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Article



## Electron Spin Resonance Study on Hydrogen Abstraction Reactions of Radiation-Induced Radicals in Synthetic Silica Clathrate with Ethylamine and Ethanol

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Abstract: Intermolecular hydrogen abstraction reactions of radiation-induced radicals from guest molecules in adjacent cages, as observed in clathrate hydrates, were investigated in synthetic silica clathrate (clathrasil) with ethylamine and ethanol. ESR observation of the silica clathrate after  $\gamma$ -ray irradiation at 77 K confirmed the formation of 1-aminoethyl radical (CH<sub>3</sub>)(CH·)(NH<sub>2</sub>), 1-hydroxyethyl radical (CH<sub>3</sub>)(CH·)(OH), and hydrogen atom at 225 K. In isothermal annealing experiments, the amount of hydrogen atoms decreased at around 225 K following first-order kinetics, while the amount of 1-aminoethyl radical simultaneously increased by a similar amount. The amount of 1-hydroxyethyl radical decreased at temperatures around 280 K with first-order kinetics, while the amount of 1-aminoethyl radical increased at these temperatures. These results suggest that hydrogen abstraction reactions occur not only between the hydrogen atom and ethylamine at around 280 K. Furthermore, observation of 1-hydroxyethyl radical in silica clathrate with only a small amount of ethanol indicated that ESR measurements could be used to detect traces of guest molecules in clathrates if the radicals derived from them are stably stored in the cages.

**Keywords:** silica clathrate; hydrogen abstraction reaction; chibaite; electron spin resonance; alkylamine; ethanol

## 1. Introduction

Silica clathrates have SiO<sub>2</sub> framework structures of cage-like voids occupied by guest molecules such as hydrocarbons, and their structures are analogous to those of clathrate hydrates, with molecular compounds enclosed within cage-like structures of water molecules [1,2]. Each cage is occupied by a single guest molecule, such as methane or ethane. Melanophlogite, chibaite, and bosoite occur in nature [3–5]. Chibaite, which was first found in Chiba prefecture, Japan [4], has a structure composed of two different cages: a small one with twelve pentagonal faces and a large one with sixteen faces (twelve pentagonal and four hexagonal). The small cage stores methane, and the large one stores methane, ethane, propane, and isobutane among alkanes. Chibaite occurs in quartz veins, ranging in thickness from a few mm to 1 cm, in tuffaceous sandstone and mudstone [4], which has been irradiated by natural radiation, such as  $\beta$ - and  $\gamma$ -rays, from natural radioisotopes in



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Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). host rocks. This phenomenon indicates that radical species are formed by natural radiation and may be stored within the cages of silica clathrate if they are thermally stable.

To investigate radiation-induced radicals in chibaite, we observed electron spin resonance (ESR) spectra in chibaite at 120 K after  $\gamma$ -ray irradiation at 77 K [6]. The formation of five organic radicals along with hydrogen atoms was confirmed. Although the amounts of hydrogen atoms and organic radicals except *tert*-butyl radical decreased at temperatures around 240 K, the amount of *tert*-butyl radical increased at these temperatures. Based on this, Yokoyama et al. [6] proposed that intermolecular hydrogen abstraction reaction occurred between organic radicals (methyl, ethyl, *n*-propyl, and isopropyl radicals) and isobutane, similar to the hydrogen abstraction reactions observed in clathrate hydrates [7–9]. However, the individual physicochemical processes of these reactions in silica clathrates are not easily revealed using naturally found chibaite because multiple gaseous molecules are generally enclathrated.

To understand the processes of hydrogen abstraction reaction in silica clathrates, it is necessary to use a synthetic silica clathrate with one or two gaseous molecules. However, it is difficult to synthesize a silica clathrate with propane or isobutane because alkanes have almost no solubility in liquid water. Previously, following the paper by Gies and Marler [10], silica clathrate enclathrating isopropylamine instead of isobutane was synthesized from a mixed solution of orthosilicic acid and isopropylamine to investigate the behavior of radiation-induced radicals in silica clathrate with the same structure as chibaite [11]. After  $\gamma$ -ray irradiation at 77 K, hydrogen atom and 2-aminoprop-2-yl radical (CH<sub>3</sub>)<sub>2</sub>C·(NH<sub>2</sub>) were observed. Hydrogen atoms decayed at around 230 K following first-order kinetics. The decrease in the amount of hydrogen atoms was similar to the increase in the amount of 2-aminoprop-2-yl radical, suggesting that hydrogen atoms abstract hydrogen from isopropylamine in the silica clathrate. However, a hydrogen atom is small enough to migrate through the pentagonal or hexagonal faces of the cage to other cages [12]; this means that the observed hydrogen abstraction reaction occurs within a cage rather than between two adjacent cages.

In fact, a hydrogen abstraction reaction between radiation-induced radicals and guest molecules was not clearly observed in irradiated isopropylamine silica clathrate [11]. The large molecular size of isopropylamine and the amino group polarization prevented the radicals from rotating freely at low temperatures, leading to broad ESR signals from the radicals, even at 240 K. This means that it is difficult to properly distinguish two different radicals (2-aminoprop-2-yl radical and ( $CH_3$ )<sub>2</sub> $CH(NH \cdot)$ ) derived from isopropylamine at around 240 K [13]. This distinction is necessary if hydrogen abstraction reactions between radiation-induced radicals and guest molecules in silica clathrates are to be investigated.

In this study, to investigate the hydrogen abstraction reactions of  $\gamma$ -ray-induced radicals with guest molecules in silica clathrates, we focused on ethylamine. Ethylamine has a smaller molecular size than isopropylamine and can be transformed into two different radicals [13]. It is also enclathrated in silica clathrate with the same structure as chibaite [10]. Furthermore, to avoid the possibility that only one radical from ethylamine was observed, a solution of orthosilicic acids, ethylamine, and ethanol was used to synthesize ethylamine and ethanol binary silica clathrate. Ethanol can be transformed into 1-hydroxyethyl radical by  $\gamma$ -ray irradiation [14].

#### 2. Results and Discussion

The ESR spectra of the unirradiated and  $\gamma$ -irradiated samples of ethylamine and ethanol binary silica clathrate are shown in Figure 1. In the irradiated sample (Figure 1b), a doublet signal with hyperfine coupling constant *A* of 50.4 mT was observed at 120 K; because of the hyperfine coupling constant, this signal was assigned to hydrogen atoms [15].

Other ESR signals split into several peaks were also observed between 320 and 335 mT (near g = 2.0) in the center of the spectrum. These signals were attributed to radiation-induced radicals because no ESR signal was observed in the unirradiated silica clathrate (Figure 1a). In the irradiated sample measured at 330 K, the doublet signal due to the hydrogen atom disappeared, and the shaper peaks were observed in the center of the spectrum (Figure 1c).



(a)

**Figure 1.** ESR spectra of (**a**) unirradiated synthetic ethylamine and ethanol binary silica clathrate, and (**b**) a  $\gamma$ -irradiated sample observed at 120 K, and (**c**) at 330 K. Microwave power was 0.1 mW. Hydrogen atom (a doublet signal) and radiation-induced radicals (several peaks around 328 mT) were observed at 120 K after  $\gamma$ -irradiation, while only radiation-induced radicals around 328 mT were observed at 330 K. The signal intensity of the hydrogen atom was evaluated by adjusting the spectral simulation at the position indicated by the arrow.

Enlarged ESR spectra are shown in Figure 2. Relatively broad signals can be observed at 120 K (Figure 2a). It can also be seen that when the measurement temperature increases, multiple split sharp peaks appear at 330 K (Figure 2b). This change in the spectrum shape between 320 and 335 mT is dependent on measurement temperature and may be the result of the free rotation of the radicals at higher temperatures. This would mean that the rotation of the radicals derived from ethylamine is slow and/or hindered at low temperatures; the same phenomenon has been observed in isopropylamine silica clathrate [11]. The signals at 330 K in Figure 2b can be attributed to 1-aminoethyl radical  $(CH_3)(CH_2)(NH_2)$  from a comparison with the simulated spectrum in Figure 2c. The simulation reveals ESR parameters as follows: the g-value is 2.0027, and the hyperfine coupling constant A is 2.05 mT for hydrogen in CH<sub>3</sub>, 1.46 mT for hydrogen in CH, 0.52 mT for hydrogen in NH<sub>2</sub>, and 0.48 mT for nitrogen. These hyperfine splitting values are in good agreement with previously reported values (~2.2 mT for hydrogen in CH<sub>3</sub>, ~2.2 mT for hydrogen in CH,  $\leq$ 0.5 mT for hydrogen in NH<sub>2</sub>, and  $\leq$ 0.5 mT for nitrogen) observed in  $\gamma$ -irradiated solid ethylamine [13]. Although the other radicals, i.e., nitrogen-centered radical (CH<sub>3</sub>)CH<sub>2</sub>(NH·) from ethylamine and 1-hydroxyethyl radical  $(CH_3)(CH)(OH)$  from ethanol, would also be formed by  $\gamma$ -ray irradiation [13,14], these were not observed at 330 K in the irradiated silica clathrate (Figures 2d and 3d).



**Figure 2.** ESR spectra of the  $\gamma$ -irradiated synthetic ethylamine and ethanol binary silica clathrate: (a) at 120 K and (b) at 330 K. Receiver gain was the same in both spectra. Simulated spectra: (c) for 1-aminoethyl radical (CH<sub>3</sub>)(CH·)(NH<sub>2</sub>) and (d) for nitrogen-centered radical (CH<sub>3</sub>)CH<sub>2</sub>(NH·) [13].



**Figure 3.** (a) ESR spectrum observed at 225 K in the  $\gamma$ -irradiated synthetic ethylamine and ethanol binary silica clathrate. The spectrum in (b) is a linear combination of the spectra in (c,d). (c) The spectrum at 225 K after heating at 330 K. (d) A simulated spectrum of 1-hydroxyethyl radical. Receiver gain was the same for spectra in (a,c). A linear combination of spectra (c,d) was used for the evaluation of the signal intensities of the organic radicals in isothermal annealing experiments by adjusting the heights of the peaks, especially at the positions indicated by the arrows.

Although only 1-aminoethyl radical was observed at 330 K, in annealing experiments, the ESR spectra at 225 K changed gradually with annealing time. Figure 3a shows the first

ESR spectrum observed at 225 K in isothermal annealing experiments. To retrieve the ESR spectrum of the 1-aminoethyl radical at 225 K, the spectrum was measured at the same temperature (225 K) using the sample after heating at 330 K (Figure 3c) because no other radicals were observed at 330 K, as shown in Figure 2b. It should be noted that the vertical axis is nearly 1/3 because the amount of 1-aminoethyl radical increased after heating up to 330 K. A comparison between Figure 3a,c shows that the spectra were slightly different.

The spectrum in Figure 3b is a linear combination of the spectrum of 1-aminoethyl radical (Figure 3c) and the simulated spectrum of 1-hydroxyethyl radical (Figure 3d), assuming that 1-hydroxyethyl radical rotates freely in the silica clathrate at 225 K. The coefficients of the combination were determined by adjusting the heights of the peaks, especially where indicated by the arrows in Figure 3a,d. The simulation of 1-hydroxyethyl radical revealed the following ESR parameters: a g-value of 2.0027 and a hyperfine coupling constant A of 1.5 mT for hydrogen in CH and 2.23 mT for hydrogen in CH<sub>3</sub>. These hyperfine splitting values are in good agreement with previously reported values (1.5 mT for hydrogen in CH, 2.2 mT for hydrogen in CH<sub>3</sub>) observed in a UV-irradiated solid mixture of ethanol and hydrogen peroxide [14]. The similarity between the spectra in Figure 3a,b indicates that the irradiated sample contained both 1-aminoethyl radical and 1-hydroxyethyl radical at 225 K. Both radicals were observed in isothermal annealing experiments at 200, 210, 220, and 230 K. However, the nitrogen-centered radical, as shown in Figure 2d, could not be observed even at 200 K (the lowest temperature in isothermal annealing experiments). This might change to 1-aminoethyl radical or non-radical species under 200 K.

Raman observation of the silica clathrate showed that the peaks were mostly due to ethylamine (see Section 3), indicating that the synthetic silica clathrate included ethylamine together with a small amount of ethanol. In the isopropylamine silica clathrate, 1-hydroxyethyl radical was not obviously detected, even though the initial solution contained ethanol [11]. This suggests that isopropylamine is preferably enclathrated, rather than ethylamine, in the large cages of the silica clathrate.

The typical results of isothermal annealing experiments at 225 K are summarized in Figure 4. The integrated ESR intensity of 1-aminoethyl radical increased with annealing time, whereas that of 1-hydroxyethyl radical remained almost unchanged. These trends were observed between 200 K and 230 K. Additionally, the integrated ESR intensity of hydrogen atoms decayed around 225 K with a first-order kinetics model, as shown in Figure 5.

If dimerization of hydrogen atoms to form hydrogen molecules occurs in the silica clathrate, the decay should follow second-order kinetics. However, the hydrogen atom in this silica clathrate decays by following first-order kinetics, indicating that the dimerization is not the main decay process. The Arrhenius plots of the decay of hydrogen atoms are shown in Figure 6. The activation energy was evaluated to be  $66 \pm 1$  kJ/mol. The rate constant was not obtained for the results at 200 K because there was hardly any reduction in the intensity of the hydrogen atom.

Figure 7 shows the correlation between the amount of hydrogen atom and the amount of 1-aminoethyl radical (excluding the first three points) in isothermal annealing experiments at 225 K. Using least-square fitting, the slope was found to be  $-1.04 \pm 0.13$ . This meant that the decrease in the amount of hydrogen atoms was almost the same as the increase in the amount of 1-aminoethyl radical in annealing experiments after 50 min. This suggests that a hydrogen abstraction reaction between the hydrogen atom and ethylamine occurs in the silica clathrate, as follows:

$$H \cdot + (CH_3)CH_2(NH_2) \rightarrow H_2 + (CH_3)(CH \cdot)(NH_2)$$

This reaction is a pseudo-first-order reaction because the amount of hydrogen atoms is much smaller than that of ethylamine. This is confirmed by the first-order decay kinetics shown in Figure 5. A similar reaction between hydrogen atom and isopropylamine has been observed in  $\gamma$ -irradiated isopropylamine silica clathrate with almost the same activation energy,  $65 \pm 4 \text{ kJ/mol}$  [11]. Furthermore, similar levels of activation energy have been obtained in simulated hydrogen abstraction reactions between alkylamine and hydrogen atoms [16]. This suggests that a hydrogen abstraction reaction will generally occur between hydrogen atoms and alkylamines in alkylamine silica clathrates. In chibaite, most hydrogen atoms decay without reacting with hydrocarbons [6]. The main decay mechanism of hydrogen atoms is different in alkylamine silica clathrates and chibaite.



**Figure 4.** Variation in the integrated ESR intensity of the organic radicals and hydrogen atom in isothermal annealing experiments at 225 K. Solid squares represent 1-aminoethyl radical, solid circles represent 1-hydroxyethyl radical, and solid diamonds represent hydrogen atom.



Figure 5. Decay in the ESR intensity of hydrogen atoms between 200 K and 230 K.



Figure 6. Arrhenius plot of the decay of hydrogen atom.



**Figure 7.** The correlation between the amount of hydrogen atom and the amount of 1-aminoethyl radical in isothermal annealing experiments at 225 K.

In contrast, the intensity of 1-aminoethyl radical increased drastically within the first 50 min of annealing time in comparison with the intensity change in hydrogen atoms, as shown in Figure 4. Although a similar trend was observed at 230 K, the drastic increase in 1-aminoethyl radical was observed within the longer duration of the early part of annealing time, at temperatures less than 220 K. Because two radicals and hydrogen atom were observed using ESR, and because only the intensity of 1-aminoethyl radical changed greatly, it could be that other reactive species which are insensitive to ESR measurements are involved in this reaction. The reason for this relatively faster reaction, compared with the hydrogen abstraction reaction by hydrogen atoms, remains unknown at this time and must be investigated in future works.

Further isothermal annealing experiments at 270, 280, and 290 K showed that the 1-hydroxyethyl radical decayed and the 1-aminoethyl radical formed. The decay of the 1-hydroxyethyl radical was evaluated, as shown in Figure 8. This also followed first-order kinetics, and its activation energy was  $53.1 \pm 0.6$  kJ/mol, as estimated from the Arrhenius

plot shown in Figure 9. In fact, the increase in the amount of 1-aminoethyl radical was almost twice the decrease in the amount of 1-hydroxyethyl radical. Although the reason why the amount of 1-aminoethyl radical increases around 280 K is not yet fully understood, it may be because the hydrogen abstraction reaction of the 1-hydroxyethyl radical from ethylamine occurs in the silica clathrate so that

 $(CH_3)(CH \cdot)(OH) + (CH_3)CH_2(NH_2) \rightarrow (CH_3)CH_2(OH) + (CH_3)(CH \cdot)(NH_2)$ 



Figure 8. Decay in the ESR intensity of 1-hydroxyethyl radical between 270 K and 290 K.



Figure 9. Arrhenius plot of the decay of 1-hydroxyethyl radical.

The features of our obtained results for the  $\gamma$ -irradiated ethylamine and ethanol binary silica clathrate are summarized in Table 1, together with previously obtained results for the other silica clathrates. This study reveals that intermolecular hydrogen abstraction reactions occur not only between hydrogen atoms and ethylamine but also probably between 1-hydroxyethyl radical and ethylamine. The latter case suggests that the radicals interact with guest molecules in adjacent cages, even in silica-framework clathrates. This supports the previous proposal of intermolecular hydrogen abstraction reactions between alkyl radicals and isobutane in chibaite [6]. Furthermore, observation of 1-hydroxyethyl radical in the

silica clathrate with only a small amount of ethanol indicates that ESR measurements can be used to detect traces of guest molecules in clathrates if the radicals derived from them are stably stored in the cages.

Sample	Ethylamine and ethanol binary silica clathrate (synthetic) [this work]	Isopropylamine silica clathrate (synthetic) [11]	Chibaite (natural) [6]
Guest molecules	Ethylamine, ethanol	Isopropylamine	Methane, ethane, propane, isobutane
Decay of hydrogen atom	Pseudo-first-order reaction	Pseudo-first-order reaction	Not first-order reaction
Hydrogen abstraction reaction	<ul> <li>(1) Between hydrogen atoms and ethylamine</li> <li>(2) Between</li> <li>1-hydroxyethyl radical and ethylamine</li> </ul>	Between hydrogen atoms and isopropylamine	Between organic radicals and isobutane

Table 1. Features of observations of radicals in silica clathrates.

#### 3. Materials and Methods

The synthetic procedure followed Gunawardane et al. [17] and Tamai et al. [11]. Orthosilicic acid solution (0.50 mol/L) was prepared by hydrolyzing tetraethyl orthosilicate (TEOS, Fujifilm Wako Pure Chemical Corp., Osaka, Japan) with ultrapure water so that

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

Ethylamine aqueous solution (6.1 mol/L) was prepared by diluting ethylamine (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) with ultrapure water. These two solutions were mixed with a 10:3 volume ratio of orthosilicic acid solution to ethylamine solution. The mixed solution was sealed in a PTFE inner container, and the container was set in a stainless pressure vessel. The vessel was then stored at 190 °C for 2 months. The storage temperature was higher, and the duration was longer in comparison with the synthetic procedure of isopropylamine silica clathrate [11] because a much smaller amount of ethylamine silica clathrate was synthesized at the same condition (180 °C for 1.5 months) in the preliminary experiments.

After the vessel was opened, synthetic particles with ~0.5 mm in diameter were collected (Figure 10). The particles had a euhedral shape, specifically, that of a regular octahedron. This suggested that the synthetic crystal has a cubic system similar to that of chibaite. Several pieces of the synthetic ethylamine and ethanol binary silica clathrate were ground in a mortar, and its powder X-ray diffraction (PXRD) was measured using Ultima IV (Rigaku Holdings Corp., Tokyo, Japan) under the following conditions: scan speed 1 deg/min, scan step 0.01 deg, and wavelength 0.15412 nm. The PXRD pattern (Figure 11) showed that the synthetic crystal had the same crystal structure as chibaite [4,18].



Figure 10. Photo of synthetic ethylamine and ethanol binary silica clathrate.



**Figure 11.** Powder X-ray diffraction (PXRD) pattern of the synthetic ethylamine and ethanol binary silica clathrate in black. A pattern of the synthetic isopropylamine silica clathrate is also shown in blue [11].

Raman spectra of the synthetic ethylamine and ethanol binary silica clathrate together with ethylamine and ethanol were measured using RAMANview (Nanophoton, in Bruker Corp., Osaka, Japan). These spectra in a range of 2550–3600 cm<sup>-1</sup> are shown in Figure 12. Baseline correction was performed upon the spectrum of the silica clathrate, and the intensities in all spectra were normalized. Raman spectra, especially peak ratios in the range of 2800–3400 cm<sup>-1</sup>, indicated that ethylamine was mainly enclathrated in the synthetic samples. As discussed above, observation of 1-hydroxyethyl radical in the silica clathrate supports the suggestion that ethanol should be enclathrated. We therefore concluded that the silica clathrate was successfully synthesized, and that it enclathrated ethylamine and a small amount of ethanol. This conclusion is supported by the results of a previous work [10] in which a small amount of methanol was enclathrated in silica clathrate when the orthosilicic acid solution was prepared with tetramethyl orthosilicate (TMOS).



**Figure 12.** Raman spectra of the synthetic ethylamine and ethanol binary silica clathrate (**upper**) together with ethylamine (**middle**) and ethanol (**lower**). The spectrum of the silica clathrate around  $2900 \text{ cm}^{-1}$  and around  $3350 \text{ cm}^{-1}$  is close to that of ethylamine.

The synthetic particles were divided into two parts. One part was placed in plastic vials, irradiated by  $\gamma$ -ray at 77 K, and divided into four ESR glass tubes at 77 K for ESR measurement. The other part was first divided into five ESR glass tubes, sealed, and irradiated by  $\gamma$ -ray at 77 K to avoid sample loss during the procedures. Both of the plastic vials and the five sample tubes were immersed in liquid nitrogen and irradiated at 77 K with 5 kGy  $\gamma$ -rays from a <sup>60</sup>Co source at the Research Laboratory for Quantum Beam Science, Institute of Scientific and Industrial Research, Osaka University. The samples were measured using X-band ESR spectrometry (JES-FA200, JEOL Ltd., Tokyo, Japan). The measurement temperature was controlled using a nitrogen gas flow unit (ES-DVT4, JEOL Ltd., Tokyo, Japan). In most ESR measurements (except hydrogen atom observation), the microwave power was 0.1 mW, the time constant was 0.1 sec, and the sweep time was 8 min. In the evaluation of the hydrogen atom, the microwave power was 0.001 mW, the time constant was 0.3 sec, and the sweep time was 4 min. In all the measurements, the number of scans was 1, and the 100 kHz field modulation width was 0.02 mT. The irradiated ESR tubes were partially heated to eliminate any ESR signals arising from quartz glass. No significant differences in ESR spectra were observed at 120 K for all samples.

One sample was measured at various temperatures between 120 K and 330 K. Isothermal annealing experiments for organic radicals and hydrogen atoms were performed using the other eight samples at 200, 210, 220, 225, 230, 270, 280, and 290 K for up to 360 min. The ESR spectrum was measured at each temperature at 15 min after annealing. Subsequently, ESR spectra were measured at 15 min intervals without pulling out the sample tube from the cavity.

The integrated signal intensities of the organic radicals and hydrogen atoms were evaluated using spectrum simulation. Following Yokoyama et al. [6], the integrated signal intensities of the observed signal were evaluated from a double integration of the simulated spectra after adjusting the signal intensities of the simulated spectra to those of the observed spectra. In the case of the hydrogen atom, the simulated spectra were adjusted at the position indicated by the arrows in Figure 1, then integrated twice and doubled to account for another peak near 351 mT. In the case of the 1-aminoethyl radical  $(CH_3)(CH \cdot)(NH_2)$ , the amount of the radical was evaluated by matching the simulated spectra to the observed ones at 330 K (Figure 2b,c). Subsequently, the ESR spectra were measured at the annealing temperatures using the sample after heating at 330 K and adjusted with the spectra observed in isothermal annealing at the positions indicated by the arrows (Figure 3a,c) to obtain the amount of the radical in isothermal annealing experiments. For the 1-hydroxyethyl radical, the amount of the radical was evaluated by integrating the simulated spectra (Figure 3d) twice after a linear combination of spectra of 1-aminoethyl radical and 1hydroxyethyl radical was performed to adjust the heights of the peaks, especially at the positions indicated by the arrows in Figure 3. Isotropic simulation software provided by JEOL was used to simulate the ESR spectra.

#### 4. Conclusions

To investigate hydrogen abstraction reactions of radiation-induced radicals in silica clathrates, ethylamine, and ethanol binary silica clathrate was synthesized from a solution of orthosilicic acids, ethylamine, and ethanol. ESR observation of the silica clathrate irradiated by  $\gamma$ -rays at 77 K revealed the formation of 1-aminoethyl radical, 1-hydroxyethyl radical, and hydrogen atom. The amount of hydrogen atom decreased at temperatures around 225 K with first-order kinetics, while a similar amount of 1-aminoethyl radical increased simultaneously. In addition, the amount of 1-hydroxyethyl radical decreased at temperatures around 280 K with first-order kinetics, while the amount of 1-aminoethyl radical increased gradually at these temperatures. These results suggest that hydrogen abstraction reactions occur not only between hydrogen atom and ethylamine at around 225 K but may also occur between 1-hydroxyethyl radical and ethylamine at around 280 K. Understanding these physicochemical processes of radicals in silica clathrates will be worthwhile not only in physical chemistry of radical species but also in ESR dating for natural silica clathrates using radical species formed by natural radiation. Furthermore, observation of 1-hydroxyethyl radical in the silica clathrate with only a small amount of ethanol indicated that ESR measurements could be used to detect traces of guest molecules in clathrates if the radicals derived from them are stably stored in the cages.

**Author Contributions:** Conceptualization, S.I. and A.T.; methodology, S.I. and A.T.; validation, S.I. and A.T.; formal analysis, S.I., K.M., and K.D.; investigation, S.I., K.M., and K.D.; resources, A.T. and S.T.; data curation, S.I., K.M., and K.D.; writing—original draft preparation, S.I.; writing—review and editing, A.T. and S.T.; visualization, S.I. and K.M.; supervision, A.T.; project administration, A.T.; funding acquisition, S.I., A.T. and S.T. All authors have read and agreed to the published version of the manuscript.

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