

POSSIBILITY OF CARBOXYLIC ACID FORMATION BY RADIOLYSIS OF CO₂ HYDRATE ON MARS.

M. Oshima¹, A. Tani¹, K. Kitano², T. Sugahara³ and K. Ohgaki³, ¹Department of Earth and Space Science, Graduate School of Science, Osaka University, ²Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University and ³Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Osaka, Japan (moto-o@astroboy.ess.sci.osaka-u.ac.jp).

Introduction: To look for evidence of life on Mars, explorations of organic matters are important. There are some possibilities of the formations of organic matters on Mars; for example, by biological activity and by radiolysis and photolysis of mixtures of icy materials. Investigating the reaction products and their quantities by radiolysis and photolysis of the mixtures can distinguish organic matters by biological activity from ones by radiolysis and photolysis.

They have been reported that H₂O ice and dry ice exist on Martian polar caps and below subsurface, and the dry ice forms on the surface of polar H₂O ice. [e.g. 1,2]. The production reactions of organic materials will less occur in the mixture of H₂O ice and dry ice by radiolysis and photolysis, because the reactions occur only between contact surface of H₂O ice and dry ice. On the other hand, it is suggested that gas hydrates would exist on Martian surface, based on the discussion of temperature and pressure conditions on Mars [3]. Gas hydrates are crystalline inclusion-compounds, which are composed of hydrogen bonded water molecules encaging gas molecules (e.g. CH₄, CO₂). Most of them are stable at high pressures and/or low temperatures. For example, CO₂ hydrate is stable below 220 K at 0.1 MP [4]. Average temperature of Martian surface is about 210 K, the Martian atmosphere consists of about 95% CO₂ and the average atmospheric pressure is about 0.56 kPa [e.g. 5]. In Martian condition, it is suggested that CO₂ hydrate is formed in about 5 m below the ground and on the polar caps in winter [3,6]. Since water ice exists on Martian surface [e.g. 2], the environment on the Martian surface should be enough to form CO₂ hydrate.

In this case, Martian CO₂ hydrate should be irradiated by natural radiation from radioisotopes in sediments as well as cosmic rays, which may cause radical formation in CO₂ hydrate. Radiation-induced radicals in CH₄ hydrate have been investigated by electron spin resonance measurement [7,8]. Methyl radical (CH₃·) is mainly formed by gamma-ray irradiation at 77 K in CH₄ hydrate. However, it is not stable above 180 K at 0.1 MPa. Since natural CH₄ hydrate is found in deep-sea sediments and permafrost region on the Earth, no methyl radical remains and radical reactions occur in natural CH₄ hydrate. Main products in these reactions are ethane, methanol, and formaldehyde [9,10]. The results indicate that larger molecules are

formed from methane and water in methane hydrate by irradiation. Radiation-induced radicals in CO₂ hydrate have been investigated [11]. Carboxyl radical (HOCO·), hydrogen atom (H·) and hydroxyl radical (OH·) are formed by gamma-ray irradiation at 77 K in CO₂ hydrate. However, H· and OH· are not stable above 120 K at 0.1 MPa, and HOCO· quickly disappears at 180 K.

In this study, to investigate the reaction products of induced radicals in CO₂ hydrate, we analyzed the aqueous solution after dissociation of CO₂ hydrates irradiated at 195 K by ion chromatography.

Experimental: We used a high-pressure vessel based on the system by Tani et al. [8]. Totally about 2.5 MPa of CO₂ gas (1.5×10^{-2} mol of CO₂) was used to form CO₂ hydrate. After CO₂ gas was supplied up to ~2.0 MPa, the vessel was stored at ~193 K in a deep freezer.

The synthetic CO₂ hydrate samples were irradiated through the high-pressure vessel using a ⁶⁰Co source with a 6 kGy dose at 195 K.

The irradiated CO₂ hydrates and unirradiated ones were dissociated at room temperature by decreasing pressure in the vessel. Samples of the aqueous solution after dissociation of irradiated/unirradiated CO₂ hydrate were analyzed by means of ion chromatography (SHIMAZU, Prominence HIC-SP) using the anion-exchange column (Shim-pack IC-SA3), the eluent (sodium carbonate aqueous solution, 3.6 mM), and the electric conductance detector (SHIMAZU, CDD-10ASP).

Results: Ion chromatograms of the aqueous solution after dissociation of CO₂ hydrate irradiated at 195 K, unirradiated CO₂ hydrate, and standard aqueous solution of formic acid (HCOOH, 10 μM) and oxalic acid ((COOH)₂, 10 μM) are shown in Figure.

From the comparison of these retention times, formic acid (about 6.8 min) and oxalic acid (about 28.3 min) are observed in the aqueous solution from the irradiated sample, while they are not in the unirradiated sample. The peaks at 8.8, 16.3, and 23.6 min are due to impurities. From a data book (Shimadzu data book of ion chromatograph, 2008.), the intense peak at 10.2 min is caused by carbonate ion that could not be removed by a deaeration unit.

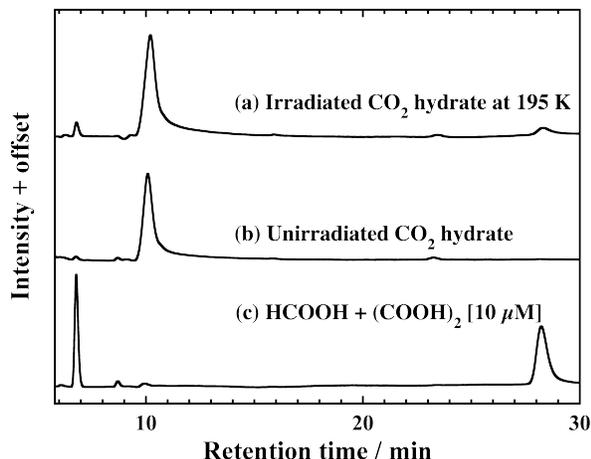
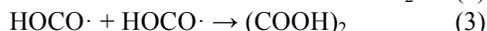
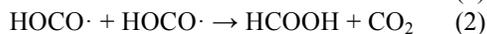


Figure. Chromatograms of the three aqueous solutions from (a) CO₂ hydrate irradiated at 195 K, (b) unirradiated CO₂ hydrate, and (c) a standard for formic acid (10 μM, 6.8 min) and oxalic acid (10 μM, 28.3 min).

Discussion: From the previous study [11], HOCO·, H· and OH· are formed by in irradiated CO₂ hydrate, and all the radicals quickly disappear at 195 K and 0.1 MPa. It suggested that some radical reactions occur in CO₂ hydrate, because CO₂ hydrate is stable below 220 K at 0.1 MPa. The observed formic acid and oxalic acid will be formed by reactions of these radicals. These results suggest that the following radical reactions may occur in irradiated CO₂ hydrate, once we focus on the decay of HOCO· which may be trapped in a water cage.



The reaction (1) is caused by self-diffusion of H· between the cages. The reaction (2) is due to hydrogen abstraction reaction from one HOCO· to the other in an adjacent cage. Since hydrogen transfer between gas hydrate cages was observed in hydrocarbon gas hydrates like propane [12], the reaction (2) may occur in this system as well. The reaction (3) is a dimerization reaction of HOCO·. If the reaction (3) occurs in CO₂ hydrate, oxalic acid might lie astride two cages where hydrogen bonds are partially broken, because it cannot be trapped in one hydrate cage due to its large molecular size. The possibility that two HOCO· are simultaneously induced in adjacent cages would be very low, because there is more CO₂ molecules than HOCO· in CO₂ hydrate. If the reactions (2) and (3) occur in CO₂ hydrate, it is necessary that there are two HOCO· in adjacent cages. Based on the study of propane hydrate [12], it is speculated that hydrogen atom transfers from one HOCO· to CO₂ molecule in an adjacent cage. Therefore, one HOCO· may adjoin to other, and react.

In Martian atmosphere, carboxylic acids will be hardly formed, because the concentration of H₂O is very low. If CO₂ hydrate is on Mars, the induced radicals were not unstable, and formic acid and oxalic acid will be formed in CO₂ hydrate and accumulated on Martian polar caps and below subsurface.

References:

- [1] Smith D. E. et al. (2001) *J. Geophys. Res-Planet*, 106, 23689-23722. [2] Boynton W. V. et al. (2002) *Science*, 297, 81-85. [3] Max and Clifford (2001) *Geophys. Res. Lett.*, 28, 1787-1790. [4] Sloan and Koh (2008), *Clathrate hydrates of natural gases, third edition*. CRC Press, Boca Raton. [5] Kieffer et al. (1993), *Mars*, University of Arizona Press, Tucson. [6] Trainer et al. (2010) *Icarus*, 206, 707-715. [7] Takeya et al., (2004) *Jpn. J. Appl. Phys.*, 43, 353-357. [8] Tani et al. (2006) *Radiat. Meas.*, 41, 1040-1044. [9] Ishikawa et al. (2007) *Jpn. J. Appl. Phys.*, 46, 455-460. [10] Tani et al. (2011) *In: Proceedings of the 7th International Conference on Gas Hydrates, Edinburgh*. [11] Oshima et al., submitted. [12] Ohgaki et al. (2008) *Phys. Chem. Chem. Phys.*, 10, 80-82.