June, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 54, 1627—1631 (1981)* 1627

The Characteristic Behavior of Recoil Tritium Atom in Solid Neopentane at 77 K. The Application of a Hot Zone Model

Yasuyuki Aratono, Enzo Tachikawa, Tetsuo Miyazaki,*,† Masayuki Sakurai,† and Kenji Fueki†

Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-Mura, Ibaraki 319-11

†*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464*

(Received October 21, 1980)

The behavior of recoil tririum atoms in solid neopentane containing a small amount of alkane has been studied at 77 K by means of ESR spectroscopy and radio-gas chromatography. Though it was reported that the H (or D) atoms produced in the radiolysis and photolysis of solid neopentane react selectively with the solute alkane, the T atoms neither diffuse into the matrix at 77 K nor react selectively with the solute alkane. Most of the recoil T atoms react in their own track. The results are explained by a hot-zone model. The radius and the duration time of the hot zone are estimated to be $\approx$60 Å and $\approx 10^{-10}$ s respectively.

Tritium-technology in fusion reactors requires the elucidation of the behavior of hot tritium atoms in solid materials, which involve the integrity of the constructing materials as well as a tritium inventory. So far many studies have been undertaken on the hot tritium reaction in the gas phase, and the fundamental reaction modes have well been established,[1] but many fewer studies have been reported for the solid phase. In the condensed phases, there exist two important factors controlling the final product-distributions. One is the rapid collisional stabilization of excited primary products, and the other is a cage effect. The latter effect, due to the confinements of both radicals and a thermalized atom, constitutes one of the central interests in the condensed phases. However, it has been verified experimentally that the cage effect is much less important in the hot tritium atom because of its small size and because of the high probability of diffusing out from the cage wall.[2] For example, the change from the high-pressure gas phase to the liquid leaves the H substitution reaction by T in 1,2-dichloro-1,2-difluoroethane almost unaffected.[3] Furthermore, the increase in the yield of c-C_4H_7T, found in the phase change of deuterated cyclobutane from gas to a liquid or to a solid was well interpreted by the rapid collisional stabilization of excited c-$C_4D_7T^*$ molecules in the condensed phase.[4]

Recently, the behavior of H (or D) atoms, produced by the photolysis of hydrogen iodide or by the γ-radiolysis of alkane, have been studied in the solid alkane at 77 K.[5] When hydrogen atoms with an initial kinetic energy of 2—3 eV are produced in solid neopentane containing a small amount of alkane at 77 K, they migrate through the solid matrix and abstract hydrogen atoms selectively from the solute alkane. The selective hydrogen-atom abstraction has the following characteristic features: (1) The ratio of the rate constant for the hydrogen atom abstraction from the solute to that from the solvent ($k_{\text{solute}}/k_{\text{solvent}}$) is 700 for neopentane-alkane mixtures at 77 K. (2) The selective hydrogen-atom-abstraction reaction by H or D atoms in the neopentane-alkane mixtures at 77 K becomes more favored with a decrease in the initial energy of the H or D atoms. (3) The selective hydrogen atom abstraction is suppressed above a certain temperature (140 K). (4) The selective hydrogen-atom abstraction is effectively caused by both H and D atoms: there exists no definite isotope effect between them. Thus, it can be expected that the T atom in the energy range of the photolysis and the radiolysis also reacts selectively with solute alkanes at 77 K if the T atom migrates through the matrix at that temperature.

The recoil tritium atoms produced by the ^{6}Li(n,α)T reaction have an initial energy of 2.7 MeV. After the consequences of collisional energy losses, they enter the reaction-energy range and react there. However, certain fractions of them continue to escape reactions and finally become thermalized T atoms. In the cooling processes down to thermalization, the T atoms must pass through the energy range of 2—3 eV, which is equal to the initial energies of the hydrogen atoms formed in the photolysis. The effects of scavengers, such as O_2 and Br_2, on the recoil T-atom reaction in CH_4,[6] C_2H_6,[7] and i-C_4H_{10}[1a] systems indicated that 30—40% of the total recoil T atoms are thermalized in the gas phase.

The question raised here is whether or not such T atoms can migrate through the solid alkane at 77 K, as the hydrogen atoms formed in the photolysis can. Here, in order to solve this problem, the reactions of T atoms were studied in neopentane–alkane mixtures. Although the preliminary experiments[8] provided no evidence for the selective H abstraction reaction of recoil T atoms, the failure in the observation might have been because the sample temperature was raised during the neutron irradiations. In the present experiments, the sample temperature during the irradiation was checked through the ESR measurements of radicals formed concomitantly. The results obtained were analyzed by comparison with the characteristic features of the behavior of the H (or D) atoms formed in the photolysis and radiolysis.

Experimental

The LiF, used as the target for ^{6}Li(n, α)T, was purchased from the Johnson Mathey Chemicals. The mass-spectroscopic analysis showed that the ^{6}Li/^{7}Li ratio in the LiF is 0.04. The neopentane and propane were more than 99.9 mol% and 99.7 mol% respectively in purity. At least 95% of the isobutane-2-d_1 (i-C_4H_9D) was correctly labeled with the deuterium at the tetriary position. The 2-methyl-d_3-propane-1,1,1,3,3,3-d_6 (i-C_4D_9H), supplied by Merck Sharp and Dohm, Canada, Ltd., has a listed isotopic purity of 98 mol%.

In order to make solid neopentane–alkane–LiF mixtures, the liquid mixtures were immersed rapidly in liquid nitrogen.

H atoms, produced by the radiolysis of neopentane, react effectively with the alkane solute to form alkyl radicals. The yields of the alkyl radicals increase with an increase in the concentration of the solute alkane.[5c] Thus, most of the alkane solute may be dissolved uniformly in the neopentane matrix at 77 K. A part of the LiF may be dissolved in the neopentane matrix, while the rest is precipitated in the solvent. Thus, T atoms may be produced from the dissolved LiF as well as the precipitated LiF.

The reagents were sealed into a quartz cell. The sealed cell was inserted into a polyethylene capsule packed with powered dry ice. Subsequently, the capsule was immersed in liquid N_2 until it reached an equilibrium and was then immediately irradiated in the pneumatic tube of the JRR-4 reactor of the Japan Atomic Energy Research Institute. The neutron flux and the dose rate of γ-rays from the reactor were 3×10^{13} n cm^{-2} s^{-1} and 2×10^{8} rad h^{-1} respectively.[9] At the end of the irradiation, some capsules were immersed in liquid N_2 to make them ready for the subsequent ESR measurements.

The free radicals of the irradiated samples were measured at 77 K with a JEOL-PE3X ESR spectrometer at a microwave power level of 0.2 mW, which did not result in a saturation of the signals of the alkyl radicals. The tritiated products were analyzed by means of radio-gas chromatography. A 5-m ferric oxide γ-alumina column at 77 K was used for the separation of HT and DT, and a 3-m Parapak Q column at 380 K, for the organic products. The two columns were combined by means of a double-column technique,[10] in which a whole sample can be injected at a time.

Results and Discussion

ESR Spectra of Irradiated Sample. Figure 1a shows the ESR spectrum of a *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %)–LiF mixture irradiated at 77 K in the reactor. The spectrum of eight lines, indicated by arrows (↓), is ascribed to the *t*-C_4H_9 radical.[11] The spectrum of three broad lines, indicated by arrows (⇩), is ascribed to the *neo*-C_5H_{11} radical.[11] The unsymmetrical spectrum, indicated by arrows (↓), is due to a color center of irradiated quartz. Figure 1b shows the ESR spectrum of a *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %) mixture γ-irradiated at 77 K with Co-60. The spectrum consists of spectra of *neo*-C_5H_{11} and *t*-C_4H_9 radicals. The amount of the *t*-C_4H_9 radical is about 30% of the total radical yield. Similarly, C_3H_7 or *t*-C_4D_9 radicals are remarkably produced in the γ-radiolysis of *neo*-C_5H_{12} containing C_3H_8(2 mol %) or *i*-C_4D_9H(2 mol %) at 77 K.

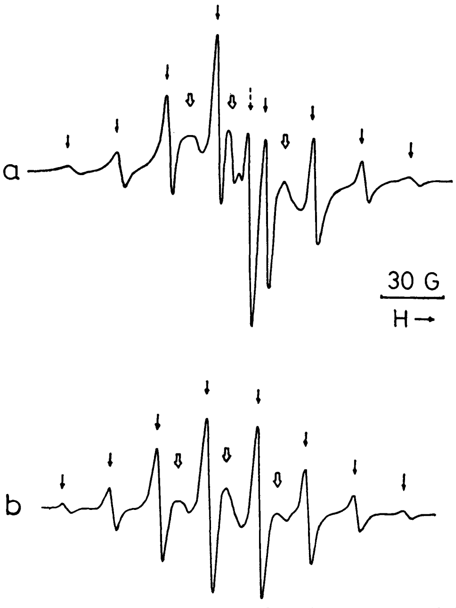


Fig. 1a. ESR spectrum of irradiated *neo*-C_5H_{12}–*i*-C_4H_9D-(2 mol %)–LiF mixture at 77 K with a reactor for 15 s at a dose of 0.8 Mrad. b. ESR spectrum of irradiated *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %) mixture at 77 K with γ-rays of Co-60 at a dose of 0.1 Mrad.

A comparison of Fig. 1a with Fig. 1b makes it obvious that the neutron-irradiation of the *neo*-C_5H_{12}–*i*-C_4H_9D-(2 mol %)–LiF mixture gives approximately the same ESR spectra of *neo*-C_5H_{11} and *t*-C_4H_9 radicals as in the γ-irradiation. This is reasonable since, during the neutron-irradiation in the reactor, the sample is also exposed to a high dose of γ-rays. The chemical damage caused by the recoil T and ^{3}He atoms amounts to only 1—2% of that caused by γ-rays.

According to the previous studies,[5] the *t*-C_4H_9 radicals are produced by the selective hydrogen-atom-abstraction reaction by H atoms produced from the radiolysis of neopentane (Reactions 1 and 2):

$$neo\text{-}C_5H_{12} \rightsquigarrow neo\text{-}C_5H_{11} + H \qquad (1)$$

$$H + i\text{-}C_4H_9D \longrightarrow HD + t\text{-}C_4H_9. \qquad (2)$$

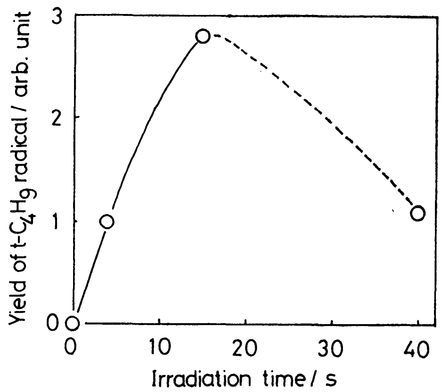


Fig. 2. Yield of *t*-C_4H_9 radical in the irradiation of *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %)–LiF mixture with a reactor against irradiation time.

Figure 2 shows the effect of the irradiation time in the reactor on the amount of the *t*-C_4H_9 radical produced in the irradiated *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %)–LiF mixture. The amount of the *t*-C_4H_9 radical increases almost linearly up to an irradiation time of 15 s, while the amount decreases drastically at 40 s. In the case of an irradiation time of 40 s, most of the *t*-C_4H_9 radicals may disappear as a result of the elevation of the temperature of the sample during the irradiation.[12] Thus, a sample temperature of near 77 K is assured within the irradiation time of 15 s, during which time the selective hydrogen-atom-abstraction reaction by T atoms can proceed. Therefore, the irradiation of the samples in the reactor was restricted to within 15 s.

Recoil T Atoms in Neopentane–Alkane Mixtures at 77 K. Table 1 shows the yields of tritiated products in the neopentane–alkane mixtures at 77 K. The DT/HT ratio in the *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %) system is only

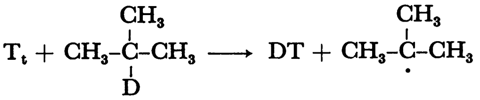
TABLE 1. YIELDS OF TRITIATED PRODUCTS OF THE RECOIL TRITIUM REACTION IN NEOPENTANE AT 77 K

Sample[a)]	Irradiation time / s	Relative yield/%						DT/HT
		HT	DT	CH_3T	RT[b)]	P[c)]	neo-$C_5H_{11}T$	
neo-C_5H_{12}–i-C_4H_9D(2)	40	42	1	14	2	4	37	0.020
neo-C_5H_{12}–i-C_4H_9D(2)	15	37	2	16	2	4	39	0.055
neo-C_5H_{12}–i-C_4H_9D(2)	4	37	2	—	—	—	—	0.056
neo-C_5H_{12}–i-C_4D_9H(2)	15	38	1	15	3	4	39	0.029
neo-C_5H_{12}–C_3H_8(2)	15	40		14	2	6	38	
neo-C_5H_{12}–i-C_4H_{10}(2)–DI(0.5)	15	45	1	14	3	—	37	0.022
neo-C_5H_{12}	15	36		15		7	42	

a) The unit of concentration in mol% is shown in parentheses. LiF (0.05 g/1 g of solvent) is added to all the samples. The yields at the irradiation time of 15 s are the mean values of three or four runs, and the errors are about 10%. b) RT represents a tritiated solute, such as i-C_4H_9T, i-C_4D_9T, or C_3H_7T. c) P may be i-C_4H_7T. d) Since not all the tritiated products were analyzed in this sample, it is assumed that the yield of hydrogen (HT+DT) is equal to that of *neo*-C_5H_{12}–i-C_4H_9D(2 mol%) at the irradiation time of 15 s.

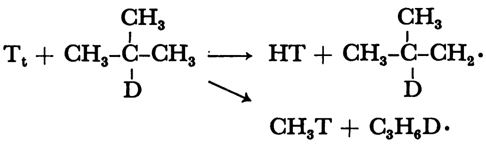
0.055 for the irradiation time of 15 s.

Now, we will try to estimate the DT/HT ratio from the previously accepted mechanisms. Though the recoil T atoms have an initial energy of 2.7 MeV, a part of them may continue to lose energy through a series of collisional deactivations to the energy range of the H (or D) atoms produced by the photolysis. The scavenger study showed that about one-third of the total recoil T atoms are deactivated.[1a,6,7] If the deactivated T atoms (T_t)[13] behave in a manner similar to that of H (or D) atoms in the photolysis, they should migrate through the *neo*-C_5H_{12}–i-C_4H_9D mixture and react selectively with the isobutane solute (Reaction 3):[5)]



$$T_t + CH_3\text{-}\underset{D}{\overset{CH_3}{C}}\text{-}CH_3 \longrightarrow DT + CH_3\text{-}\underset{\bullet}{\overset{CH_3}{C}}\text{-}CH_3 \qquad (3)$$

Furthermore, the possibility of the occurrence of Reactions 4 and 5 can be dismissed on the basis of the following results of H-atom reactions in the photolysis:



$$T_t + CH_3\text{-}\underset{D}{\overset{CH_3}{C}}\text{-}CH_3 \longrightarrow HT + CH_3\text{-}\underset{D}{\overset{CH_3}{C}}\text{-}CH_2\cdot \qquad (4)$$

$$\searrow \quad CH_3T + C_3H_6D\cdot \qquad (5)$$

When H atoms are produced by the photolysis of HI in the *neo*-C_5H_{12}–i-C_4H_9D mixtures at 77 K, only t-C_4H_9 radicals are produced by Reaction 3.[5b)] The isobutyl or propyl radicals, which should be formed in Reactions 4 and 5, were not observed by ESR spectroscopy in the reaction of H atoms with i-C_4H_9D at 77 K. Thus, most of the T_t atoms can be expected to react with i-C_4H_9D to form DT by means of Reaction 3.

The amounts of hot T atoms with a high energy (T_h) are about 60—70% of the total-recoil T-atom reactions in alkanes.[1a,6,7] These T atoms react with alkane by means of abstraction, replacement, and fragmentation reactions. Since the ratio of the D atom to the H atom in the *neo*-C_5H_{12}–i-C_4H_9D(2 mol %) mixture is only 0.002, the hot T_h atoms in the abstraction reaction react virtually with the H atom to form HT by means of Reaction 6:

$$\begin{matrix} T_h + neo\text{-}C_5H_{12} & \longrightarrow & HT + C_5H_{11}\cdot \\ (i\text{-}C_4H_9D) & & (C_4H_8D) \end{matrix} \qquad (6)$$

Thus, the maximun yield of HT is less than 60—70% of the total tritiated products. The T_t atoms, the amounts of which are about 40—30% of the total recoil T atoms, form DT by means of Reaction 3.

Therefore, the ratio of DT to HT can be expected to be higher than 0.4:

$$\frac{DT}{HT} = \frac{40-30\%}{\leqq 60-70\%} \geqq 0.4. \qquad (7)$$

The expected ratio (DT/HT) dose not coincide at all with the experimental value (0.055) in Table 1. The quite low value of the experimental DT yield indicates that most of the T_t atoms neither diffuse into the neopentane matrix at 77 K nor abstract D atoms selectively from i-C_4H_9D.

Hot-zone Model for Recoil-T-atom Reactions. If the thermalization process of recoil-T atoms in the solid phase is approximately the same as that in the gas phase, the question arises of why the thermalized recoil T_t atoms do not diffuse into the neopentane matrix at 77 K. The hot-zone model, proposed previously by Seitz *et al.*,[14)] Harbottle *et al.*,[15)] and others,[16)] gives a hypothetical explanation for this question. The ratios of the rate constants ($k_{i\text{-}C_4H_9D}/k_{neo\text{-}C_5H_{12}}$) for hydrogen-atom

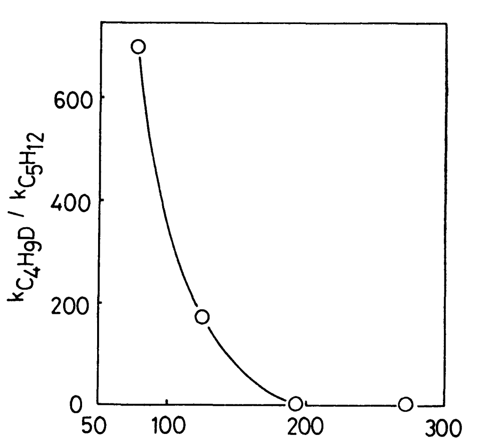


Fig. 3. Temperature effect of rate constants($k_{solute}/k_{solvent}$) for hydrogen atom abstraction by hydrogen atom produced by the UV-photolysis of *neo*-C_5H_{12}–i-C_4H_9D(2 mol %)–HI(0.5 mol %) mixture. The values are estimated from the results of previous papers.[5b,5d)]

abstraction by H atoms in the photolysis of *neo*-C_5H_{12}–*i*-C_4H_9D-HI mixtures were determined previously,[5b,5d] and they are summarized in Fig. 3. The ratio of the rate constants, which represents the selectivity of the abstraction reaction, decreases drastically with an increase in the temperature. The selective hydrogen-atom-abstraction reaction in a neopentane matrix is suppressed at temperatures higher than 140 K, which is the transition point of solid neopentane.

A recoil-T-atom produces a "track," *i.e.* "continuous spurs," around its trajectory. If the temperature of the track is much higher than 77 K and the T atom reacts in its track, the T_t atom does not abstract a D atom selectively from solute *i*-C_4H_9D, but it may react with solvent *neo*-C_5H_{12} and free radicals in the track.

We can estimate the size of a hot zone from the negative temperature effect on the selective hydrogen-atom-abstraction reaction. A cylindrical hot-zone model is used for a high-LET track produced by a recoil T atom. The excess temperature distribution (T_{ex}) in space (r) and time (t) is given for this geometry by:

$$T_{ex} = T_0(1+4\delta t/r_0^2)^{-1}\exp[-r^2/(r_0^2+4\delta t)], \qquad (8)$$

where T_0 is the initial temperature excess on the track axis and where r is the distance from it.[17] The quantity r_0 denotes the size parameter of the track cylinder, where 0.56 r_0 corresponds to the mean radius of the track. If S denotes the energy loss per unit length, then T_0 is given by the equation $T_0=S/(\pi\rho c\ r_0^2)$, where ρ and c are the density and the specific heat of the solid. Equation 8 is, in principle, the same as that proposed by Seitz *et al.*[14] except that the size of the initial track is considered according to the method of Mozumder.[17] The quantity δ, called the thermal diffudivity, equals $\kappa/\rho c$, where κ denotes the heat conductivity.

Recently the experimental and theoretical results on the stopping powers and path lengths of hydrogen and helium have been summarized by Ziegler.[18] The path lengths of the D atom and the ^{4}He atom with 1 keV through carbon are 160 Å and 100 Å respectively. It is assumed here that the length of the T atom with 1 keV through hydrocarbon is 130 Å. Thus, the average stopping power (S) is 7.7 eV Å^{-1}. The heat conductivity (κ), the specific heat (c), and the density (ρ) of solid neopentane at 77 K are 1.4×10^{-3} J s^{-1} cm^{-1} deg^{-1},[19] 0.80 J g^{-1} deg^{-1},[20] and 0.72 g cm^{-3} respectively. According to the experimental and theoretical studies of radiation chemistry, the radii of the track produced by β-rays are about 15 Å in water[17] and 25 Å in methanol[21] respectively. Thus, two values of 20 and 40 Å are tentatively taken here for the size parameters of the track (r_0). Since the selective hydrogen-atom-abstraction reaction in the *neo*-C_5H_{12}–*i*-C_4H_9D mixture is suppressed at 140 K (*cf.* Fig. 3), the lower limit of the temperature of the hot zone is assumed to be 140 K. Then, $T_{ex}=140-77=63$ K. If the excess temperature (T_{ex}) at the boundary of the hot zone is 63 K, the radius (r) of the hot zone can be calculated by Eq. 8 as a function of the duration time (t).

Figure 4 shows the size of the hot zone. The maximum radius and the duration time of the hot zone are found to be ≈60 Å and $\approx10^{-10}$ s respectively, both of which values are roughly independent of the initial size parameter (r_0) of the track. The radius increases with an increase in the duration time from 10^{-13} s to 3×10^{-11} s, and then decreases drastically at 10^{-10} s. The increase in the radius is caused by the diffusion of the initial energy deposited by a recoil T atom. The subsequent drastic decrease in the radius is due to the cooling of the hot zone. Most of the recoil T atoms may react in this hot zone within $\approx10^{-10}$ s, while only a few of them diffuse out of the zone.

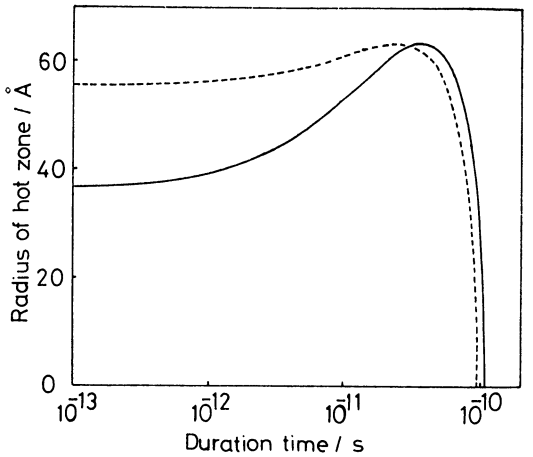


Fig. 4. Time dependence of hot zone produced by recoil T atom in solid neopentane.
——, A size parameter (r_0) of a track is 20 Å.
……, A size parameter (r_0) of a track is 40 Å.

Amount of T Atoms Leaking out of the Hot Zone. Though most of the recoil T atoms react in the hot zone, some of them may diffuse out of the zone. Now, we will attempt to estimate the upper limit of T_t atoms which may leak out of the zone. Table 1 shows the volatile tritiated products in the neopentane system. As no polymeric products are produced in a butane system,[2] most of the activity in the neopentane system may also appear in a volatile form. Thus, the yields in Table 1 represent roughly the overall reaction products.

The most possible reaction of the T_t atoms which diffuse out of the hot zone is a selective hydrogen-atom-abstraction reaction with the alkane solute in the neopentane matrix at 77 K. For example, the T_t atom reacts with *i*-C_4H_9D in the *neo*-C_5H_{12}–*i*-C_4H_9D(2 mol %) mixture to form DT (Reaction 3). The DT yield, however, amounts to only 2% of the total tritiated products.

There is a possibility that T_t atoms may migrate through the matrix and recombine with trapped radicals produced by the radiolysis of the sample. In order to examine this possibility, the reaction of T atoms has been studied in the *neo*-C_5H_{12}–C_3H_8(2 mol %) system. The ESR measurements of this mixture, after it has been γ-irradiated at 77 K, verified the production of a large amount of C_3H_7 radicals. If the C_3H_7 radicals are also produced by reactor-irradiation, the T_t atoms would recombine with the trapped C_3H_7 radicals.

$$T_t + C_3H_7 \longrightarrow C_3H_7T. \qquad (9)$$

The yield of C_3H_7T is only 2% of the total tritiated products (*cf.* Table 1). Since C_3H_7T may also be formed by the substitution reaction of hot T atoms with

C_3H_8, the amount of T atoms which recombine with the trapped C_3H_7 radicals is much less than 2%.

There is also the additional possibility that the T_t atoms react with the trapped radicals by means of a disproportionation reaction. The disproportionation reaction between an H atom and a butyl radical occurs at such a low temperature as 90 K.[22] The ESR measurement of the γ-irradiated *neo*-C_5H_{12}–*i*-C_4D_9H(2 mol %) mixture shows the predominant formation of C_4D_9 radicals. It is expected that the C_4D_9 radicals are also produced by the reactor-irradiation. If the T_t atoms migrate through the *neo*-C_5H_{12}–*i*-C_4D_9H mixtures at 77 K and react with the trapped C_4D_9 radicals by means of the disproportionation reaction, DT should be formed by Reaction 10:

$$T_t + C_4D_9 \longrightarrow DT + C_4D_8. \qquad (10)$$

Table 1 shows that the yield of DT is only 1% of the total tritiated products.

The effect of a radical scavenger, such as DI, has also been studied in the *neo*-C_5H_{12}–*i*-C_4H_{10}–DI mixtures at 77 K. It is expected that the T_t atoms may react with DI, with the resultant formation of DT:

$$T_t + DI \longrightarrow DT + I. \qquad (11)$$

Table 1 shows that the yield of DT is only 1% of the total tritiated yield. This result also indicates that the amount of the diffusively mobile T atoms may be quite small.

The authors wish to thank Prof. Noriaki Ito of Nagoya University for his fruitful discussion. The authors wish also to thank Dr. Shigeo Tsujimura of the Japan Atomic Energy Research Institute for his encouragement throughout the work and Dr. Yasuo Ito of the University of Tokyo for his helpful advice concerning the ESR measurement. This work was done under the Collaboration Program between Japan Atomic Energy Research Institute and Nagoya University. It was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) a) R. Wolfgang, *Progress Reaction Kinetics*, **3**, 97 (1965); b) F. S. Rowland, "MTP Int. Review of Science," *Phys. Chem. Ser.*, **9**, 109 (1972); c) D. S. Urch, "MTP Int. Review of Science," *Inorg. Chem. Ser.*, One, **8**, 149 (1972).

2) M. Menzinger and R. Wolfgang, *J. Phys. Chem.*, **72**, 1789 (1968).

3) H. J. Machulla and G. Stöcklin, *J. Phys. Chem.*, **78**, 658 (1974).

4) A. Hosaka and F. S. Rowland, *J. Phys. Chem.*, **75**, 3781 (1971).

5) a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **77**, 2365 (1973); b) T. Miyazaki and T. Hirayama, *J. Phys. Chem.*, **79**, 566 (1975); c) T. Miyazaki, K. Kinugawa, and J. Kasugai, *Radiat. Phys. Chem.*, **10**, 155 (1977); d) T. Miyazaki, J. Kasugai, M. Wada, and K. Kinugawa, *Bull. Chem. Soc. Jpn.*, **51**, 1676 (1978); e) T. Miyazaki, S. M. L. Guedes, and K. Fueki, *ibid.*, **53**, 1813 (1980). Other related papers are cited therein.

6) D. See and R. Wolfgang, *J. Chem. Phys.*, **47**, 143 (1967).

7) a) D. S. Urch and M. J. Welch, *Trans. Faraday Soc.*, **62**, 388 (1966); b) R. T. K. Baker and R. Wolfgang, *ibid.*, **65**, 1153 (1969).

8) Y. Aratono, E. Tachikawa, and T. Miyazaki, *Radiat. Phys. Chem.*, **13**, 115 (1970).

9) Y. Aratono and E. Tachikawa, *J. Inorg. Nucl. Chem.*, **39**, 555 (1977).

10) E. Tachikawa, Ph. D. Thesis 1967, University of California. First, hydrogen and other products were separated by the use of a cooling trap. HT and DT were analyzed by the use of the first column of ferric oxide γ-alumina. Then, the other products were analyzed by the use of the second column of parapak Q.

11) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

12) Since the irradiation time of the previous study (Ref. 8) was 60 s, the temperature of the sample was not kept at 77 K during irradiation.

13) T_t means a T atom equal to, or less than, the epithermal energy.

14) F. Seitz and J. S. Koehler, "Solid State Physics," ed by F. Seitz and D. Turnbull, Academic Press, New York, N. Y. (1956), Vol. 2.

15) G. Harbottle and N. Sutin, *J. Phys. Chem.*, **62**, 1344 (1958).

16) G. Harbottle, "Chemical Effects of Nuclear Transformations in Inorganic Systems," ed by G. Harbottle and A. G. Maddock, North-Holland Publ. Co., Amsterdam (1979), Chap. 3, The related papers are cited therein.

17) A. Mozumder, "Advances in Radiation Chemistry," ed by Burton and J. L. Magee, Wiley-Interscience, New York (1969), Vol. 1, p. 1.

18) J. F. Ziegler, "Stopping Powers and Ranges in All Elements," Pergamon Press, New York (1977), Vols. 3 and 4.

19) "Handbook of Chemistry and Physics," ed by R. C. Weast, CRC Press, Cleveland, (1976).

20) H. Enokido, T. Shinoda, and Y. Mashiko, *Bull. Chem. Soc. Jpn.*, **42**, 84 (1969).

21) R. I. Samoilova, A. M. Raitsimring, and Yu. D. Tsvetkov, *Radiat. Phys. Chem.*, **15**, 553 (1980).

22) R. Klein, M. D. Scheer, and R. Kelley, *J. Phys. Chem.*, **68**, 598 (1964).