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Non-statistical formation of $J = 1$ T_2 (*ortho*-T_2) in recombination reaction of $T + T + M \rightarrow T_2 + M$ in liquid helium at 1.42–2.50 K

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Abstract

During the course of an investigation on chemical behaviors of hydrogen isotopes in quantum media, non-statistical formation of *ortho*-T_2 was observed in recombination reaction of $T + T + {}^{3,4}He \rightarrow T_2 + {}^{3,4}He$ in liquid ${}^3He$–${}^4He$ mixture at 1.42–2.50 K. The experimental *ortho*-T_2 fractions are larger than 0.9. The values are considerably higher than the equilibrium fraction of 0.75 at room temperature. Similar results have been reported in H–H recombination at low temperature. These facts suggest that similar reaction mechanism would be applied to both H and T atoms, which have the same nuclear spin number of 1/2. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

An atom–atom recombination reaction between hydrogen atoms is the simplest and prototype chemical process and thus many theoretical and experimental works have been carried out [1–8]. According to the resonant recombination theory [1–3,5], the reaction proceeds through collisional deactivation with third body,

$$H + H \rightarrow H_2^*$$

$$H_2^* + M \rightarrow H_2 + M + \Delta E \quad (M : \text{third body})$$

because vibrationally and rotationally excited hydrogen molecule (H_2^*) cannot be stabilized via radiative process of the recombination energy, $\Delta E = 4.476$ eV [9]. A collision with a third body causes the quasi-bound state to relax to a stable truly bound state.

Since T has nuclear spin number of 1/2, T_2 has two nuclear spin isomers of *para*- and *ortho*-states [10]. The former has the rotational quantum number (J) of even and the latter the odd number. Though the theoretical investigation of hydrogen recombination reaction has been devoted primarily to calculation of rate constant and to understanding of reaction mechanism, it can predict *ortho* to *para* ratio in the recombined molecular hydrogen [3–5]. Though some discrepancies between theoretical prediction and experimental

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results have been reported on the *ortho* to *para* ratio, non-statistical and preferential formation of *ortho*-H_2 (o-H_2) at low temperature predicted theoretically has been qualitatively proved by experimental studies. Most of the investigations are on H atom, one on D atom [2] but no report has been published on T atom, to the best of our knowledge.

Two of the authors (Kumada and Aratono) have been studying tunneling abstraction reaction of H and D in solid hydrogen and T in liquid ^{3}He–^{4}He mixture at very low temperatures [11,12]. Similar radiochemical methods used in the previous paper, i.e., nuclear activation for T formation and radio-gaschromatographic analysis of reaction products, were successfully applied in the present experiments. Here we report non-statistical ratio of o-T_2 against p-T_2 in the recombination reaction of T in the liquid ^{3}He–^{4}He mixture at 1.42–2.50 K.

2. Experimental

Helium-3 supplied by Isotec, has a listed isotopic enrichment of more than 99.9 at.%. Tritium content in the gas is less than 1×10^{-11}%, which is below detection limit of radioactivity counting system. The purity of ^{4}He is higher than 99.999%. According to the phase diagram of the liquid ^{3}He–^{4}He mixture [12], the solution takes on a normalfluid or superfluid state depending on temperature and composition. The atomic fraction of ^{3}He in liquefied mixture solution was measured by quadrupole mass spectrometer and ranged from 0.3 to 1. Cold neutron irradiation was performed at neutron beam guide of JRR-3M (upgraded Japan Research Reactor No. 3) for about 40 h at 1.42–2.50 K. Neutron flux measured by Au-foil activation method was about 5×10^{11} m^{-2} s^{-1}. Since the irradiation port is 30 m far from reactor core, γ-ray dose rate is very low and γ-ray radiolysis of T_2 can be neglected. After the irradiated sample was recovered from irradiation vessel to analyzing system, o-T_2 and p-T_2 were separated by radio-gaschromatograph equipped with a gas-flow proportional counter. Gamma alumina column was used at 77 K. Iron(III) hydroxide [FeO(OH)] from Nakarai Tesque, which has been used for conversion of o-H_2 to p-H_2 as catalyst [13], was also utilized for the conversion of o-T_2 to p-T_2 at room temperature. The fraction of o-T_2, $f_{o\text{-}T_2}$, was calculated as follows:

$$f_{o\text{-}T_2} = \frac{\text{radioactivity of } o\text{-}T_2}{\text{radioactivity of } p\text{-}T_2 + \text{radioactivity of } o\text{-}T_2}.$$

3. Results and discussion

Tritium atom is formed with a very high recoil energy of 192 keV by the neutron absorption of ^{3}He with a concomitant release of 576 keV proton (p) as $^3He + n \rightarrow T^{**} + p^{**}$, where T^{**} and p^{**} mean translationally excited tritium atom and proton.

The possible reaction pathways leading to the formation of H_2, HT and T_2 can be considered as follows:

(1) Thermalization of T^{**} and p^{**} by successive collisions with liquid ^{3,4}He and neutralization of p to H.

$$T^{**} + {}^{3,4}He \rightarrow T + {}^{3,4}He \tag{1}$$

$$p^{**} + {}^{3,4}He + e^- \rightarrow H + {}^{3,4}He \tag{2}$$

Thermalization of T^{**} and p^{**} in liquid ^{3,4}He occurs very efficiently due to very close mass to collision entity. The kinetic energy of T or H after N head-on collisions, E_N, can be written as

$$E_N = E_i \times \{m_2/(m_1 + m_2)\}^N,$$

where E_i is the initial kinetic energy of T or p and m_1 and m_2 are the masses of ^{3}He or ^{4}He and T or p, respectively. Thermal energy at reaction temperatures is 1.22×10^{-4} eV (1.42 K) to 2.15×10^{-4} eV (2.50 K). Thus, N can be calculated to be less than 100 for all the experimental conditions. Even if the collision is not always head-on, energy loss process proceeds in condensed phase and thus recoil T and p is thermalized sufficiently prior to recombination reaction.

(2) Recombination reactions of the thermalized H and T.

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H}_2^* \tag{3}$$

$$\mathrm{H} + \mathrm{T} \rightarrow \mathrm{HT}^* \tag{4}$$

$$\mathrm{T} + \mathrm{T} \rightarrow \mathrm{T}_2^* \tag{5}$$

$$\mathrm{H}_2^*, \mathrm{HT}^*, \mathrm{T}_2^* + {}^{3,4}\mathrm{He} \rightarrow \mathrm{H}_2, \mathrm{HT}, \mathrm{T}_2 + {}^{3,4}\mathrm{He} \tag{6}$$

H_2^*, HT^* and T_2^* are vibrationally and rotationally excited hydrogen molecules and stabilized by collisional energy transfer with liquid helium (third body).

Fig. 1 shows radio-gaschromatograms at 2.25 K (a) and 1.42 K (b). The first peak was assigned to HT by standard HT/DT mixture gas. In addition to the reaction (4), so-called wall effect, which arises from tunneling abstraction and hot atom reactions of T with surface impurity hydrogen of the reaction vessel, will be responsible for the formation of HT. The detailed reaction mechanism of the reactions (3)–(6) including the wall effect will be discussed after theoretical calculation now in progress by our group. In the present Letter, we focus on nuclear spin isomer ratio in T_2 formation. The second peak in Fig. 1a is small and was not observed in some experiments, as is seen in Fig. 1b. The retention time of the second peak is close to that of DT. However formation of DT is negligible because natural abundance of D is 0.015%. Second and third peaks were considered to be originated from *p*- and *o*-T_2 and identified as follows. One of the samples irradiated at 2.50 K was divided into two parts. One was analyzed as such. Catalytic conversion of *o*-T_2 to *p*-T_2 was applied to the second part at room temperature for 12.5 h. Radio-gaschromatographic results are shown in Fig. 2. Two peaks are seen before conversion (Fig. 2a). After treatment by catalyst, new peak grows between these two peaks (Fig. 2b). The fraction of the third peak (radioactivity of third peak/total radioactivity of second and third peaks) is 0.89 and different from equilibrium value (0.75) at room temperature [15]. This is due to relatively short contacting time of sample with catalyst. The new peak was assigned to *p*-T_2 on the basis of the following considerations. (a) In the present radio-gaschromatographic condition, only tritiated hydrogen isotopes can be detected. (b) The tritiated hydrogen isotopes produced by (3)–(6) and wall effect are HT and T_2. (c) HT is not responsible for the formation of the new peak because chemical reaction of HT with catalyst does not occur. These suggest that the new peak originates from T_2. (d) The retention time of the new peak is shorter than that of the third peak. In H_2 and T_2 molecules, *ortho*-state is more strongly bound to the surface of absorbant because *para*-state is spherically symmetric and *ortho*-state is in p orbital-like in rotation [14]. This means *p*-T_2 elutes faster than *o*-T_2. Same order was observed also for *p*-H_2 and *o*-H_2 in the present experiments.

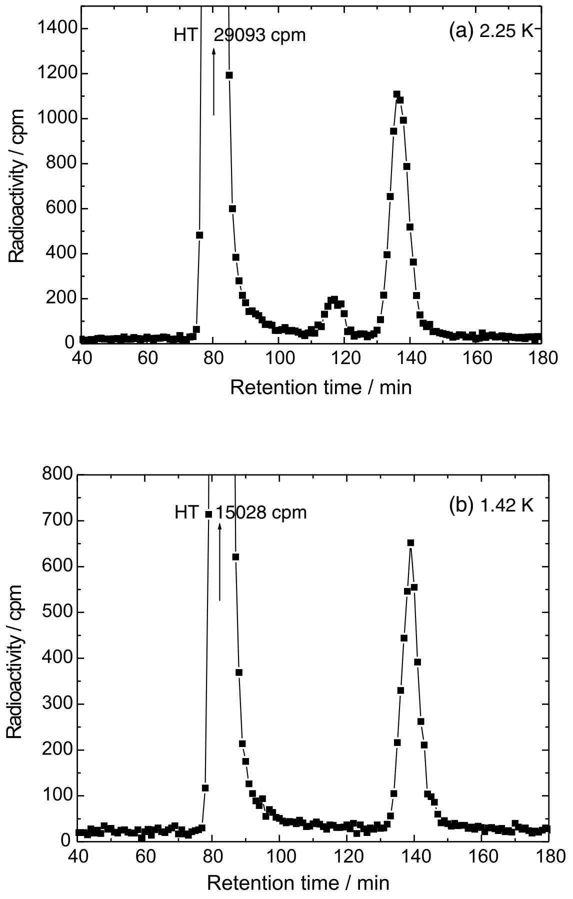

Fig. 1. Radio-gaschromatograms of cold neutron irradiated ${}^3He$–${}^4He$ mixture solutions at 2.25 K (a) and 1.42 K (b).

Table 1 shows fraction of *o*-T_2 as functions of temperature and atomic fraction of ${}^3He$ in normal and superfluid states. The values are the average of

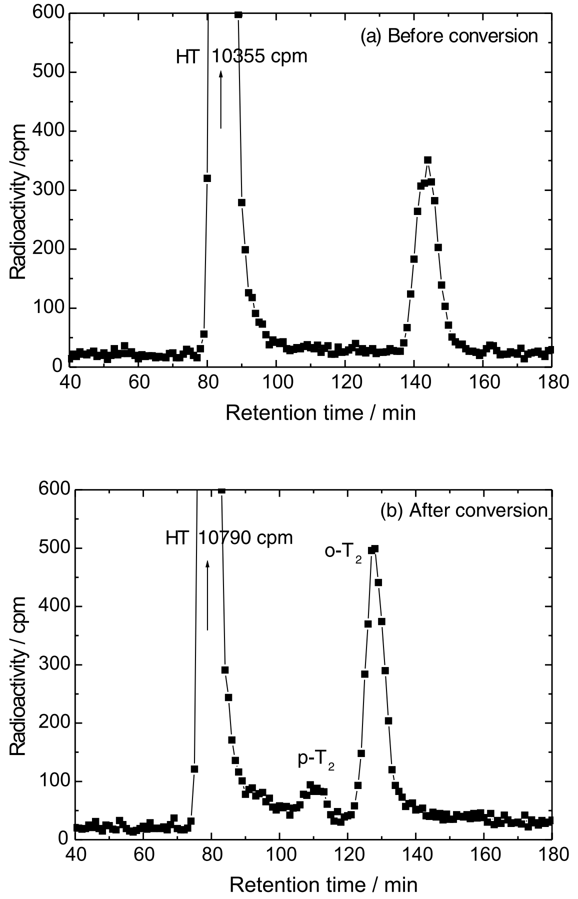

Fig. 2. Assignment of peaks by catalytic conversion of o-T_2 to p-T_2. (a) Before conversion of o-T_2 to p-T_2. (b) After conversion of o-T_2 to p-T_2.

twice experiments except at 2.25 K (three times). As is seen from Table 1, the o-T_2 fractions are higher than 0.9 over the entire range of temperatures. If p-T_2 or mixture of p-T_2 and o-T_2 is produced in initial stage and is converted during neutron irradiation, storage and separation, the fraction of o-T_2 should be less than 0.75. The present results exceeding 0.9 indicate that conversion does not occur under the present experimental conditions and hence o-T_2 is preferentially formed at the reaction temperatures. No appreciable difference is seen between superfluid and normalfluid states.

Some theoretical studies based on orbiting resonance complex mechanism have been carried out in 1970s [1–3,5]. According to the theory, the resonance complex is in a quasi-bound state with lifetime longer than vibrational period of the complex and has the characteristic rotational and vibrational quantum numbers [1,2,5]. Because of conservation of the overall symmetry, the rotational selection rule for H_2 is $\Delta J = -2$ so that odd J resonance complex contributes to the formation of o-H_2 while even J-state will results in the formation of p-H_2. Calculations show the recombination of H atoms occurs through six resonance states with vibrational and rotational quantum numbers (v, J) of (14, 5), (14, 4), (13, 8), (12, 12), (12, 11) and (11, 13) in descending order of importance and predict preferential formation of o-H_2 [1–5]. This is qualitatively in consistent with experimental results. The preferential formation of o-T_2 obtained in the present experiments seems to support the similar reaction mechanism to that for hydrogen molecule. We believe that comparison of experimental recombination behaviors with theoretical calculation among three hydrogen isotopes, H, D and T, is important for better understanding of the reac-

Table 1
Fractions of o-T_2 as functions of reaction temperature and atomic fraction of ^{3}He

Temp. (K)	$^3He/(^3He + ^4He)$	$o\text{-}T_2/(o\text{-}T_2 + p\text{-}T_2)^a$	Phase
1.42	0.38 ± 0.05	1.00 ± 0.00	Superfluid
1.75	1.00 ± 0.00	1.00 ± 0.00	Normalfluid
2.00	0.42 ± 0.00	0.98 ± 0.02	Normalfluid
2.25	0.40 ± 0.12	0.91 ± 0.06	Normalfluid
2.50	0.43 ± 0.00	0.98 ± 0.02	Normalfluid

[a] The values are the average of twice experiments except at 2.25 K (three times).

tion mechanism. From such a point of view, theoretical calculation is in progress.

4. Conclusion

Preferential formation of *o*-T_2 in tritium atom–tritium atom recombination reaction has been observed in liquid helium at very low temperature. The non-statistical formation of *ortho*-state in the present experiments are qualitatively in consistent with the theoretical prediction and experimental results in H–H recombination reaction. Details on the reaction mechanism will be reported in the near future based on the theoretical calculation which is currently under way.

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