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Thermal stability of methyl radical in γ-ray irradiated methane hydrate under different pressure from 0.003 to 1 MPa

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Abstract

Synthetic methane hydrate irradiated by γ-rays at 77 K was measured by electron spin resonance (ESR) to investigate the thermal stability of the methyl radical under different pressures from 0.003 to 1 MPa. The decay of the radical was composed of at least two decay processes. The first decay process was observed within an annealing time of 150 min and the second one on a longer time scale. The decay constant for the second process was estimated using a second order decay model. An Arrhenius plot gave almost the same activation energy at lower temperature under each pressure, and it was estimated to be $20.0 \pm 2.7\,\mathrm{kJ/mol}$.

Keywords: Methane hydrate; Methyl radical; Electron spin resonance (ESR); Pressure; Thermal stability

1. Introduction

Methane hydrate, a clathrate compound of water molecules surrounding a methane molecule, is found in permafrost and deep-sea sediment (e.g. Max, 2000). Natural methane hydrate will be exposed to radiation from α-, β- and γ-rays emitted from natural radioisotopes like ^{40}K and isotopes in the U and Th decay series in sediment.

In our previous study, synthetic methane hydrate irradiated by γ-rays at 77 K was measured by electron spin resonance (ESR) to identify radiation-induced radicals and reveal their thermal stability at atmospheric pressure (Takeya et al., 2004). The methyl radical was the most thermally stable and decayed at around 200 K, close to the dissociation temperature of methane hydrate at atmospheric pressure (Sloan, 1998). Takeya et al. (2005) suggested that decay of the radical might be associated with dissociation of methane hydrate because the activation energy of the radical decay was close to the enthalpy change in dissociation of the hydrate to water ice and methane gas. However, additional experiments showed that the methyl radical decayed even at 210 K under 10 MPa conditions under which methane hydrate is stable (Tani et al., 2005), implying that the decay, at least under high pressure, was not caused by dissociation of methane hydrate.

In this study, we performed annealing experiments on the γ-ray induced methyl radical in methane hydrate especially at low pressures of 0.003 and 0.01 MPa as well as at atmospheric pressure (0.1 MPa) and high pressure of 1 MPa to investigate the thermal stability.

2. Experimental

Methane hydrate was synthesized at 277 K by the mixing of methane gas (99.95%) and degassed ultrapure water in a high-pressure vessel (Fig. 1). The pressure was initially about 10 MPa. Additional methane gas was provided twice into the vessel up to 10 MPa because the pressure was decreased by hydrate formation. The sample was kept at 10 MPa for several hours to reduce the residual water on/between the sample grains by forming additional methane hydrate, after the water was evacuated from the vessel using high-pressure methane gas. The sample was obtained at 243 K and atmospheric pressure in low-temperature chamber. Small pieces of 1–2 mm in diameter were collected using metal sieves and kept in plastic vials,

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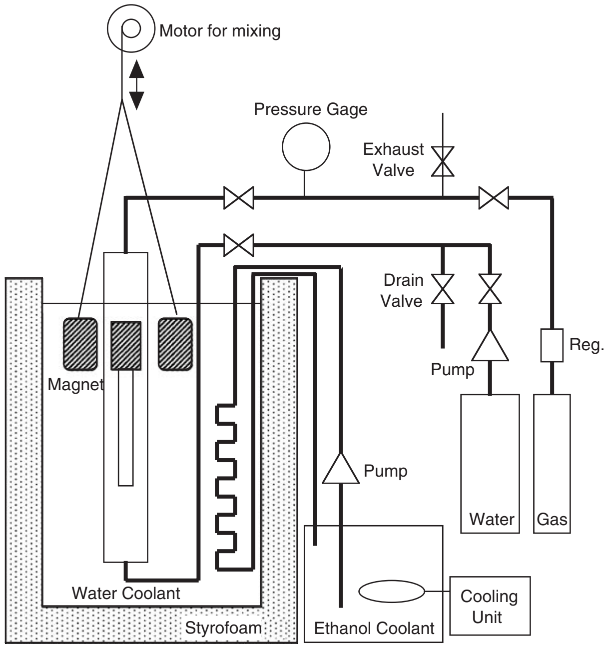

Fig. 1. Schematic illustration of the system used in synthesizing methane hydrate.

called cryovials. The vials were immediately immersed in liquid nitrogen. The dissociation is likely to be negligible during this process because of the low dissociation rate of methane hydrate (Stern et al., 2003). Irradiation was performed at 77 K using a ^{60}Co γ-ray source. The dose was about 10 kGy.

The sample was measured at 120 K using a commercial X-band ESR spectrometer (JEOL RE-1X) with 100 kHz field modulation of 0.1 mT and a nitrogen gas flow unit system (JEOL ES-DVT2). The microwave power was 1 mW.

The nitrogen gas flow unit system for ESR was also used for isothermal annealing experiments at 0.003, 0.01 and 0.1 MPa. The annealing procedure for pressures of 0.003 and 0.01 MPa was (1) immersing the ESR sample tube in liquid nitrogen, (2) reducing pressure to 0.003 or 0.01 MPa at 77 K using a vacuum pump with a constant-pressure regulator, (3) setting the sample tube in the thermostatic cavity with the nitrogen gas flow unit, (4) keeping it there for 30 min, (5) immersing it in liquid nitrogen and (6) opening the valve to 0.1 MPa. For the annealing at 0.1 MPa, steps (1), (3)–(5) above were used.

The isothermal annealing experiments at 1 MPa were performed using homemade apparatus (Fig. 2) by (1) setting the sample in the high-pressure vessel immersed in liquid nitrogen, (2) applying pressure to 1 MPa at 77 K using helium gas, (3) immersing the vessel in a thermostatic coolant of ethanol and dry ice mixture, (4) keeping it there for 30 min, (5) immersing it in liquid nitrogen and (6) reducing the pressure to 0.1 MPa. During step (3), the inner pressure was controlled by opening the exhaust valve to prevent the pressure from increasing by thermal expansion of inner gas. The annealing temperature in the coolant of ethanol and dry ice was monitored by a Pt thermometer. The sample was measured by ESR before any heating, and after every 30 min heating, in all experiments.

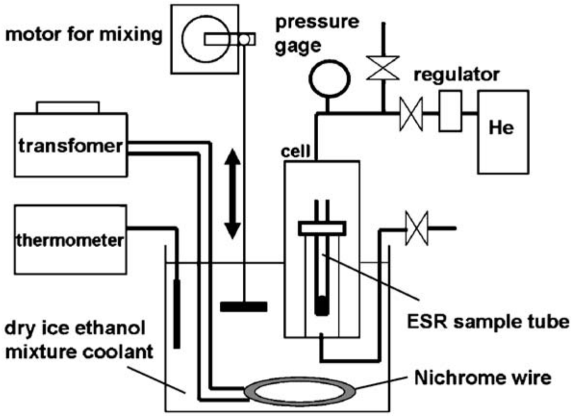

Fig. 2. Schematic illustration of the annealing system at high pressure.

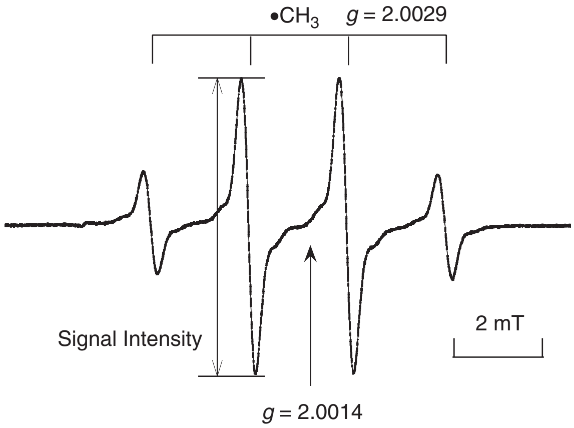

Fig. 3. ESR powder spectrum of the methyl radical at 120 K in γ-ray irradiated methane hydrate. No signal was observed at $g = 2.0014$.

3. Results and discussion

The methyl radical was observed at 120 K and the powder spectrum is shown in Fig. 3. The quartet signal split with the intensity ratio of 1:3:3:1 is due to hyperfine interaction between electron spin and nuclear spin of three equivalent hydrogen atoms in the radical. The peak-to-peak height at the second signal (Fig. 3) was evaluated as the signal intensity in this paper because the difference of the spectrum shapes for all measurements was negligible. Although an unidentified signal at $g = 2.0014$ was reported by Takeya et al. (2004), it was not observed in this sample. This signal may be caused by some impurities.

Fig. 4 shows the decay of the normalized signal intensity (I/I_0) under different pressures of 0.003, 0.01, 0.1 and 1 MPa. The decay curves at 200 K show that the intensity of the methyl radical decreased more quickly at lower pressure.

The inverse of the signal intensity (I_0/I) was plotted in Fig. 5 because Takeya et al. (2004) mentioned that the radical decayed according to a second order decay model through the dimerization process to form ethane (see Appendix). Fig. 5 indicates that the decay process was not simple and composed