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Electronic Supplementary Information for

Reactions of HOCO Radicals through Hydrogen-Atom Hopping Utilizing Clathrate Hydrates as an Observational Matrix

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I. Information of induced radicals on ESR measurements

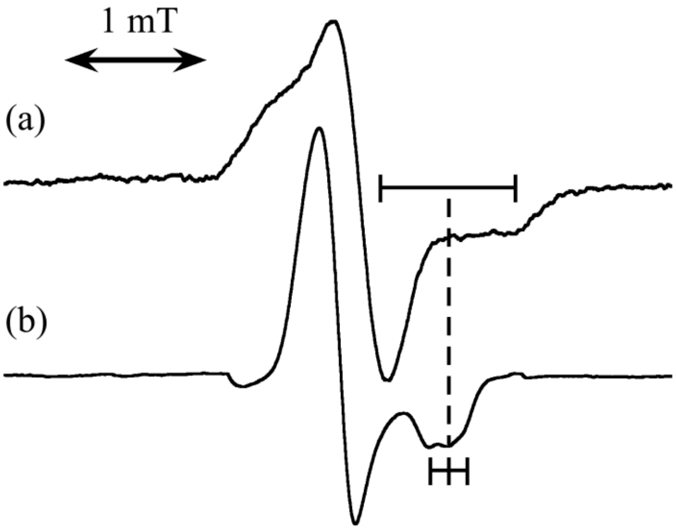

Figure S1. ESR spectra magnified at *Signal (i)* in Fig. 1, recorded at 77 K after annealing at 170 K for 15 min. (a) Irradiated CO_2 hydrate prepared with H_2O, (b) irradiated CO_2 hydrate prepared with D_2O.

Figure S1 (a) and (b) show ESR spectra magnified at *Signal (i),* which was recorded at 77 K after annealing at 170 K for 15 min in the irradiated CO_2 hydrates prepared with H_2O and D_2O, respectively. HOCO and/or CO_2 anion (CO_2^-) radicals are mainly formed from CO_2 and H_2O in the magnetic field range of Fig. S1.[1] *Signal (i)* has a similar *g*-factor as that of the HOCO and CO_2^- radicals. Hyperfine constants of hydrogen (A_H = 0.93 mT) and deuterium (A_D = 0.13 mT) around g = 1.9974 are observed on the peak of signals in the high magnetic field of Fig. S1. When the CO_2^- radical is induced in CO_2 hydrate, the spectral shapes in Fig. S1 (a) and (b) should show the same ones; however, they are intrinsically different. Therefore, the signals in Fig. S1 (a) and (b) are assigned to HOCO and DOCO radicals, respectively. The spectrum of the hydrogen atom (*Signal (ii)*) in Fig. 1 (a) is observed at g = 2.0025 with a large hyperfine constant (A = 50.3 mT). The spectrum of the OH radical (*Signal (iii)*) in Fig. 1 (a) is observed at *g*-parallel ($g_{//}$) = 2.0479, though *g*-perpendicular (g_{∞}) is only partially observed due to the overlap with *Signal (i).*

These radicals are induced in CO_2 hydrate through the following reactions.

$$H_2O + \text{gamma-rays} \rightarrow OH\cdot + H\cdot \qquad \text{(a)}$$

$$H_2O + \text{gamma-rays} \rightarrow H_2O^+ + e^- \rightarrow H^+ + OH\cdot + e^- \qquad \text{(b)}$$

$$CO_2 + e^- \rightarrow CO_2^-\cdot \qquad \text{(c)}$$

$$CO_2^-\cdot + H^+ \rightarrow HOCO\cdot \qquad \text{(d)}$$

Generally, hydrogen atom, OH radical, H_2O cation (H_2O^+) and electron (e^-) are induced by the radiolytic reaction of H_2O (reaction (a) and (b)). H_2O^+ is unstable at 77 K, and can quickly decompose to proton (H^+) and OH radical (reaction (b)). HOCO radical would be formed by additional reactions of CO_2 with secondary electron (reaction (c)) and proton induced from H_2O (reaction (d)) because the direct addition of a hydrogen atom to CO_2 is endothermic.

II. Thermal stabilities of HOCO radicals

Figure 2 indicates that the decay process is not readily achieved and consists of at least two steps. The spectral shape of *Signal (i)* slightly changes at an early stage at each annealing temperature. The change in the spectral shape may be caused by overlap of less stable signals of HOCO radicals. Most results show that the unstable factors decreased with the annealing time within the range denoted by the open markers shown in Fig. 2, and the data sets represented by solid markers are used for the discussion of the more stable HOCO radicals.

RERENCES

(1) Tseng, S.S.; Chang, S. *Origins Life Evol. B.* **1975**, *6*, 61–73.