Isotope Effect on Hydrogen Atom Abstraction Reaction by Recoil T Atoms in Solid n-$C_{10}D_{22}$-n-$C_{10}H_{22}$ Mixtures. Comparison of Recoil T Atoms with D Atoms in γ-Radiolysis

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Synopsis. An isotope effect on the hydrogen atom abstraction reaction by recoil T atoms in the n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures in the solid phase is compared with the reaction by D atoms in the γ-radiolysis. A small isotope effect for the recoil T atoms is explained by a track model.

So far many studies have been undertaken on hot tritium reactions in the gas phase,[1] but only a few studies have been reported for solid organic compounds. It has been reported for solid neopentane that most of the recoil T atoms react in their own tracks and the thermal diffusion of the T atoms in the bulk matrix plays only a minor role.[2] Recently a large isotope effect on the hydrogen atom abstraction by D atoms produced by γ-radiolydis has been found in n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures at 77 K.[3]

Here the isotope effect on the hydrogen atom abstraction reaction by recoil T atoms is examined in n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures in the solid phase and compared with the results for D atoms produced by γ-radiolysis of decane.

Experimental

n-$C_{10}D_{22}$ and n-$C_{10}H_{22}$ were the same as used before.[3c] ^{6}Li enriched LiF, used as a target for ^{6}Li (n, α) T, has the ^{6}Li/(^{7}Li+^{6}Li) ratio of 0.95. The details of the neutron irradiations, performed in the KUR reactor of Kyoto University[4] and the JRR-4 reactor of the Japan Atomic Energy Research Institute, were described in the previous papers.[2] The irradiation times were 54 h at 20 K and 15 s at other temperatures. HT and DT were analyzed by radio-gas chromatog-r aphy (5 m ferric oxide γ-alumina column at 77 K).

Results and Discussion

Though recoil T atoms cause abstraction, replacement, and fragmentation reactions with alkanes, the discussion in this paper will be confined only to the abstraction reaction which is one of the main processes in the T atom reactions and is closely related to the reaction by D atoms in the radiolysis. An apparent overall abstraction reaction in the n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ system will be represented by the following scheme.

$$\underset{(D)}{T} + n\text{-}C_{10}D_{22} \xrightarrow{p_D} \underset{(D_2)}{DT} + C_{10}D_{21}, \quad (1)$$

$$\underset{(D)}{T} + n\text{-}C_{10}H_{22} \xrightarrow{p_H} \underset{(HD)}{HT} + C_{10}H_{21}, \quad (2)$$

where p is the relative probability of the reactions. The T and D atoms are produced by the ^{6}Li(n, α)T reaction and the radiolysis of n-$C_{10}D_{22}$, respectively. The ratios of the HT yields to the DT yields at 77 K are shown in Fig. 1 and compared with HD/D_2 ratios for D atoms.[3]

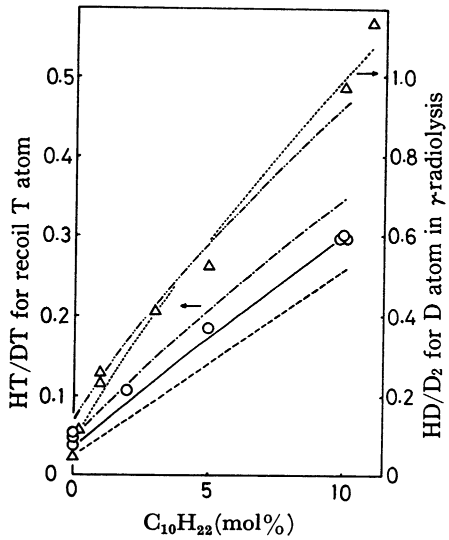

Fig. 1. Concentration dependence of HT/DT for recoil T atoms in the n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures at 77 K. ○: Experimental value for recoil T atoms, △···△, experimental value for D atoms in the radiolysis,[3a–c] –··–··: calculated value for x=0.1, –·–·: calculated value for x=0.05, ——: Calculated value for x=0.03, ----: calculated value for x=0.01. x is a fraction of diffusive T atoms to total recoil T atoms.

HT/DT is much lower than HD/D_2. Since 38% of the D_2 yield is formed by molecular detachment from n-$C_{10}D_{22}$ in the γ-radiolysis,[3c] HD/D_2 by the hydrogen atom abstraction reactions should be higher than the values in Fig. 1, resulting in the large difference between HT/DT and HD/D_2.

Recent studies show that thermal H atoms easily abstract H or D atom from alkanes at low temperature by a quantum mechanical tunneling.[5] Thus, both hot and thermal T atoms can abstract a hydrogen atom in Reactions 1 and 2. The ratio of relative probabilities for Reactions 1 and 2 is approximated by the following equation:

$$P = \frac{p_H}{p_D} = \frac{[HT][C_{10}D_{22}]}{[DT][C_{10}H_{22}]}. \quad (3)$$

The temperature effect on p_H/p_D for recoil T atoms is shown in Fig. 2. p_H/p_D for D atoms in the γ-radiolysis is also shown in Fig. 2.[3b,3c] Though the $(p_H/p_D)_D$ depends remarkably upon temperature, the $(p_H/p_D)_T$ shows little temperature effect.

The remarkable difference between the recoil T atom reaction and the D atom reaction in the γ-radiolysis can be explained by the following track model. The recoil T atom produced by the ^{6}Li(n, α)T reaction has an initial energy of 2.7 MeV and produces a high LET

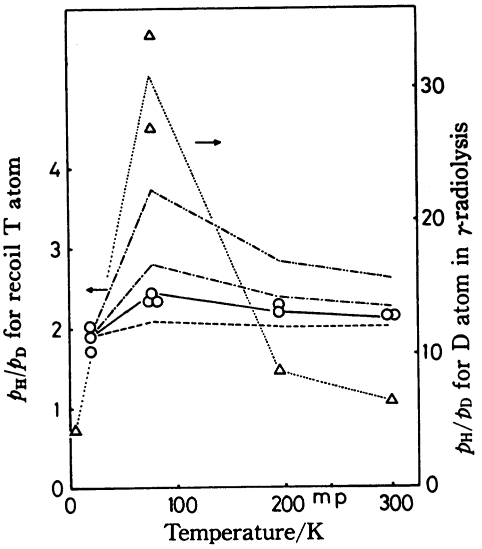

Fig. 2. Temperature dependence of p_H/p_D for recoil T atoms in the n-$C_{10}D_{22}$–n-$C_{10}H_{22}$ mixtures.
○: Experimental value for recoil T atoms, △···△: experimental value for D atoms in the radiolysis,[3a–c) ·–·–·–: calculated value for $x=0.1$, –·–·–·: calculated value for $x=0.05$, ——: calculated value for $x=0.03$, ----: calculated value for $x=0.01$. x is a fraction of diffusive T atoms to total recoil T atoms. Mp denotes a melting point of decane.

track along its trajectory in the solid phase. Some of the energetic T atoms react with n-$C_{10}D_{22}$ in the track by a hot atom reaction. However, a certain fraction of them escape reaction and finally become thermalized T atoms in the track. A fraction of the thermalized T atoms react near the end of the track, while the rest of them diffuse into the bulk matrix and react in a similar manner to D atoms in the γ-radiolysis.[6] Therefore the reaction of the recoil T atoms in the solid phase consists of two types; one occurs in the track of the recoil T atom and the other in the bulk matrix by diffusive T atoms. Then, Reactions 1 and 2 take place both in the track and in the bulk matrix. $P^t(=p_H{}^t/p_D{}^t)$ and $P^b(=p_H{}^b/p_D{}^b)$ can be defined in the track and in the bulk matrix, respectively. If x is the fraction of the T atoms, which diffuse into the bulk matrix, to the total T atoms, [HT]/[DT] can be evaluated by the following equation.

$$\frac{[\mathrm{HT}]}{[\mathrm{DT}]}=\frac{\dfrac{0.42(1-x)P^tm}{1+P^tm}+\dfrac{xP^bm}{1+P^bm}}{\dfrac{0.42(1-x)}{1+P^tm}+\dfrac{x}{1+P^bm}}, \qquad (4)$$

where m is $[C_{10}H_{22}]/[C_{10}D_{22}]$.

It has been reported in solid neopentane that almost all the recoil T atoms react in the track at 20 K without diffusion into the bulk matrix and that 42% of the total T atoms produce hydrogen.[2b)] Thus, it is assumed here that 42% of the recoil T atoms in the track reaction also produce hydrogen in the decane mixture. Then, the first and second terms in the numerator of Eq. 4 represent HT yields in the track and in the bulk matrix, respectively. The denominator represents the DT yields. Since the thermal diffusion of T atoms is suppressed at 20 K, the ratio $P(=p_H/p_D)$, calculated from [HT]/[DT] at 20 K, represents the ratio in the track reaction (P^t). P^b for diffusive T atoms may be equal to that for diffusive D atoms produced by γ-radiolysis.[6]

Then, [HT]/[DT] can be estimated in the cases of $x=0.1$, 0.05, 0.03, and 0.01 by using Eq. 4 (*cf.* Fig. 1).[7] The experimental data fit the cuves for $x=0.03$ or 0.05, suggesting that the amount of the diffusive T atoms is only 3—5% of the total T atoms. p_H/p_D can also be estimated at each temperature (*cf.* Fig. 2). The experimental data fit the curve for $x=0.03$.

In conclusion most of the recoil T atoms react in their own track and only a few percent of them diffuse into the decane matrix.

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6) The selective hydrogen atom abstraction from a solute is effectively caused by both H and D atoms. There exists no definite isotope effect between them (*cf.* T. Miyazaki *et al.*, *Bull. Chem. Soc. Jpn.*, **53**, 1813 (1980)). Thus, the T atoms with energies similar to those of the atoms produced by the radiolysis should also cause the selective hydrogen atom abstraction.

7) n-$C_{10}D_{22}$ contains H atoms equivalent to 1% $C_{10}H_{22}$. Thus some HT formation is expected in the n-$C_{10}D_{22}$ sample used here.