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Tunneling Abstraction Reactions of Tritium Atoms with HD and with Mixtures of H_2 and D_2 in Superfluid and Normal-Fluid ^{3}He−^{4}He Media at 1.3 K

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The abstraction reactions, T + HD(DH) → HT(DT) + D(H) and T + $H_2(D_2)$ → HT(DT) + H(D) were studied experimentally in liquid ^{3}He−^{4}He media at 1.3 K and theoretically using the gas-phase reaction model. The experimental reaction system has two characteristics; one is that the tritium atom (T) is produced from one of the constituents, ^{3}He, through ^{3}He(*n*, *p*)T nuclear reaction, and the other is that superfluid or normal-fluid reaction medium can be chosen arbitrarily by changing the composition and temperature of the sample. The experimental isotope effect defined by $\{[HT]/[H_2]\}/\{[DT]/[D_2]\}$ for the reactions T + $H_2(D_2)$ → HT(DT) + H(D) was found to be 158 in superfluid and 146 in normal-fluid solutions. The large isotope effects observed were qualitatively explained via quantum mechanical tunneling on the basis of the theoretical calculations of thermal rate constants for these reactions. In the T + HD(DH) → HT(DT) + D(H) reactions, the experimental isotope effect was <19.8. From the considerations on both the reaction processes based on the experimental results and the theoretical calculations, it has been suggested that the quantum mechanical tunneling abstraction through van der Waals complex plays a predominant role for both the reactions.

Introduction

Liquid and solid helium are the most typical quantum media and show very significant quantum effects because of the small mass and very weak van der Waals interaction of helium. Many peculiar phenomena of liquid helium arising from its quantum properties, such as superfluid, formation of snow ball, and electron bubble, have been attracting many scientists. However, the studies have been focused mostly on the physical aspects, such as spectroscopy of alkali atoms introduced by laser abrasion or ion implantation, motions of electrons, and cluster formation of helium with H_2.[1] Observation of the chemical reactions in liquid helium medium has not been attempted previously.

The tunneling abstraction reactions by H and D in hydrogen molecules (H_2, HD, D_2, and their mixtures) have been investigated experimentally[2−6] in the solid state at very low temperature. However, no report has been published on the reaction in liquid helium. One of the most difficult points in the study of the chemical reaction of hydrogen isotopes in liquid helium is how to introduce reactive species in it and how to detect reaction products at very low concentration. To solve these difficulties, the nuclear activation method and radioactivity analysis of reaction products were successfully applied to the study of the reaction of T, which is one of the hydrogen isotopes, by choosing a mixture of ^{3}He and ^{4}He as a reaction medium. Helium-3 (^{3}He) has a very large activation cross section for thermal neutron (5.33×10^3 barns) to give T through a ^{3}He(*n*, *p*)T process. Because T is a radioactive nuclide that emits β-rays, even a trace amount of tritiated products can be detected with high sensitivity. In addition, the mixture of ^{3}He and ^{4}He has the very interesting property that it takes on a superfluid or normal-fluid state depending on the composition and temperature (Figure 1). Therefore, the reaction medium can be chosen arbitrarily. In the present paper, by applying these characteristics, the abstraction reactions of T + HD(DH) → HT(DT) + D(H) and T + $H_2(D_2)$ → HT(DT) + H(D) are experimentally investigated in the superfluid and normal-fluid ^{3}He−^{4}He mixtures from the viewpoint of how the chemical reaction of T proceeds in such a quantum liquid at ultralow temperature. Though there are some studies on the theoretical calculation of rate constants for the abstraction reactions of H or D with H_2, HD and D_2,[7−11] no report has been published on the rate constants of T with them. In the present work, theoretical calculation of the rate constants was carried out, and the reaction mechanism is discussed both from the experimental results and from the theoretical prediction.

Experimental Section

Helium-3 was purchased from Isotec Inc., and isotopic enrichment was >99.9 atom %. Tritium content in the gas was below the detection limit for the present T counting system. Deuterium gas (D_2) was also the product of Isotec Inc., and the isotopic content of D was >99.96%. The purity of HD gas was 96 mol %. The main impurities in HD gas were H_2 (2 mol %) and D_2 (2 mol %). The purity of other gases was >99.999%.

The mixture of ^{3}He, ^{4}He, and 1 mol % of the reactants, H_2, HD, D_2, or $H_2 + D_2$, was introduced into a Pyrex glass reaction vessel ($\sim 3.8 \times 10^3$ cm^3) with a quartz irradiation tube (6 mm i.d., 1 m in length) and cooled to 1.3 K. The atomic

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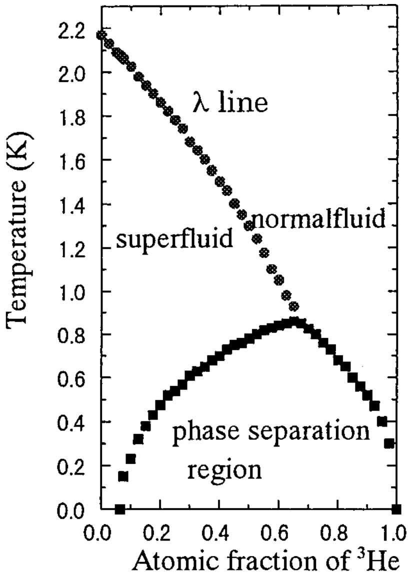

Figure 1. Phase diagram of ^{3}He $-^4$He system under saturated vapor pressure.

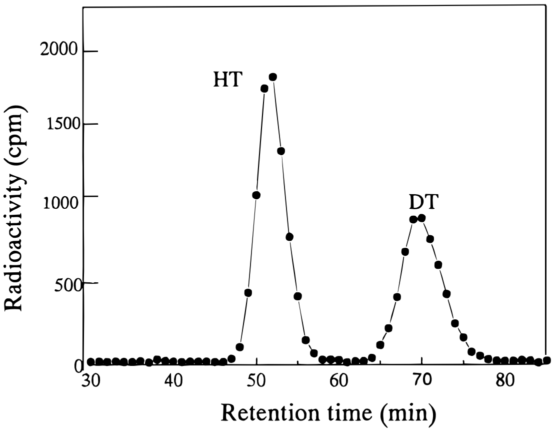

Figure 2. Typical radio-gas chromatogram of HT and DT.

compositions of the liquefied solution were ^{3}He:^{4}He = 0.670:0.330 (normal-fluid solution), and ^{3}He:^{4}He = 0.282:0.718 (superfluid solution).

Deuterization of the OH group in the quartz irradiation tube was carried out by heating for 1 day at 1273 K under D_2 pressure of 4.4 × 10^4 Pa. The conversion of the OH group to the OD group was monitored with an infrared (IR) spectrometer.

Thermal neutron irradiation was performed at JRR-2 (Japan Research Reactor No. 2) for ~50 h at 1.30 ± 0.02 K. Because the irradiation port was designed for neutron scattering experiment, the γ-ray dose rate was very low and the secondary effect caused by γ-ray could therefore be neglected. The thermal neutron flux measured by the Au-foil activation method was 8.41×10^{10} m^{-2} s^{-1}. The irradiated sample was analyzed with a radiogas chromatograph equipped with a gas-flow proportional counter. The reaction products, HT and DT, were separated at 77 K with a γ-alumina column coated with Fe_2O_3. A typical gas chromatogram is shown in Figure 2. A complete separation is seen for HT and DT. Total radioactivity was $1-2.5 \times 10^4$ counts for each experiment.

Results and Discussion

Product Distribution and Isotope Effects for HT and DT Formation. Table 1 shows the product distribution and isotope effects under the various experimental conditions. Though T atoms are formed through the nuclear reaction with an initial kinetic energy of 192 keV, they are thermalized very efficiently prior to reaction by the successive collision with liquid helium due to close mass among T, ^{3}He, and ^{4}He and to very high concentration of ^{3}He and ^{4}He in the reaction medium.[12] In addition, as the recoil range of T (14 μm) is very short compared with the inner diameter of the quartz tube, almost all T is considered to react in the sample and thus the reaction with surface hydrogen can be neglected. This assumption is supported by the experimental results in the H_2 addition − deuterated quartz tube system; that is, no DT was observed even though the deuterated quartz tube was used (first column in Table 1).

The effect of D_2 addition is very suggestive. Although there was no addition of H_2, 62.8 ± 2.9% of T is observed as HT. The most plausible source of H is considered to be an impurity included in the D_2 gas. If so, the result suggests a large isotope effect for HT and DT formation. To confirm the isotope effect definitely, a predetermined amount of H_2/D_2 was added in the system. Clear evidence of preferential formation of HT over DT was observed in this reaction system. From the yields of HT and DT shown in Table 1, the isotope effects, defined as {[HT]/[H_2]}/{[DT]/[D_2]}, were calculated to be 158 for superfluid and 146 for normal-fluid solutions. These results are also shown in the last column of Table 2 for comparison with higher temperature experiments.

Reaction Mechanism. The possible pathways leading to the formation of HT and DT in the T + H_2 (D_2) → HT(DT) + H(D) system can be considered as follows.

(1) Formation of Tritium. As T is formed through the nuclear reaction, it is initially in its translationally excited (T*) state.

$$^3\mathrm{He} + n \rightarrow \mathrm{T}^* + p \qquad (1)$$

(2) Thermalization of T.* T* loses its kinetic energy very efficiently by the successive collision with a large amount of ^{3}He and ^{4}He and is finally thermalized before subsequent reactions (reactions 3, 4, 7, and 8) occur. During thermalization, a translationally and electronically excited state of He(He*) will be produced along the track of T:

$$\mathrm{T}^* + \mathrm{He} \rightarrow \mathrm{He}^* + \mathrm{T} \qquad (2)$$

(3) Formation of HT and DT. Two pathways are possible for the formation of HT and DT; one is the abstraction reaction

TABLE 1: Distribution of HT and DT under the Various Experimental Conditions and Experimental Isotope Effects

^{3}He:^{4}He	state	additives	HT (%)	DT (%)	isotope effects
0.282:0.718^a	*s*	H_2, 1 vol %	100	0	-------
—^{b}	*s* and *n*	D_2, 1 vol %	62.8 ± 2.9	37.2 ± 2.9	-------
0.282:0.718	*s*	H_2/D_2 = 1/9, 1 vol %	94.6 ± 1.1	5.4 ± 1.1	158
670:0.330	*n*	H_2/D_2 = 1/9, 1 vol %	94.2 ± 0.8	5.8 ± 0.8	146
0.282:0.718	*s*	HD, 1 vol %	95.2 ± 0.1	4.8 ± 0.1	19.8

[a] Deuterated quartz tube. [b] ^{3}He:^{4}He = 0.670:0.330 and 0.282:0.718.

TABLE 2: Isotope Effects for $T + H_2(D_2) \rightarrow HT(DT) + H(D)$ at Various Temperatures

phase	temp.	isotope effect	I.K.E.[a]	remarks	ref.
gas	room	2.7	192 keV[b]	scavenged	15
gas	room	1.55 ± 0.06	192 keV[b]	unscavenged	15
gas	room	0.98 ± 0.03	2.8 eV[c]	-------	16
solid	77 K	7	2.7 MeV[c]	-------	14
liquid	1.3 K	146, 158	192 keV[b]	present results	

[a] I.K.E., Initial Kinetic Energy. [b] Tritium atom was produced by $^{3}He(n, p)T$. [c] Tritium atom was produced by TBr—(photolysis) → T + Br. [d] Tritium atom was produced by $^{6}Li(n, \alpha)T$.

of thermalized T with H_2 and D_2 (reactions 3 and 4) and the other one is the recombination of the thermalized T with H and D (reactions 7 and 8), which are formed by the energy transfer process from He* to H_2 and D_2 (reactions 5 and 6):

$$T + H_2 \rightarrow HT + H \tag{3}$$

$$T + D_2 \rightarrow DT + H \tag{4}$$

$$He^* + H_2 \rightarrow H + H + He \tag{5}$$

$$He^* + D_2 \rightarrow D + D + He \tag{6}$$

$$T + H \rightarrow HT \tag{7}$$

$$T + D \rightarrow DT \tag{8}$$

First of all, we consider the processes 5 and 6. If the efficiency of the energy transfer from He* to H_2 and D_2 is different very much between reactions 5 and 6, then the subsequent recombination reactions 7 and 8 result in the preferential formation of HT or DT if the reactivity of reactions 7 and 8 is identical. To evaluate the formation fraction of H against D, [H]/([H] + [D]), as a function of H_2 fraction, $[H_2]/([H_2] + [D_2])$, the amount of H and D was experimentally determined in γ-ray irradiated Xe$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.2 K and X-ray irradiated Ar$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.5 K by ESR spectroscopy. In these systems, Xe* or Ar*, formed by γ- or X-ray absorption, transfers its excited energy to H_2 and D_2 and decomposes them into H and D. Because these atoms cannot diffuse in the matrix at the experimental temperatures, the initial distribution of H and D is preserved in these systems. The results are shown in Figure 3. From the figure, it is clear that [H]/([H] + [D]) is approximately proportional to $[H_2]/([H_2] + [D_2])$. Therefore, the energy transfer efficiency from He* is supposed to be nearly equal both for H_2 and D_2 and the preferential formation of HT over DT observed experimentally cannot be explained by the difference in the reactions 5 and 6 if the reactivities of reactions 7 and 8 are identical.

In general, the isotope effect of recombination reaction between hydrogen isotopes is small. Even at ultralow temperature like the present case, the reactivity difference among hydrogen isotopes cannot be expected because the recombination is a no-barrier radical−radical reaction. The recent experiment by Hyden et al.[13] at ultralow temperature supports the aforementioned prediction. They determined the gas-phase recombination reaction rate constants k_{HD} and k_{DD} for $H + D + {}^{4}He \rightarrow HD + {}^{4}He$ and $D + D + {}^{4}He \rightarrow D_2 + {}^{4}He$ in the superfluid helium-coated wall under zero magnetic field at ~1 K. They obtained $k_{H\bullet D}/k_{D\bullet D} = 1.03$. Thus, the preferential formation of HT over DT is not due to the difference in the recombination reactions 7 and 8.

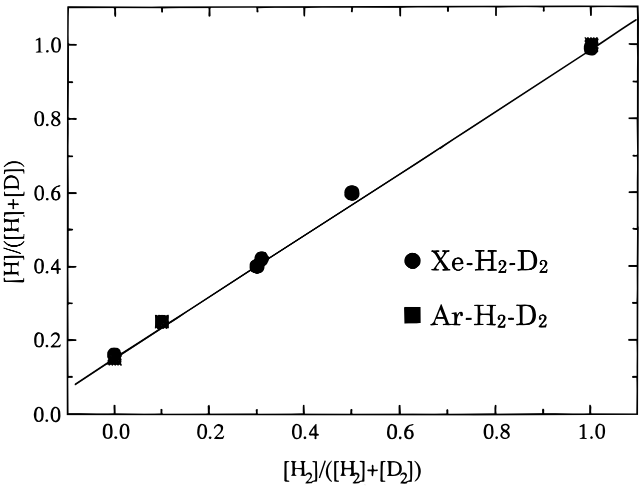

Figure 3. Fraction of H produced by γ-ray irradiated Xe$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.2 K and X-ray irradiated Ar$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.5 K. Key: (●) Xe$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.2 K; (◆) Ar$-H_2$-D_2($H_2 + D_2 = 1$ mol %) at 4.5 K.,

In conclusion, reactions 3 and 4 are supposed to be the most plausible processes to result in the very large isotope effects, $k_{(T + H_2)}/k_{(T + D_2)} = 158$ for superfluid and 146 for normal-fluid solutions, and the tunneling abstraction is considered to be the main reaction mechanism. More detailed discussions on the reaction mechanism will be given in a later section together with the consideration of $T + HD(DH) \rightarrow HT(DT) + D(H)$ system by using the theoretical rate constants and the experimental results.

Comparison of Isotope Effects of the Abstraction Reactions of $T + H_2 \rightarrow HT + H$ and $T + D_2 \rightarrow DT + H$ at Various Temperatures. The isotope effects for $T + H_2(D_2) \rightarrow HT(DT) + H(D)$ at >77 K have been experimentally examined by some workers.[14−16] Table 2 summarizes the results including the present results. Though the isotope effects in the gas phase somewhat depend on the experimental conditions, the values lie below 2.7. On the other hand, the value of 7 obtained by some of the present authors at 77 K in the highly moderated Xe$-H_2$-D_2 system is 2.5 times higher than those in the gas phase. This result suggests the partial contribution of the tunneling in the abstraction reaction. The present results exceed by about two orders of magnitude the gas-phase values and are rather close to the isotope effects of the abstraction reactions of H and D in the solid H_2, D_2, and HD at ~4 K where the importance of the tunneling in the abstraction reaction was well established.[2−6]

Theoretical Calculation of Thermal Rate Constants for the T + H_2, D_2, and HD Reactions. We employed gas-phase reaction rate theory to study isotope effect of rate constants at low temperatures. As mentioned previously, the present experiment has been done in condensed phase, liquid He media. Although the use of the gas-phase reaction model is, of course, a crude approximation, there are important advantages for this. The first advantage is that highly accurate potential energy surface for the T reaction system is now available.[17] The second advantage is that computational methodology to calculate absolute values of the thermal rate constants has been well established. These advantages mean that we can obtain accurate thermal rate constants without any adjustable parameters if the potential energy surface is given.

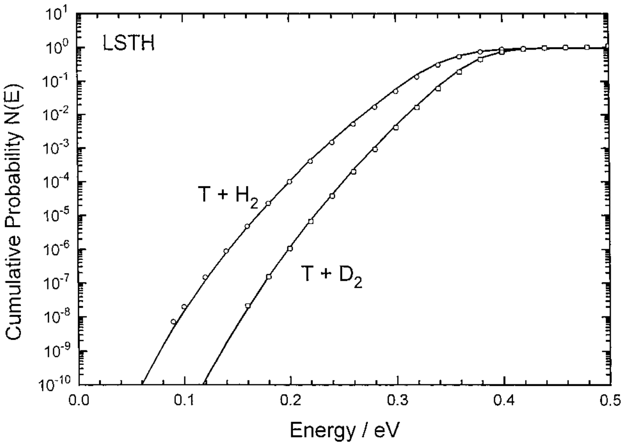

Figure 4. Cumulative reaction probabilities for T + H_2 and D_2 as a function of energy. The energy is measured from the ro-vibrational ground state of H_2 or D_2. Open circles and squares are the accurate three-dimensional quantum scattering results. Solid lines are the reduced-dimensionality results.

The thermal rate constant, k(T), for the bimolecular A + BC reaction is written as[18,19]:

$$k(\mathrm{T}) = \frac{1}{hQ_{\mathrm{int}}(\mathrm{T})Q_{\mathrm{trans}}(\mathrm{T})}\sum_{J=0}^{\infty}(2J+1)\int_0^{\infty}N^J(E)e^{-E/k_{\mathrm{B}}T}\mathrm{d}E \qquad (9)$$

where J is the total angular momentum; Q_{int}(T) and Q_{trans}(T) are the internal partition function of BC and the relative translational partition function, respectively, h and k_{B} are Planck's constant and Boltzmann's constant, respectively, $N^J(E)$ is the cumulative reaction probability, which is the sum over all initial and final open channels, for total angular momentum J as a function of the energy, E.

The cumulative reaction probability, $N^J(E)$, can be calculated accurately using three-dimensional quantum scattering theory. We have employed a time-independent hyperspherical coulpled-channel method. The computational code we used has been described in detail in ref 18. The scattering calculations were done only for $J = 0$ using the ab initio LSTH (Liu-Siegbahn-Truhlar-Horowitz)[17] potential energy surface. Figure 4 shows the $J = 0$ cumulative reaction probabilities for the T + H_2 and T + D_2 reactions as a function of energy that is measured from the ground ro-vibrational state of H_2 or D_2. As is expected, the cumulative reaction probability for T + H_2 is much larger than that for T + D_2 by a factor of 100 at low energies because the contribution of quantum mechanical tunneling for T + H_2 may be more significant.

To calculate accurate thermal rate constants below 100 K, we need to calculate $N^J(E)$ at very low energies. However, we could not obtain converged results at low energies where the cumulative reaction probabilty is $<10^{-8}$ using our quantum scattering code because the coordinate transfer from the hyperspherical coordinates to the Jacobi coordinates was not done in the asymptotic region; the reaction probability was calculated using simple averaging procedure.[18] In addition, we have to carry out the scattering calculations for $J > 0$ to obtain accurate thermal rate constants. Instead of these time-consuming calculations, we employed the reduced-dimensionality method[19,20] developed by Bowman to calculate the cumulative reaction probability at low energies. This method is essentially based on the two-dimensional collinear scattering model, where the rotational degree-of-freedom is treated as an adiabatic bending vibration during collision. Although fully state-to-state information cannot be obtained from this method, Bowman shows that this approximate method gives reliable cumulative reaction probabilities for several chemical reactions, such as D + H_2, for which accurate quantum scattering results are available. This result indicates that the reduced dimensionality method also gives accurate thermal rate constants. The reduced dimensionality Schrödinger equation was numerically solved using a standard R-matrix propagation on a natural collision coordinate system. Bending vibrational energies were calculated on all the two-dimensional grid points by a standard Harminic basis expansion method. The details of the computational procedure are described elsewhere.[9] The J-shifting approximation[19,20] was not employed in the reduced dimensionality calculations because the rate constants at low temperatures are very sensitive to the choice of the rotational constant used in the approximation.

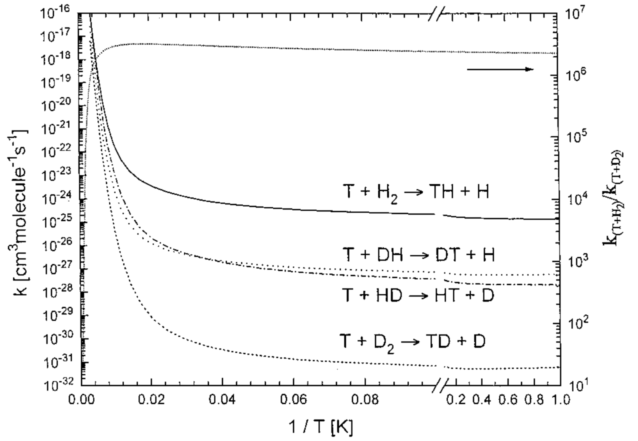

Figure 5. Arrhenius plot of thermal rate constants for T + H_2, D_2, and HD in the temperature range 10−300 K.

TABLE 3: Thermal Rate Constants k(T) Calculated with the Reduced Dimensionality Theory (in units of cm^3 $molecule^{-1}$ s^{-1})

T/K	T + H_2	T + D_2	T + DH	T + HD
300	1.4(−16)	6.5(−18)	2.6(−17)	9.7(−17)
200	1.6(−18)	2.9(−20)	1.6(−19)	7.7(−19)
100	2.1(−22)	4.7(−26)	2.4(−24)	1.3(−23)
50	3.4(−24)	6.9(−30)	1.2(−26)	2.0(−26)
10	2.5(−25)	8.2(−32)	8.2(−28)	4.4(−28)
5	1.8(−25)	5.7(−32)	6.1(−28)	2.7(−28)
1.3	1.4(−25)	5.9(−32)	5.8(−28)	2.2(−28)

In Figure 4 we compare the $J = 0$ cumulative reaction probabilities for T + H_2 and D_2 calculated using the reduced-dimensionality theory with the accurate results. The agreement with accurate three-dimensional results is excellent. In addition, we could obtain converged cumulative reaction probability down to very low energies where the cumulative reaction probability is $\sim10^{-20}$. Table 3 reports the calculated thermal rate constants in the temperature range 1.3−300 K for the T + H_2, D_2 and HD reactions. Figure 5 shows the Ahhrenius plot of the calculated thermal rate constants. Also plotted in Figure 5 is the ratio of rate constants, $k_{(\mathrm{T+H_2})}/k_{(\mathrm{T+D_2})}$, because this value is important for the present experiment.

From Figure 5 a significant curvature of the Ahhrenius plot is seen around 80 K for all the reactions. This result is consistent with the previous calculations[9,11] for other isotopic variants. The ratio of rate constants, $k_{(\mathrm{T+H_2})}/k_{(\mathrm{T+D_2})}$, is calculated to be larger than 10^6 below 50 K. This large isotope effect at low temperatures has also been reported in the comparison of the rate constants between D + H_2 and D + D_2.[9,11] It is interesting to note that the difference in the rate constants between the T + HD → HT + D and T + DH → TD + H is not so large for all the temperatures considered in this calculation. It may be expected that the rate constant for the former reaction would be larger than that for the latter reaction because quantum mechanical tunneling would be significant in light atom transfer. However, for these reactions, we found that this simple consideration cannot be applied from a reaction path analysis. For example, saddle point zero point energies of symmetric stretch and bending vibration for T + HD are larger than those for T + DH. This result indicates that the vibrational adiabatic barrier height for T + HD is larger than that for T + DH.

Consideration of Reaction Mechanism Based on the Experimental Results and Theoretical Abstraction Rate Constants. Here, we discuss the reaction mechanisms of T + HD(DH) → HT(DT) + D(H) and T + $H_2(D_2)$ → HT(DT) + H(D) (reactions 3 and 4) based on the experimental results and theoretical abstraction rate constants shown in Table 3.

The experimental isotope effect for the abstraction reactions of T + HD → HT + D and T + DH → DT + H was 19.8. In the present experimental system, H_2 and D_2 are included as the impurities and the reactions, HD −γ-ray radiolysys → H, D, --recombination → $H_2 + D_2$, during the irradiation period could be neglected because γ-ray dose rate at the irradiation port is low (2.58×10^{-6} C kg^{-1} h^{-1}).

HT and DT are produced not only by the reaction with HD but also by the reactions with H_2 and D_2. The total processes leading to HT and DT formation can be written as,

$$\mathrm{T + HD \rightarrow HT + D} \tag{10}$$

$$\mathrm{T + H_2 \rightarrow HT + H} \tag{11}$$

$$\mathrm{T + DH \rightarrow DT + H} \tag{12}$$

$$\mathrm{T + D_2 \rightarrow DT + D} \tag{13}$$

The formation rate of HT and DT are expressed as:

$$d[\mathrm{HT}]/dt = k_{10}[\mathrm{T}][\mathrm{HD}] + k_{11}[\mathrm{T}][\mathrm{H_2}] \tag{14}$$

and

$$d[\mathrm{DT}]/dt = k_{12}[\mathrm{T}][\mathrm{DH}] + k_{13}[\mathrm{T}][\mathrm{D_2}] \tag{15}$$

where k_{10}, k_{11}, k_{12}, and k_{13} are the rate constants of the reactions 10−13, respectively. Therefore, the isotope effect, [HT]/[DT], is written as:

$$[\mathrm{HT}]/[\mathrm{DT}] = \{k_{10}[\mathrm{T}][\mathrm{HD}] + k_{11}[\mathrm{T}][\mathrm{H_2}]\}/\{k_{12}[\mathrm{T}][\mathrm{DH}] + k_{13}[\mathrm{T}][\mathrm{D_2}]\} \tag{16}$$

Because k_{13} is expected to be much lower than k_{12} (cf. Table 3) and the concentration of the impurity D_2 is much smaller than that of HD, $k_{13}[\mathrm{T}][\mathrm{D_2}]$ can be neglected in eq 16. However, $k_{11}[\mathrm{T}][\mathrm{H_2}]$ may be the same order of magnitude as $k_{10}[\mathrm{T}][\mathrm{HD}]$ because k_{11} is expected to be large in Table 3. Thus, a part of HT yields is formed by reaction 11 in addition to reaction 10. Therefore, the isotope effect (k_{10}/k_{12}) on the abstraction reactions 10 and 12 is probably much <19.8. The smaller isotope effect (∼0.4) is expected from the theoretical calculation in Table 3.

The large isotope effects of 158 and 146 on reactions 3 and 4, respectively, is qualitatively explained by the large isotope effect of $\sim 10^6$ (cf. Figure 5) calculated theoretically for the tunneling reactions 3 and 4. There exist, however, two questions on the tunneling reactions. The first question is why is the experimental isotope effect much smaller than the calculated values? The second question concerns the following: the experimental rate constant for the tunneling reaction D + H_2 → HD + H at 4 K is 6×10^{-25} cm^3 molecule^{-1} s^{-1},[5] which is approximately similar to the theoretical rate constant (1.4×10^{-25} cm^3 molecule^{-1} s^{-1}) for the tunneling reaction T + H_2 → HT + H at 1.3 K. Therefore, the frequency of the tunneling reaction T(D) + H_2 is ∼1/60 s^{-1}. Therefore, the second question is why does such a slow reaction take place in liquid helium?

The most plausible solution to these questions might be given by taking the formation of a van der Waals complex prior to the abstraction reaction into consideration. Because the interaction of T and H_2 or D_2 has a long-range and attractive force and the experimental temperature is very low, the formation of a van der Waals complex $(\mathrm{T{\cdots}H_2})_{\mathrm{comp.}}$ or $(\mathrm{T{\cdots}D_2})_{\mathrm{comp.}}$ prior to the abstraction reaction is considered to be reasonable. Actually, the van der Waals complex of a hydrogen atom and a hydrogen molecule has been predicted theoretically[9, 21] and observed experimentally very recently by the authors in tunneling reaction HD + D → H + D_2 in argon matrix at 20 K.[22] According to the ab initio calculation by Boothroyd et al.,[21] well depth of van der Waals interaction is reported to be 0.047 kcal mol^{-1}. The geometry at the minimum of the van der Waals Well is colinear and the distance between H and the center of mass of H_2 is 3.7A. If we take the formation of this van der Waals complex into our kinetic model, the possible pathways leading to the formation of HT and DT may be expressed as follows:

$$\mathrm{T + H_2 + (He) \rightarrow (T{\cdots}H_2)_{comp.} - (reaction) \rightarrow HT + H} \tag{17}$$

or the complex would dissociate by the collision with He:

$$\mathrm{(T{\cdots}H_2)_{comp.} + He - (dissociation) \rightarrow T + H_2} \tag{18}$$

The following similar reaction scheme will hold for T + D_2:

$$\mathrm{T + D_2 + (He) \rightarrow (T{\cdots}D_2)_{comp.}\text{-}(reaction) \rightarrow DT + H} \tag{19}$$

or

$$\mathrm{(T{\cdots}D_2)_{comp.} + He - (dissociation) \rightarrow T + D_2} \tag{20}$$

Although the branching ratio of the reaction to the dissociation has not been well-known, it seems reasonable that the lifetime of $(\mathrm{T{\cdots}D_2})_{\mathrm{comp}}$ is longer than that of the complex $(\mathrm{T{\cdots}H_2})_{\mathrm{comp}}$ and, thus, reaction 17 might prevail over reaction 19 to lead to the preferential formation of HT.

As for the reaction rate, the question on the higher rate at 1.3 K still remains. However, it seems that the interaction of T with H_2 or D_2 within the complex surrounded by liquid helium promotes the reaction. Further theoretical and experimental investigations are necessary for the quantitative understanding of the reaction mechanism.

Conclusion

The abstraction reactions, T + HD(DH) → HT(DT) +D(H) and T + $H_2(D_2)$ → HT(DT) + H(D) were studied at 1.3 K by introducing T directly through the nuclear reaction of ^{3}He(n, p)T in superfluid and normal-fluid ^{3}He−^{4}He media. The rate constants of these abstraction reactions were theoretically calculated with the gas-phase reaction model. Based on the experimental isotope effects and theoretical rate constants, the tunneling abstraction reaction through van der Waals complex has been proposed. This is the first experimental study on the chemical reactions in quantum liquid helium. The more detailed study using the superfluid helium as a new solvent for chemical reaction is now in progress.

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(12) The kinetic energy of T after n collisions, E_n, can be written as follows if head-on collision is assumed. $E_n = E_i\, x\, \{m_2/(m_1 + m_2)\}^n$, where E_i is the initial kinetic energy of T and m_1 and m_2 are the masses of He and T. E_i can be calculated to be 192 keV by using the Q value for the nuclear reaction of ^{3}He(n, p)T. The thermal energy at 1.3 K is 1.12×10^{-4} eV. By introducing $E_n = 1.12 \times 10^{-4}$ and $m_1 = 3$ for ^{3}He or 4 for ^{4}He and $m_2 = 3$, n can be calculated as $n = 31$ for ^{3}He and $n = 38$ for ^{4}He. The concentration of He is higher than that of $H_2 + D_2$ by $\sim 10^4$ times. Moreover, T is uniformly produced. Though the collision is not always head-on, the concentration of He is sufficient for thermalization when taking the necessary number of collisions into consideration.

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