*Article*

# Intermolecular Hydrogen Transfer in Isobutane Hydrate

**Naohiro Kobayashi [1], Takashi Minami [1], Atsushi Tani [2], Mikio Nakagoshi [1], Takeshi Sugahara [1], Kei Takeya [3] and Kazunari Ohgaki [1,\*]**

[1] Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan; E-Mail: sugahara@cheng.es.osaka-u.ac.jp (T.S.)

[2] Department of Earth and Space Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan; E-Mail: atani@ess.sci.osaka-u.ac.jp

[3] Department of Electrical and Electronic Engineering and Information Engineering, Graduate School of Engineering, Nagoya University, Furo, Chikusa-ku, Nagoya, Aichi 464-8603, Japan; E-Mail: takeya@nuee.nagoya-u.ac.jp

**\*** Author to whom correspondence should be addressed; E-Mail: ohgaki@cheng.es.osaka-u.ac.jp; Tel.: +81-6-6850-6290.

**Abstract:** Electron spin resonance (ESR) spectra of butyl radicals induced with γ-ray irradiation in the simple isobutane (2-methylpropane) hydrate (prepared with deuterated water) were investigated. Isothermal annealing results of the γ-ray-irradiated isobutane hydrate reveal that the isobutyl radical in a large cage withdraws a hydrogen atom from the isobutane molecule through shared hexagonal-faces of adjacent large cages. During this "hydrogen picking" process, the isobutyl radical is apparently transformed into a *tert*-butyl radical, while the sum of isobutyl and *tert*-butyl radicals remains constant. The apparent transformation from isobutyl to *tert*-butyl radicals is an irreversible first-order reaction and the activation energy was estimated to be $35 \pm 3$ kJ/mol, which was in agreement with the activation energy ($39 \pm 5$ kJ/mol) of hydrogen picking in the γ-ray-irradiated propane hydrate with deuterated water.

**Keywords:** hydrogen abstraction; clathrate hydrate; radical; electron spin resonance; activation energy

## 1. Introduction

Clathrate hydrates are solid inclusion compounds formed by rearranging the hydrogen bonding between water (host) molecules to form polyhedral cages in which guest molecules can be trapped. Three common structures of clathrate hydrates are structure I (s-I), II (s-II), and H (s-H). Generally, the size of the guest molecule determines which structure is formed. The s-II is a cubic structure and the unit cell consists of 16 small and eight large cages. The small cage (hereafter, S-cage) is a dodecahedron comprised of 20 water molecules arranged to form 12 pentagonal faces. The large cage (L-cage) is a hexakaidecahedron comprised of 28 water molecules forming 12 pentagonal and four hexagonal faces. An isobutane molecule occupies every L-cage of s-II hydrate. The L-cage shares a hexagonal plane with adjacent L-cages. The S-cage of the s-II isobutane hydrate is vacant.

We have reported the thermal stabilities of methyl, ethyl, and propyl radicals in the γ-ray-irradiated simple methane [1,2], ethane [3], and propane [4] hydrate systems. The radicals in other clathrate hydrates have been investigated [5–7]. Alkyl radicals induced from relatively small alkanes seem to be stable in hydrate cages below the three-phase (hydrate, ice, and gas phases) equilibrium temperature of each simple hydrate system at atmospheric pressure. In the hydrate cages, the concentrated radicals of light hydrocarbons are more stable than those in any other environment [8]. In the γ-ray-irradiated propane hydrate system, we have reported that *n*-propyl radicals directly pick a hydrogen atom from the propane molecule in the adjacent L-cages (Scheme 1) [4].

**Scheme 1.** Intermolecular hydrogen-picking through a hexagonal face of L-cages in the γ-ray-irradiated propane hydrate system [4].
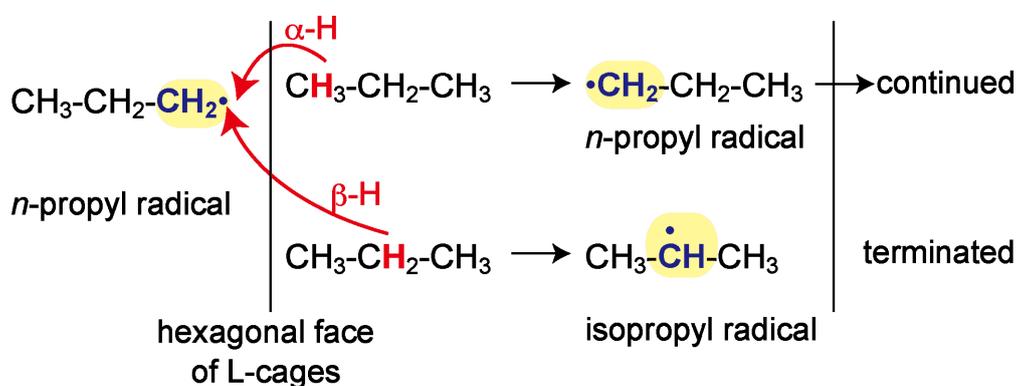


If, during the "hydrogen-picking" process, the α-hydrogen of propane is removed by the *n*-propyl radical, then an *n*-propyl radical is produced again; thus, a chain reaction should follow. When the β-hydrogen of propane is removed, an isopropyl radical is produced instead of an *n*-propyl radical; thus, the reaction is terminated. That is, the "hydrogen-picking" seems apparently to be the reaction from *n*-propyl radical to isopropyl radical, while the sum of the propyl radicals remains constant. Such an intermolecular hydrogen-picking has been also observed between methyl radical (in S-cage) and propane (in L-cage) in the methane + propane mixed-gas hydrates, that is, the hydrogen-picking occurs between different molecules in different cages [9]. We believe that the same hydrogen-picking phenomenon also occurs in other light hydrocarbon hydrate systems.

In the present study, we investigated the hydrogen-picking reaction in the γ-ray-irradiated simple isobutane hydrate with deuterated water ($D_2O$), which belongs to s-II hydrate, by means of electron spin resonance (ESR) measurements. The longest carbon chain of isobutane molecule is $C_3$ like in propane, but the β-hydrogen of isobutane would be less accessible than that of propane due to the stereo hindrance. The main purposes in the present study are to confirm the hydrogen-picking reaction and to evaluate its activation energy in the simple isobutane hydrate system.

## 2. Results and Discussion

### 2.1. ESR Spectrum of Induced Radicals

The ESR spectrum of the radicals induced in the γ-ray-irradiated simple isobutane hydrate (prepared with $D_2O$) is shown in Figure 1. The spectrum, which indicates the initial spectrum measured at 120 K before annealing, contains the signals of isobutyl and *tert*-butyl radicals. The hyperfine constants were determined: $A_\alpha$ = 2.20 mT, and $A_\beta$ = 3.40 mT for the isobutyl radical (sextet signals) and $A$ = 2.22 mT for the *tert*-butyl radical (dectet signals), respectively. These values are in agreement with the literature [10,11]. Other than isobutyl and *tert*-butyl radicals, the signals of H and D atoms were also observed at 120 K. OD radicals were not observed even at 77 K, which is consistent with the previous reports on the γ-ray-irradiated methane [1], ethane [3], and propane [4] hydrates.

**Figure 1.** ESR spectrum of radicals induced in the γ-ray-irradiated isobutane hydrate prepared with $D_2O$. The measurement was performed at 120 K and ambient pressure.
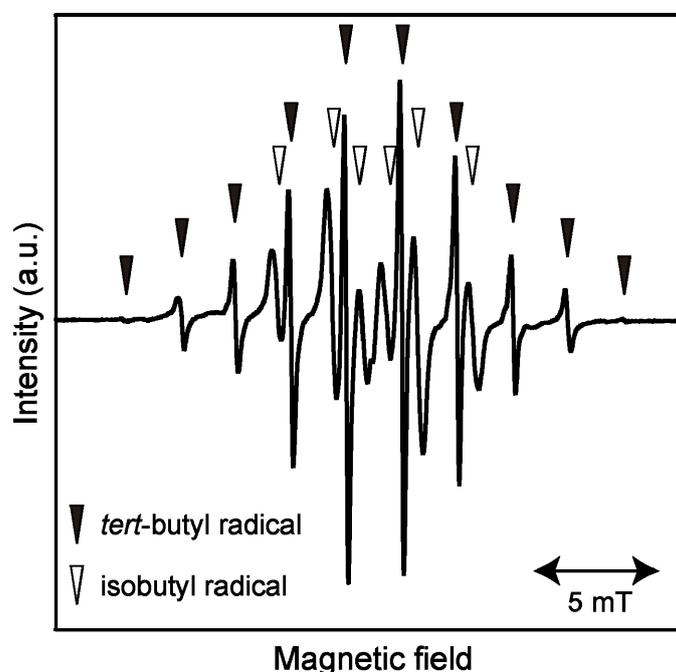


To quantify the amounts of each butyl radical, the ESR spectrum was deconvoluted based on the ESR parameters determined at each temperature. The typical deconvolution is shown in Figure 2. Figure 2a indicates the observed spectrum before annealing at 270 K. The spectra in Figure 2 (b–d) indicate the calculated spectra of *tert*-butyl radical in Figure 2c, isobutyl radical in Figure 2d, and their sum in Figure 2b. The SimFonia software provided by Bruker Biospin was used to calculate the spectra.

**Figure 2.** (**a**) Observed ESR spectrum of radicals induced in the γ-ray-irradiated isobutane hydrate with $D_2O$ at 270 K (before annealing); (**b–d**) Calculated ESR spectra of *tert*-butyl radical in (**c**), isobutyl radical in (**d**), and their sum in (**b**). In this case, the molar ratio of *tert*-butyl radical to isobutyl radical is approximately 5:4.
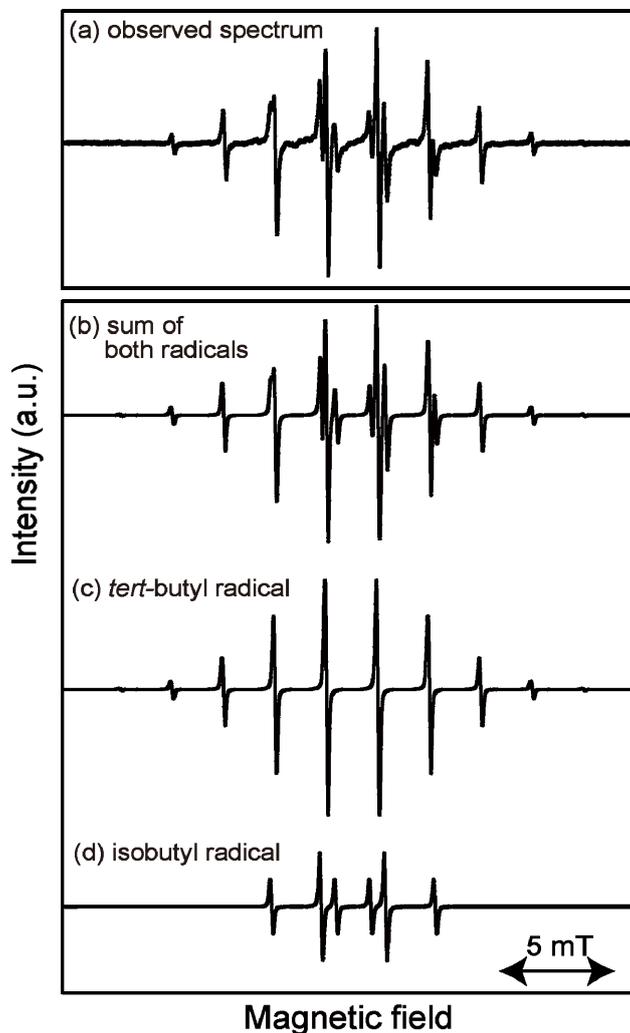


### 2.2. Isothermal Annealing Measurements

Figure 3 shows the representative results of the isothermal annealing experiment at 245 K and 260 K. Isobutane hydrate is thermodynamically stable at these temperatures under 0.1 MPa. Although the normalized total amount $[N_{all}(t)/N_{all}(0)]$ of radicals remains almost constant, the amount $[\Delta N/N_{all}(0)]$ of the isobutyl radical (solid circles) decreases while that of the *tert*-butyl radical (open circles) increases. The amounts of change for two radicals show good agreement with each other. These results reveal that isobutyl radicals directly pick a hydrogen atom from the isobutane molecule in the adjacent L-cages (Scheme 2) as in the case of the γ-ray-irradiated propane hydrate (Scheme 1) [4]. Note that no water molecule bridges between isobutyl radical and isobutane molecule because neither of the butyl radicals takes in the deuterium atom derived from $D_2O$.

The *tert*-butyl radical is more thermally stable than the isobutyl radical due to the stereostructure of the radicals. To investigate the thermal stability of the *tert*-butyl radical, the γ-ray-irradiated isobutane hydrate has been annealed at 260 K for 150 hours. The ESR spectrum after 150 hours shown in

Figure 4 is almost the same as the spectrum of *tert*-butyl radical shown in Figure 2c. That is, the hydrogen-picking reaction is irreversibly continued until all of the isobutyl radical is consumed. There is no thermodynamic equilibrium between isobutyl and *tert*-butyl radicals.

**Figure 3.** Representative results of isothermal annealing experiments at (**a**) 245 K and (**b**) 260 K in the γ-ray-irradiated isobutane hydrate ($D_2O$). Upper panel: Normalized total amount of both butyl radicals; Bottom panel: Changing amount of isobutyl (solid circles) and *tert*-butyl radicals (open circles).
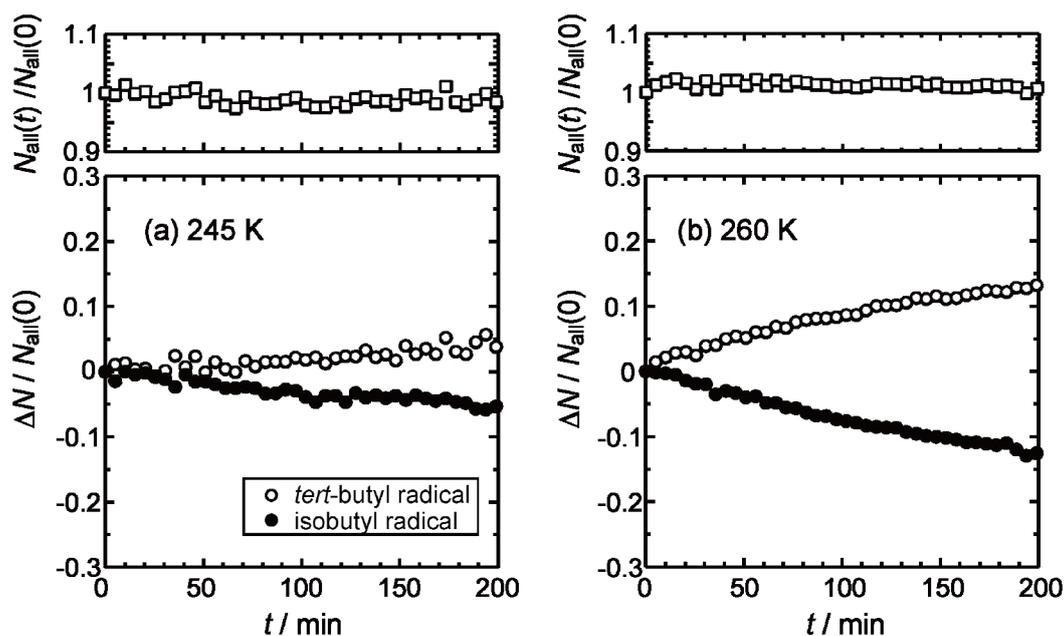


**Figure 4.** ESR spectrum after annealing at 260 K for 150 hours in the γ-ray-irradiated isobutane hydrate ($D_2O$).
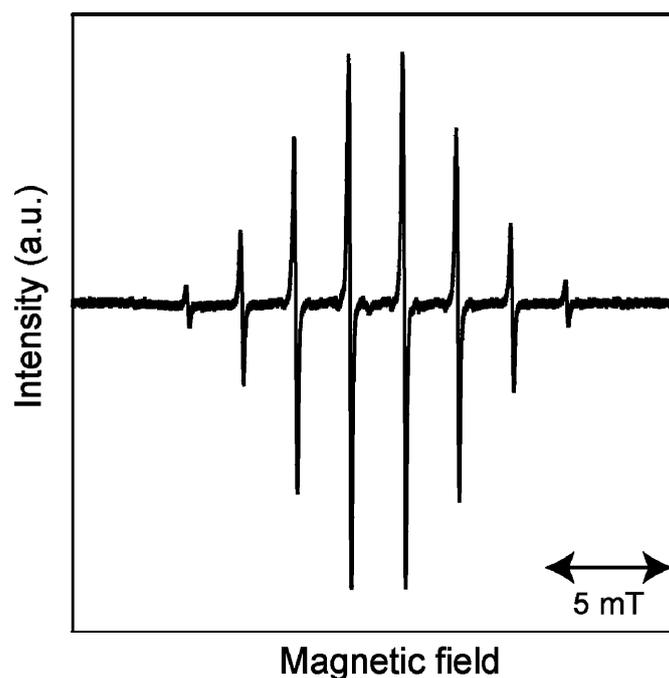
**Scheme 2.** Intermolecular hydrogen-picking through a hexagonal face of L-cages in the γ-ray-irradiated isobutane hydrate system.
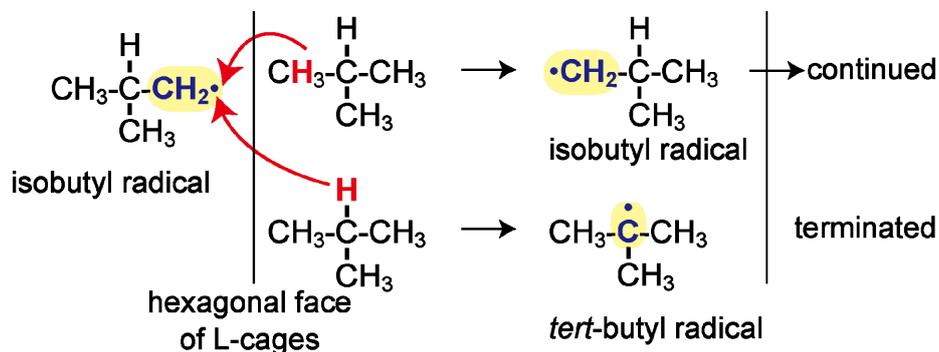


Assuming that hydrogen-picking from isobutyl to *tert*-butyl is followed by an irreversible first-order reaction, the amount of the isobutyl radical, $N_{isobutyl}(t)$, is expressed as:

$$N_{isobutyl}(t) = N_{isobutyl}(0)\exp(-kt) \tag{1}$$

where $k$ is the rate constant.

The amount of isobutyl radicals gives the exponential decay curves in annealing time as shown in Figure 3. Hydrogen-picking proceeds as a first-order reaction because the plot of log [$N_{isobutyl}(t)/N_{isobutyl}(0)$] against time ($t$) gives a straight line with a rate constant at the whole temperatures in the present study. The Arrhenius plot of the rate constant obtained from the fit of Equation (1) is shown in Figure 5.

**Figure 5.** Arrhenius plots of the decreasing rates for isobutyl and *n*-propyl radicals in the γ-ray-irradiated isobutane and propane hydrates prepared with $D_2O$, respectively.
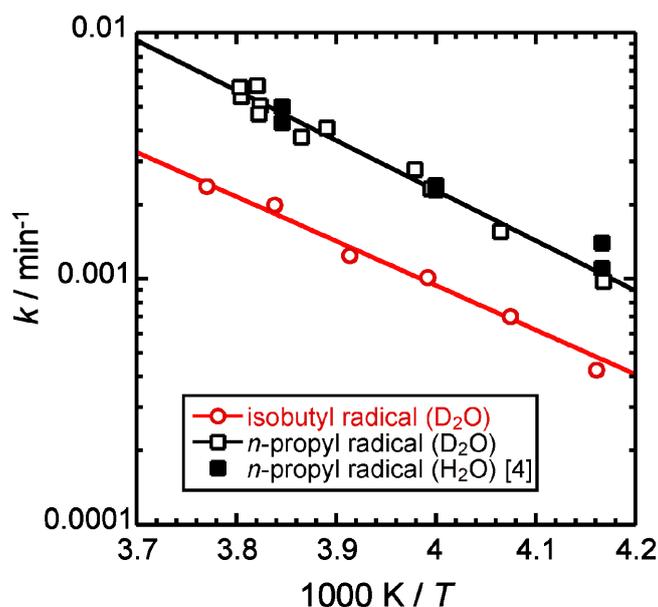


Based on the Arrhenius plot, the activation energy of the apparent transformation from isobutyl to *tert*-butyl radicals in the γ-ray-irradiated isobutane hydrate ($D_2O$) is estimated at 35 ± 3 kJ/mol. To directly compare activation energies in deuterated hydrates, the propane hydrate prepared with $D_2O$

was also investigated in a similar manner. The activation energy of the apparent transformation from *n*-propyl to isopropyl radicals in the γ-ray-irradiated propane hydrate ($D_2O$) is 39 ± 5 kJ/mol (open squares in Figure 5). The activation energy in the γ-ray-irradiated propane hydrate ($D_2O$) is similar to that (34 ± 3 kJ/mol, solid squares [4] in Figure 5) of the γ-ray-irradiated propane hydrate ($H_2O$). Comparing the activation energies between isobutane and propane hydrates ($D_2O$), the difference of the activation energies is within the estimated errors in spite of the different accessibility of β-hydrogen atom. These results imply that the potential barrier through the shared hexagonal face of adjacent L-cages is one of the most dominant factors in the hydrogen-picking process. The rate in the isobutane hydrate system slower than that of propane hydrate system may be caused by the accessibility of β-hydrogen atom, which mainly affects the frequent factor of the hydrogen-picking reaction.

## 3. Experimental Section

Isobutane hydrate was synthesized from isobutane (Takachiho Trading Co., Ltd., Shinjuku-ku, Tokyo, mole fraction purity 0.9999) and the deuterated water ($D_2O$) (Cambridge Isotope Laboratories, Inc., Andover, MA, USA, mole fraction purity 0.999). The pressure and temperature were kept at 0.14–0.17 MPa and 277.2 K. After excess $D_2O$ was removed from the mixture, the synthesized hydrate was quenched and taken from the high-pressure cell at 253 K. The hydrate samples were placed in plastic vials and kept at 77 K with liquid nitrogen. The samples were irradiated by γ-rays at a 6 kGy dose with a source of $^{60}Co$ at 77 K.

Several small pieces of isobutane hydrates with a diameter 2–4 mm were placed in the ESR sample tube at 77 K, and the liquid oxygen in the tube was carefully removed. The samples in the ESR tube were measured with a commercial X-band ESR spectrometer (JEOL, RE-1X) with 100 kHz field modulation of 0.1 mT. The sample temperature was controlled within an accuracy of ±0.5 K with a nitrogen gas flow unit system (JEOL, ES-DVT2). The power of the microwave was set at 0.01 mW for all ESR measurements and the signals of both butyl radicals observed in the present study are unsaturated at the power of 0.01 mW, because the saturation points of isobutyl and *tert*-butyl radicals at 120 K are located at 2 and 0.3 mW, respectively. In isothermal annealing experiments, the annealing and measurement temperature range was 240 K to 265 K. The equilibrium temperature of simple isobutane hydrate prepared with $H_2O$ at ambient pressure is approximately 272 K [12,13]. Generally, the equilibrium temperature of hydrate prepared with $D_2O$ is 2–4 K higher than that of $H_2O$ [14]. That is, the experimental temperatures in the present study are below the equilibrium temperature of simple isobutane hydrate ($D_2O$) at ambient pressure.

## 4. Conclusions

ESR spectra of the isobutyl and *tert*-butyl radicals in the γ-ray-irradiated isobutane hydrate were investigated. The isobutyl radical in an L-cage picks a hydrogen atom from the isobutane molecule in adjacent L-cages. The isobutyl and *tert*-butyl radicals are generated dependent on which hydrogen atom is picked by the original isobutyl radical while the original isobutyl radical is changed to an isobutane molecule. As a result, the isobutyl radical seems to be apparently transformed into the *tert*-butyl radical. The apparent transformation is an irreversible first-order reaction and the activation energy is estimated at 35 ± 3 kJ/mol.

## Acknowledgments

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