000 of that in the γ/neutron-irradiation port. The total dose of neutrons in the neutron-irradiation port is about 1/10 that in the γ/neutron-irradiation port. The dependence of the isotope effect on the dose rate cannot be explained by the mechanism of a hot-atom reaction. If hot T atoms react with H(D) atoms produced by radiolysis, as well as $H_2(D_2)$ molecules, the possibility of a reaction with H(D) atoms is determined by the ratio ([H(D)]/[$H_2(D_2)$]) of the concentration of H(D) atoms to that of $H_2(D_2)$ molecules in the irradiated samples. Since [H(D)]/[$H_2(D_2)$] is less than 10^{-3} under the present experimental conditions,[9] it is expected that hot T atoms do not react with H(D) atoms and, thus, the hot-atom reactions are not affected by any change in the dose rate of γ-rays.

The dose rate effect of γ-rays is probably due to reactions of thermal T atoms with products of γ-ray radiolysis. In a previous study the dose rate of γ-rays could not be changed and, thus, the dose rate effect on the recoil T-atom reactions, i.e., secondary reactions of T atoms with H(D) atoms produced by radiolysis, was not taken into consideration. It was thus suggested in the previous paper that hot T atoms may not be deactivated in the xenon matrix before encountering the solute hydrogen at 1 mol%. The dose-rate effect on the reaction of thermal T atoms, however, indicates deactivation of hot T atoms in the xenon matrix at 77 K under the experimental conditions in the present work.

$$^6Li + n \longrightarrow T^* + \alpha \quad (2)$$

$$T^* + Xe \longrightarrow T + Xe^* \quad (3)$$

$$T + H_2 \longrightarrow HT + H \quad (4)$$

$$T + D_2 \longrightarrow DT + D \quad (5)$$

$$Xe, H_2, D_2 \overset{\sim}{\longrightarrow} 2H \quad (6)$$

$$\overset{\sim}{\longrightarrow} 2D \quad (7)$$

$$T + H \longrightarrow HT \quad (8)$$

$$T + D \longrightarrow DT \quad (9)$$

$$H(D) + H(D) \longrightarrow H_2(D_2, HD) \quad (10)$$

Most of the hot T atoms (T*), which were produced by a nuclear reaction (Reaction 2), may be deactivated by collisions with xenon atoms (Reaction 3) before encountering solute hydrogen molecules at 1.0 or 0.2 mol%. Thermalized T atoms (T) react with H_2 or D_2 by a tunneling effect at 77 K (Reactions 4 and 5). In fact, hydrogen atoms react with hydrogen molecules by tunneling without any activation energy at ultralow temperatures.[2] A large isotope effect, i.e. a large value for the ratio of rate constants (k_4/k_5), would be expected in the tunneling reactions (Reactions 4 and 5).[10] At a high dose rate of γ-rays, a large amount of H and D atoms are produced by γ-ray radiolusis of Xe–H_2–D_2 mixtures (Reactions 6 and 7). Thus, thermal T atoms combine with H and D atoms to form HT and DT (Reactions 8 and 9), while most of H and D atoms recombine with each other (Reaction 10). It seems that there is no isotope effect in combination reactions of hydrogen atoms, since these reactions take place, perhaps, in every encounter without any activation energy. If it is assumed that there is no isotope effect on the production of H and D atoms (Reactions 6 and 7), the isotope effect is not expected in the formation of HT and DT by the combination reactions (Reactions 8 and 9) following the production reactions (Reactions 6 and 7). The isotope effect on the production of H and D atoms by γ-radiolysis will be discussed in the later section based upon the experimental results.

In order to discuss the competition between a tunneling abstraction reaction and a combination reaction at 77 K, HT formation in a simple system of a Xe–H_2 mixture is analyzed here:

$$Xe, H_2 \overset{\sim}{\longrightarrow} 2H \quad (6)$$

$$T + H_2 \xrightarrow{k_4} HT + H \quad (4)$$

$$T + H \xrightarrow{k_8} HT \quad (8)$$

$$H + H \xrightarrow{k_{10}} H_2, \quad (10)$$

where k is the rate constant. I is the production rate of H atoms, which is proportional to the dose rate of γ-rays. Since the amount of H atoms is much higher than those of T atoms,[11] most of the H atoms decay by a recombination reactions (Reaction 10). Then, the ratio of the rate (r_4) for the tunneling reaction (Reaction 4) to the rate (r_8) for the combination reaction (Reaction 8) is given by

$$\frac{r_4}{r_8} = \frac{k_4}{k_8}\left(\frac{k_{10}}{I}\right)^{0.5}\cdot[H_2] = k_4\left(\frac{1}{k_8 I}\right)^{0.5}[H_2], \quad (11)$$

where k_{10} is approximately equal to k_8. The ratio (r_4/r_8) is inversely proportional to $I^{0.5}$ and, thus, HT formation by a tunneling reaction plays an important role at such a low dose rates of γ-rays, as in the neutron-irradiation port, while a combination reaction becomes significant at a high dose rate of γ-rays in the γ/neutron-irradiation port.

We now discuss the isotope effect on the production of H and D atoms (Reactions 6 and 7). When Xe–H_2–D_2 mixtures are irradiated by γ-rays at 4.2 K, the H and D atoms produced are clearly observed by ESR (cf. Fig. 1). The relative amounts of H and D atoms can be estimated by a double integration of the ESR spectra. The relative yields of H atoms ([H]/([H]+[D])), as shown in Fig. 2 by closed circles, are approximately in accord with the dashed line. The apparent isotope effect (k_H/k_D) on production of H and D atoms is 1.3.

Since hydrogen atoms (H, D, and T atoms) are trapped in a xenon matrix at 4.2 K, the amounts of hydrogen atoms increase with an increase in the total irradiation dose. The Xe–H_2–D_2 mixture were irradiated in the neutron-irradiation port at 4.2 K for 6 h, and then the irradiated samples were warmed to 77 K. The concentrations of H and D atoms in this case were much higher than those of the atoms in the steady state during irradiation at 77 K.[12] Thus, combination reactions between T and H(D) atoms take place during warming the irradiated samples to 77 K. Since the isotope effect on the production of H and D atoms (Reactions 6 and 7) is 1.3, it is expected that the isotope effect on the formation of HT and DT by combination reactions (Reactions 8 and 9) is nearly 1. In fact, when the Xe–H_2–D_2 mixtures were irradiated at 4.2 K in the neutron-irradiation port, and the irradiated mixtures then warmed to 77 K, the relative yields of HT (denoted by ∇ in Fig. 2) agreed well with a dashed line, showing that k_H/k_D is 1.

In conclusion, the dose rate effect on HT and DT formation at 77 K can be explained as follows. In irradiation at such a low dose rate of γ-rays as that of the neutron-irradiation port, HT and DT are formed mainly by tunneling reactions of thermal T atoms with H_2 and D_2 (Reactions 4 and 5), resulting in a large isotope effect ($k_H/k_D \approx 7$) on HT and DT yields (cf. ○ and △ in Fig. 2). When samples are irradiated at high γ-ray dose rate in γ/neutron-irradiation port, HT and DT are mainly formed by combination reactions of thermal T atoms with H and D atoms produced by radiolysis (Reactions 6—9), resulting in a small isotope effect ($k_H/k_D \approx 1$) on the HT and DT yields (cf. ◇ and □ in Fig. 2).

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9) If G-value of H(D) atoms in the γ-irradiated Xe–H_2–(D_2)(1 mol%) mixtures is assumed as 1 and the lifetime of the atoms at a xenon matrix at 77 K is less than 1 sec, [H(D)]/[H_2(D_2)] is less than 7×10^{-4} for γ/neutron-irradiation port and 10^{-8} for neutron-irradiation port.

10) According to the calculation by Sato et al., k(T+H_2)/k(T+D_2) for tunneling reactions at 77 K amounts to 8.7×10^3. (T. Takayanagi, S. Sato, and S. Tsunashima, 32nd Japanese Meeting on Radiation Chemistry, Hiroshima, Oct. 1989.)

11) Total amounts of T atoms produced in the xenon–hydrogen mixtures are about 1/100000 of those of H(D) atoms produced by radiolysis. Thus, most of H and D atoms recombine with each other.

12) If the lifetime of H atoms in a xenon matrix at 77 K is less than 1 sec, the concentration of H(D) atoms accumulated at 4.2 K is about 20000 times as large as that of H(D) atoms during irradiation at 77 K.