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Radiation-induced radical reactions at different temperatures in CO_2 hydrate

Motoi Oshima[1*], Atsushi Tani[1], Katsuhisa Kitano[2], Takeshi Sugahara[3], Kazunari Ohgaki[3]

[1]Science, Osaka Univ., [2]Engineering, Osaka Univ., [3]Engineering Science, Osaka Univ.

CO_2 hydrate is one of clathrate hydrates, which is composed of water molecules encaging CO_2 molecules, and stable at atmospheric pressure below 220 K. It has been suggested that CO_2 hydrate exists in Okinawa Trough (Konno et al., 2006) and Martian surface (Max and Stephen, 2001). Natural CO_2 hydrate will have been constantly irradiated by natural radiation from sediments, and radicals will have been induced by the radiation and reacted in CO_2 hydrate.

In the case of CH_4 hydrate, methyl radicals are mainly formed by gamma-rays at 77 K (Takeya et al., 2004). Since they are not stable over 200 K, no radicals remain and radical reactions occur in CH_4 hydrate. Methanol, formaldehyde, and ethane are main products in these reactions (Ishikawa et al., 2007; Tani et al., 2010). In the case of CO_2 hydrate, HOCO radicals were observed after gamma-ray irradiation at 77 K and decayed over 130 K. Analysis of the dissociated water by ion chromatography showed that a little amount of formic acid was formed (Tani et al., 2008). These results suggest that main radical reaction may change if gas hydrate is irradiated at different temperatures because radiation-induced radicals become stable below a certain temperature.

In this study, we investigated the compounds formed by radical reactions in CO_2 hydrate after gamma-irradiation at 77, 195, and 273 K. The thermal stabilities of the induced-radicals have been investigated by electron spin resonance (ESR). The dissociated water of irradiated CO_2 hydrate has been measured by ion chromatography. HOCO radicals and H atom are observed at 120 K in irradiated CO_2 hydrate. HOCO radicals disappeared within 20 min at 195 K, though 80% of HOCO radicals remained after 6 hours at 120 K. H atoms were not observed at 130 K. As well as formic acid, oxalic acid has been newly observed in the dissociation water. The amounts of formic acid and oxalic acid were changed by temperature history of radical. Especially, the amount of oxalic acid increased with temperature. They may be partially caused by the decay processes of the radicals in CO_2 hydrate.

Keywords: CO_2 hydrate, Radicals, Carboxylic acid, Radiation, Electron spin resonance (ESR), Ion chromatography