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Reactions of HOCO radicals through hydrogen-atom hopping utilizing clathrate hydrates as an observational matrix†

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The carboxyl (HOCO) radical, which is an important species in atmospheric chemistry and combustion, is an intermediate in the reaction: CO + OH → CO_2 + H and serves as a hydrogen donor to the reaction partners. The *cis*-HOCO radical, one of the ground-state HOCO radicals, is supposed to be decomposed into CO_2 and the hydrogen atom by a tunneling effect. In order to prove the hypothesis, we performed electron spin resonance (ESR) measurements to investigate the decay mechanisms of the ground-state HOCO and DOCO radicals in gamma-ray-irradiated CO_2 hydrates, which may hold the radicals stably. The ground-state HOCO and DOCO radicals decayed according to a second-order decay model and transformed into formic acid and CO_2. The ratio of the decay rate constants of HOCO and DOCO radicals shows a good agreement with that in the kinetic isotope effect for the hydrogen and deuterium abstraction reactions. These results indicate that they react with another HOCO radical in the adjacent hydrate cage without the tunneling effect. This implies that the ground-state HOCO radicals are not decomposed by the tunneling effect but are decayed through reactions with some atoms, molecules, and/or radicals even in the gas phase. In addition, the hydrogen-atom hopping through the temporary hydrogen bonds between the HOCO radical and CO_2 results in a seeming diffusion of the HOCO radicals in the CO_2 hydrate; this would be an important concept for the studies of the radical diffusions and the supply of hydrogen atoms in gas, liquid, and solid phases.

1. Introduction

Reactions of the carboxyl (HOCO) radical are important for the carbon dioxide (CO_2) formation and reduction.[1,2] The reactive HOCO radical acts as an intermediate in the conversion of carbon monoxide (CO) and the hydroxyl (OH) radical into CO_2 and the hydrogen atom,[3] and serves as a hydrogen donor to the reaction partners (*i.e.*, other radicals and atoms). This reaction is one of the major processes in atmospheric chemistry and combustion, and has received attention in the related research fields. In addition, it has been believed that the reactions of the HOCO radical are related to CO_2 production in the interstellar clouds and planetary atmosphere.[4–6] Therefore, it is necessary to further understand the hydrogen transfer mechanisms in the reactions involving the HOCO radical.

The transfer mechanisms and dynamics of the hydrogen atom are of fundamental importance in physical chemistry. The three typical reaction processes involving hydrogen transfer are: the elimination of a hydrogen atom from a molecule (or radical) *via* the tunneling effect and subsequent addition to other molecules, the hydrogen abstraction reaction by free radicals and atoms, and the intramolecular and/or intermolecular transfer of protons or hydrogen upon photoexcitation. In order to explain the general reaction mechanism of the HOCO radical, the following reactions have been reported in many theoretical and experimental studies in the gas phase.[7–9]

$$\mathrm{CO} + \mathrm{OH}^{\bullet} \leftrightarrow \mathrm{HOCO}^{*\bullet} \rightarrow \mathrm{CO}_2 + \mathrm{H}^{\bullet} \qquad (1)$$

$$\mathrm{HOCO}^{*\bullet} + \mathrm{M} \rightarrow cis\text{-}\mathrm{HOCO}^{\bullet}/trans\text{-}\mathrm{HOCO}^{\bullet} + \mathrm{M} \qquad (2)$$

The excited state HOCO radical (hereafter, it is represented by $HOCO^{*\bullet}$) is formed through the reaction of CO and OH radical.

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Then HOCO* radical is either decomposed into CO_2 and hydrogen atom ($H^\bullet$) by the tunneling effect (reaction (1)) or decayed to the ground-state (*cis*-HOCO• and *trans*-HOCO•) through collision with a third species (reaction (2)). Generally, the *cis*-HOCO and *trans*-HOCO radicals decay *via* the following reactions with the reactive radicals ($H^\bullet$ and $OH^\bullet$), which have been reported in the experimental[10,11] and the theoretical researches.[5]

$$cis\text{-}HOCO^\bullet/trans\text{-}HOCO^\bullet + H^\bullet \rightarrow HCOOH \quad (3)$$

$$cis\text{-}HOCO^\bullet/trans\text{-}HOCO^\bullet + OH^\bullet \rightarrow CO_2 + H_2O \quad (4)$$

$$cis\text{-}HOCO^\bullet/trans\text{-}HOCO^\bullet + OH^\bullet \rightarrow H_2CO_3 \quad (5)$$

In the field of atmospheric chemistry, it is believed that the ground-state *cis*-HOCO radical is also decomposed into CO_2 and hydrogen atom by the tunneling effect as described by reaction (6). In addition, it is reported that the *trans*-HOCO radical isomerizes to *cis*-HOCO radical and then decomposes to the CO_2 and hydrogen atom through reaction (6).[12–14]

$$cis\text{-}HOCO^\bullet \rightarrow CO_2 + H^\bullet \quad (6)$$

The decay mechanisms of the HOCO radical are a missing piece of the entire reaction mechanisms because reaction (6) by the tunneling effect has not been experimentally demonstrated yet, and its details are necessary to be investigated. In the present study, the CO_2 hydrate was used as an observational matrix to investigate the decay mechanisms of the HOCO radical by using electron spin resonance (ESR) measurements.

Clathrate hydrates (or gas hydrates) are crystalline inclusion compounds, which are composed of hydrogen-bonded water molecules acting as host molecules to encage other guest molecules. The guest molecules interact weakly with the water molecules of the cages through only van der Waals forces,[15] and we have already studied the thermal stabilities of gamma-ray induced radicals in clathrate hydrates using ESR measurements.[16–19] In the case of gamma-ray irradiated hydrocarbon hydrates, alkyl radicals induced from alkanes in hydrate cages seem to be stable below the three-phase (*i.e.*, hydrate, ice and gas phase) equilibrium temperature of each hydrocarbon hydrate at atmospheric pressure. For example, the methyl radical in the methane hydrate is relatively stable in comparison with that in water ice, and this trend has also been observed in other hydrocarbon hydrate systems. It means that each hydrate cage could be a peculiar holder for a free radical. Additionally, the hydrogen-picking (hydrogen abstraction) reaction between the radical and the guest molecule is confirmed in gamma-ray irradiated propane hydrate,[20] where the normal-propyl radical withdraws a hydrogen atom from the adjacent propane molecule through the hexagonal faces of the hydrogen-bond cage. Almost all the alkyl radicals in clathrate hydrates could enable a hydrogen-picking reaction with a guest molecule in the adjacent cage.

The CO_2 hydrate is stable below 220 K at 0.1 MPa. Its structure is called ''structure I'', which consists of two different cages, known as a small one (5^{12}, dodecahedron) and a large one ($5^{12}6^2$, tetrakaidecahedron). Uchida *et al.*[21] have reported that although the ideal hydration number (n) is $n = 5.75$, it is slightly larger in the artificially-prepared CO_2 hydrate. In the case of the irradiated CO_2 hydrate, the HOCO radical would be formed because the formation of the HOCO radical is through an ultraviolet irradiation of the mixture of CO_2 and H_2O.[22] It is expected that the HOCO radical in the CO_2 hydrate would be more stable than in other matrices, and the decay process of the HOCO radical can be easily observed by ESR measurements.

2. Experimental

2.1. Sample preparation

The samples were prepared by a high-pressure vessel developed based on the system previously reported by Tani *et al.*[19] The CO_2 hydrate was prepared as per the following procedure in three steps: (i) ultrapure water (Milli-Q, 8.0 cm^3) or heavy water (Cambridge Isotope Laboratories, Inc., 99.9%, 8.0 cm^3) in a polypropylene test tube was placed in the high-pressure vessel immersed in a thermostatic bath (275–284 K); (ii) the gaseous CO_2 was supplied to the vessel until the vessel pressure increased to 3.0–3.5 MPa (Neriki Gas, 99.99% grade), and the vessel was sealed afterwards, and the pressure was measured using a pressure gauge (VALCOM, VSW2 series); and (iii) after the ultrapure water and CO_2 were mixed by agitation with a magnetic stirrer for 0.5–12 h, additional CO_2 was supplied to the vessel with the pressure up to 3.0–3.5 MPa because the pressure dropped (1.8–2.0 MPa) as a result of the formation of CO_2 hydrate.

In this procedure, approximately 2.0×10^{-2} mol of CO_2 was used to produce CO_2 hydrate. After completion of the formation, the vessel pressure was ~2.0 MPa. The vessel was stored at ~193 K in a deep freezer for more than 12 hours.

For ESR measurements, CO_2 hydrates were taken from the high-pressure vessel in a low-temperature chamber (243 ± 3 K and 0.1 MPa). Small pieces of CO_2 hydrates with a diameter of 1–2 mm were collected using metal sieves and placed in a plastic vial, which was then stored at ~77 K. The synthetic CO_2 hydrates in the vial were irradiated using a ^{60}Co source with 1.4–1.5 kGy dose at 77 K. For ion chromatography analyses, the synthetic CO_2 hydrate prepared with H_2O was irradiated in the high-pressure vessel with the same dose at 77 K.

2.2. Electron spin resonance (ESR) measurements

The irradiated samples were measured at 0.1 MPa using a commercial X-band ESR spectrometer (JEOL, JES-FA200), and the measurement temperature was controlled using a nitrogen gas flow unit system (JEOL, ES-DVT4). The microwave power was 0.2 mW in the measurements, and the 100 kHz field modulation width was 0.1 mT. The isothermal annealing experiments were performed at temperatures in the range of 120–150 K for 6–10.5 hours.

2.3. Ion chromatography analyses

The irradiated sample in the high-pressure vessel was annealed at ~145 K for 10 days, after which the hydrate was dissociated at room temperature by depressurization. The aqueous solutions obtained by the dissociation of irradiated/unirradiated CO_2 hydrates were analyzed by ion chromatography

(SHIMADZU, Prominence HIC-SP) using an anion-exchange column (Shim-pack IC-SA3) and electric conductance detector (SHIMADZU, CDD-10ASP), where the eluent was a sodium carbonate aqueous solution at 3.6 mmol m^{-3}. The column was held at 45 °C, the eluent flow rate was 0.8 cm^3 min^{-1}, and the injected volume of the sample was 50 mm^3 for all the analyses. The chromatograms were recorded at room temperature.

3. Results and discussion

3.1. Induced radicals in CO_2 hydrates

A representative ESR spectrum of the gamma-ray-irradiated CO_2 hydrate (H_2O) at 120 K is shown in Fig. 1(a). Three signals are observed, where Signal (i) is an intense signal located at the center of the spectrum, Signal (ii) is a doublet signal, and Signal (iii) is a relatively broad signal. Signal (i) comprises two signals, exhibiting similar thermal stabilities. In addition, hyperfine structures of hydrogen and deuterium were observed in Signal (i) of irradiated CO_2 hydrate prepared with H_2O and D_2O, respectively. According to the previous investigations on the Fermi contact constants of HOCO and DOCO radicals, a hyperfine constant of hydrogen (deuterium) on the *cis*-HOCO (DOCO) radical is larger than that on *trans*-HOCO (DOCO) radical.[23] Therefore, Signal (i) is assigned to two overlapping signals of *trans*-HOCO and *cis*-HOCO radicals, which has hyperfine structure of hydrogen. Signal (ii) is assigned to the hydrogen atom because of the large hyperfine constant and the same signal is observed in other gas hydrates.[16,24] Signal (iii), which is partially observed due to the overlap with Signal (i), corresponds to the OH radical, and resembles the signal of OH radical in water ice.[25] The detailed identification procedures of these radicals have been described in ESI.†

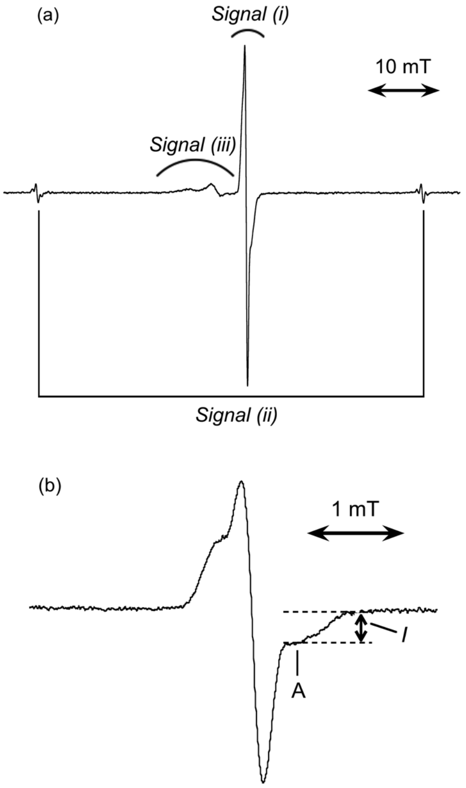

Fig. 1 ESR spectra for gamma-ray-irradiated CO_2 hydrate with H_2O at 120 K. (a) Three signals are observed: Signal (i), which is assigned to two overlapping signals of *cis*-HOCO and *trans*-HOCO radicals, Signal (ii) assigned to hydrogen atom, and Signal (iii) assigned to OH radical. (b) Magnified ESR spectrum on the location of Signal (i). ESR signal intensity *I* was evaluated at position A.

3.2. Thermal stabilities of HOCO and DOCO radicals

Fig. 1(b) shows a magnified ESR spectrum with a special focus on Signal (i) at 120 K; Signal (iii) disappeared by annealing at 140 K in advance. The thermal stability of both *cis*-HOCO and *trans*-HOCO radicals can be evaluated by the intensity (*I*) at position A, as shown in Fig. 1(b).

The amounts of HOCO radicals, hydrogen atom, and OH radical barely changed at 77 K. Especially the amounts of HOCO radicals and hydrogen atom in CO_2 hydrate were preserved at 77 K for more than one month. Hydrogen atom and OH radical quickly disappeared at 130 K; however, there was only a very small decrease (a few percent) of HOCO radicals at the same time. Considering the thermal stabilities of the radicals and CO_2 hydrate, all the radical reactions occurred below the dissociation temperature of CO_2 hydrate (220 K at 0.1 MPa).

Fig. 2 shows the typical decays of the normalized ESR signal intensity (I/I_0) of HOCO radicals at 130–150 K over time. Only the signals arising from HOCO radicals remained in the spectrum after the disappearance of the less-stable signals; the decay of HOCO radicals was better fitted with the second-order decay curves after the spectral shapes were stabilized. The decay of DOCO radicals in the gamma-ray-irradiated CO_2 hydrate prepared with D_2O showed a similar trend to that of the HOCO radicals. The Arrhenius plots for the decay curves of HOCO and DOCO radicals are shown in Fig. 3. The activation energies of HOCO and DOCO radicals, estimated from the Arrhenius plots, were $E_a^H = 13.9 \pm 1.0$ kJ mol^{-1} (0.14 ± 0.01 eV) and $E_a^D = 13.1 \pm 1.5$ kJ mol^{-1} (0.14 ± 0.02 eV), respectively.

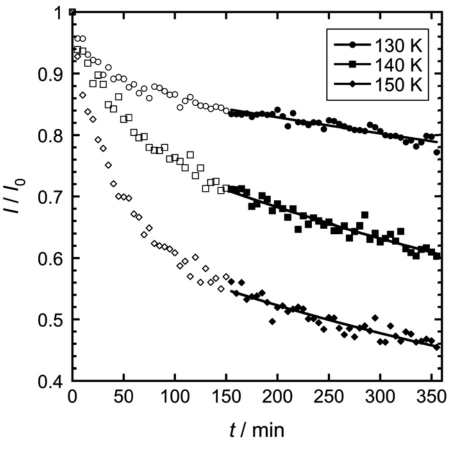

Fig. 2 Decay of the HOCO radicals in isothermal annealing experiments, where I_0 stands for the initial signal intensity at each temperature, open markers denote the data before the stabilizing of spectral shapes, and solid markers show the ones after stabilizing. The fitting curves were estimated only from the solid makers.

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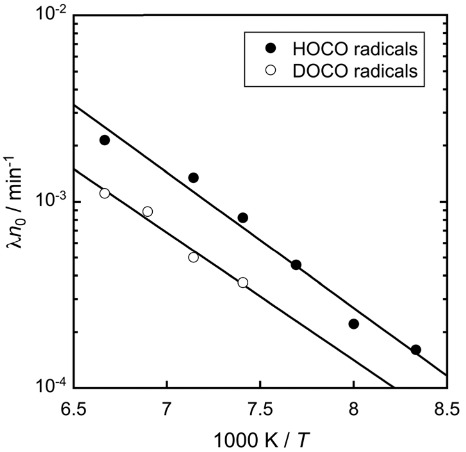

Fig. 3 Arrhenius plot for the decay reaction of the HOCO and DOCO radicals, where λ is a rate constant of the second-order decay model and n_0 is the initial concentration of the radical. The estimated activation energies of HOCO (solid circle) and DOCO (open circle) radicals are E_a^H = 13.9 ± 1.0 kJ mol^{-1} (0.14 ± 0.01 eV) and E_a^D = 13.1 ± 1.5 kJ mol^{-1} (0.14 ± 0.02 eV), respectively. The ratio of rate constants (k_a^H/k_a^D) is 1.8–2.2 for 120–150 K.

The decay mechanisms of the ground-state HOCO radicals have been proposed in previous studies, including the reactions (reactions (3)–(5)) with reactive radicals (hydrogen atom and OH radical)[5,10,11] and the decomposition (reaction (6)) by the tunneling effect.[12–14] The results in the present study reveal that the *cis*-HOCO and *cis*-DOCO radicals are not decomposed by the tunneling effect because the decays demonstrate strong Arrhenius behaviors (as shown in Fig. 3) and the amounts of radicals hardly change even at 77 K.

3.3. Decay mechanisms of HOCO and DOCO radicals

To investigate the reaction products of HOCO radicals, the samples irradiated at 77 K were annealed at ~145 K for 10 days until the amounts of the HOCO radicals reduced to several percent of the initial value. Ion chromatograms of the aqueous solution after the dissociation of irradiated CO_2 hydrate (H_2O), unirradiated CO_2 hydrate (H_2O), and standard aqueous solution of formic acid (10 mmol m^{-3}) and oxalic acid (10 mmol m^{-3}) are shown in Fig. 4. Formic acid (with the retention time of 6.5 min) and oxalic acid (about 26.3 min) were observed in the aqueous solution obtained from the irradiated sample, whereas they were not included in the unirradiated sample. The peaks at 8.3, 14.6, and 23.1 min are thought to be induced by impurities. The intense peak at 9.8 min is attributed to the carbonate ion that could not be removed by a de-aeration unit. The concentrations of formic acid and oxalic acid per kGy are 5.4 mmol m^{-3} and 0.7 mmol m^{-3}, respectively with formic acid being the main product.

The molar ratio of HOCO radicals to CO_2 (C_{HOCO}/C_{CO_2}) in CO_2 hydrate from ESR measurements is several ppm, and the concentration of formic acid in the irradiated sample approximately accords with half the amount of HOCO radicals. The difference between the activation energies of the decays of HOCO and DOCO radicals in Fig. 3 is within the estimated errors.

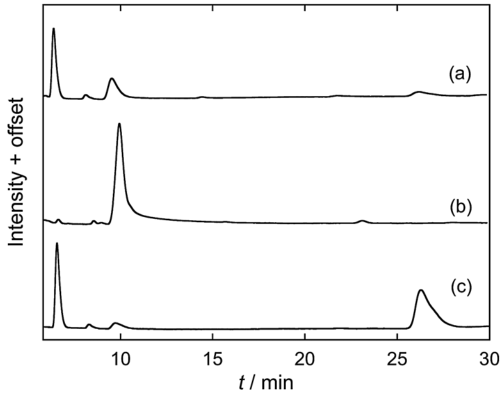

Fig. 4 Chromatograms for three aqueous solutions, (a) the sample annealed at ~145 K for 10 days after being irradiated at 77 K, (b) unirradiated CO_2 hydrate, and (c) a standard of formic acid (10 mmol m^{-3}) and oxalic acid (10 mmol m^{-3}). The retention time of formic acid is ~6.5 min, oxalic acid is ~26.3 min.

The reaction rate constant of HOCO radicals (k_a^H) is higher than that of DOCO radicals (k_a^D), with a ratio (k_a^H/k_a^D) of 1.8–2.2. The value of k_a^H/k_a^D in the present study is similar to that obtained from the kinetic isotope effect for the hydrogen (or deuterium) abstraction reaction by Ishimoto *et al.*[26] In addition, the decay of HOCO radicals is better fitted with the second-order decay model. These results suggest that the decay of HOCO (DOCO) radicals occurs through reaction (7) by hydrogen abstraction (hydrogen-picking) between two HOCO radicals.

$$HOCO^\bullet + HOCO^\bullet \rightarrow HCOOH + CO_2 \qquad (7)$$

For reaction (7) to occur in CO_2 hydrate, two HOCO radicals should occasionally exist in the adjacent cages. The probability that two HOCO radicals could exist in the adjacent cages is quite small with gamma-ray irradiation because the C_{HOCO}/C_{CO_2} in CO_2 hydrate is merely several ppm. Nevertheless, the HOCO radicals almost disappear in the sample annealed at ~145 K for 10 days. Therefore, it is necessary for the HOCO radicals to migrate in CO_2 hydrate. Generally only one molecule exists in one cage, and it is very difficult for a molecule to physically diffuse into clathrate hydrate.[15] In the irradiated hydrocarbon hydrates, alkyl radicals seemingly diffuse in hydrocarbon hydrates by hydrogen-picking reaction, where an alkyl radical withdraws a hydrogen atom from an alkane molecule in the adjacent cage.[20,27,28] In the CO_2 hydrate system, the diffusion of HOCO radicals in CO_2 hydrate is assumed to proceed with a mechanism as described: contrary to the hydrogen-picking reaction in hydrocarbon hydrates (where radicals withdraw a hydrogen atom from other molecules), CO_2 withdraws a hydrogen atom from HOCO radicals, and the seeming diffusion of HOCO radicals occurs without the self-diffusion.

3.4. Implications

It has been claimed that the ground-state HOCO radicals are decomposed by the tunneling effect, whereas the results obtained in the present study suggests different mechanisms. The decomposition of *cis*-HOCO radical by the tunneling effect cannot be avoided in the large cage, which is occupied by the HOCO radicals, because the size of $5^{12}6^2$ cage (about 0.58 nm) is slightly larger than the sum of the miner axis of CO_2 (about 0.34 nm) and the diameter of the hydrogen atom (0.24 nm). Nevertheless, the HOCO radicals barely decrease at 77 K. Assuming that the reactions of the *cis*-HOCO radical in the CO_2 hydrate are close to those in the other matrices, we can conclude that the ground-state HOCO radicals are not decomposed by the tunneling effect, but decay through the reactions with some atoms and/or radicals (*e.g.* through reactions (3)–(5) and (7)) even in the gas phase and on the surface of other ice materials, for example, planetary atmospheres, dense molecular clouds, interstellar ice mantles, and cometary ices.

Additionally, we found that because of the hydrogen transfer between the HOCO radical and CO_2, *i.e.*, ''hydrogen-atom hopping'', the HOCO radical seemingly diffuses in CO_2 hydrate, and the transfer mechanism is considered similar to the proton hopping reactions in aqueous solutions.[29,30] In addition, Kumagai *et al.*[31] demonstrated that the hydrogen-atom relay (*i.e.* hydrogen-atom hopping) reactions occur along hydrogen-bonded chains on the surface of Cu(110). The hydrogen-atom hopping reaction in the present study would also proceed through the hydrogen bonds that are temporarily formed between the HOCO radical and CO_2; these reactions should occur not only in CO_2 with the HOCO radical but also in other molecules with radicals, which have surplus hydrogen, *i.e.* in oxygen with the hydroperoxyl (HO_2) radical and in CO with the formyl (HCO) radical. If these radicals with surplus hydrogen atoms exist in gas, liquid, and other solid phases, the hopping reactions would occur between the radicals and neighboring molecules depending on the adaptive environments. For example, the diffusion of radicals and the supply of hydrogen atom in gas and liquid phases would proceed with the hydrogen-atom hopping through hydrogen bonds. In addition, it is suggested that the radicals generated on the surface of solid matter by natural radiation and cosmic rays apparently penetrate the solids by the hydrogen-atom hopping reactions, and a reaction field, deeper than the surface one, might exist.

4. Conclusions

The decay mechanisms of the ground-state HOCO and DOCO radicals in CO_2 hydrates have been investigated by means of ESR measurements. HOCO and DOCO radicals decayed according to a second order decay model, and formic acid (HCOOH) and CO_2 were produced by the reaction (7). The activation energies of these decays estimated from the Arrhenius plots were E_a^H = 13.9 ± 1.0 kJ mol^{-1} and E_a^D = 13.1 ± 1.5 kJ mol^{-1}, respectively. These results reveal that the ground-state HOCO and DOCO radicals in the hydrate are not decomposed by the tunneling effect. If the hydrate cage does not affect the self decomposition of the HOCO radical, it may not be decomposed by the tunneling effect but decayed through the reactions with some atoms and/or radicals with an Arrhenius behavior in the gas phase and other ice materials. In addition, we found that the hydrogen-atom transfer through the temporary hydrogen bonds between the HOCO radical and CO_2 (*i.e.* hydrogen-atom hopping reaction) results in a seeming diffusion of the HOCO radicals in CO_2 hydrate. These results suggest that hydrogen-atom hopping reactions would also occur between the radicals with excess hydrogen atom and neighboring molecules depending on the adaptive environments of gas, liquid and solid phases. The present results propose an important concept for the studies of the intermolecular hydrogen transfer in most elementary chemical reactions, applied chemistry, planetary science, and atmospheric chemistry.

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