Mechanism of Synergistic Methyl Radical Formation in CH4+CO2 Mixed Gas Hydrates Systems

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Clathrate hydrates are crystalline inclusion compounds, where hydrogen-bonded water molecules (host molecules) encage guest molecules – such as methane and CO2. The interactions between the hydrate cages and the guest molecules are usually through weak van der Waals forces. Using electron spin resonance (ESR) spectroscopy, our group has measured the thermal stabilities of methyl radical induced with gamma-ray in pure CH4 and CH4+CO2 mixed hydrates. Gamma-radiation has enough energy to transfer electron from water or methane molecule to CO2 molecule. Considering the low stabilities of the species formed after electron transfer, their decomposition produces an additional reaction chain, generating stable radicals. To investigate the mechanism of methyl radical formation in mixed hydrate systems, the results on gamma-ray and UV irradiated CH4+CO2 mixed hydrates were compared. Additionally, the same experiments with mixed hydrates prepared with D2O only under gamma-ray irradiation were conducted. From the analysis of the gamma-ray-irradiated mixed hydrates prepared with D2O, a dominant synergistic mechanism in radical formation was suggested. Moreover, the results show different radical formation efficiencies dependent on the irradiation sources, which contributes to the mechanism suggested. The methyl radical has an important role in combustion chemistry, in atmospheric chemistry and in planetary science – such as an oxidant and reducing agent.