

FORMATION OF CARBONIC ACID (H₂CO₃) BY SURFACE REACTIONS OF NON-ENERGETIC OH RADICALS WITH CO MOLECULES AT LOW TEMPERATURES

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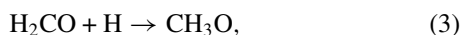
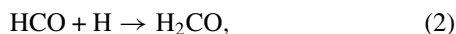
ABSTRACT

We present the experimental results of carbonic acid (H₂CO₃) formation through surface reactions of CO molecules with non-energetic hydroxyl (OH) radicals at 10–40 K. The formation of H₂CO₃ was clearly identified both in the IR spectra and in the thermally programmed desorption mass spectra. The H₂CO₃ yield was rather high, amounting to approximately 40%–70% relative to that of CO₂ formed by the reaction of CO with OH. The structure of H₂CO₃ formed by reactions of CO with OH may differ from that formed by energetic processes such as UV irradiation, ion irradiation, and electron irradiation of H₂O/CO₂ binary ices. In this paper, we envisage some of the possible roles H₂CO₃ may have in the interstellar medium, such as enriching grain mantles of new molecules via acid–base reactions with basic species and contributing to the formation of the unidentified band at 6.8 μm; we suggest possible reasons for its non-detection yet and discuss the restoration of carbonic acid molecules in the gas phase.

Key words: astrobiology – astrochemistry – ISM: clouds – ISM: molecules – molecular processes

1. INTRODUCTION

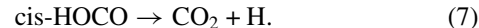
Carbon monoxide (CO) is one of the most abundant molecules observed in ice mantles of dense molecular clouds (see, e.g., Whittet et al. 2010, for a detailed study of its uptake in icy mantles). Owing to its ubiquitous existence in ice, CO has been theoretically and experimentally demonstrated to be used for various chemical reactions that occur on the surface of ice (Watanabe & Kouchi 2008). For example, formaldehyde (H₂CO) and methanol (CH₃OH), both of which are known constituents in ice mantles (e.g., Gibb et al. 2004), can be formed from the following successive hydrogenation of CO molecules:



These reactions have been both theoretically (Tielens & Hagen 1982; Cuppen et al. 2009) and experimentally (Watanabe & Kouchi 2002a; Hidaka et al. 2004; Fuch et al. 2009; Pirim et al. 2010) shown to occur on a cold (~10 K) icy grain surface.

In addition to H₂CO and CH₃OH, carbon dioxide (CO₂), which is another abundant solid component in ice mantles (e.g., Pontoppidan et al. 2008), can be synthesized from pure CO (Loeffler et al. 2005; Jamieson et al. 2006; Bennett et al. 2009) and CO-containing ices (Palumbo et al. 1998; Watanabe & Kouchi 2002b; Ioppolo et al. 2009) through energetic processes such as UV irradiation, ion irradiation, and electron irradiation. CO₂ has also been shown to be formed by surface reactions of CO + O in the presence of water ice (Roser et al. 2001), and recently, we performed an experiment involving the reactions of CO molecules with non-energetic hydroxyl radicals (OH) on a cold (10 and 20 K) surface leading to the formation of carbon

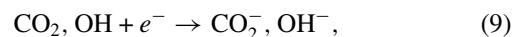
dioxide through the following pathway (Oba et al. 2010):

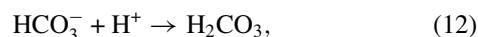
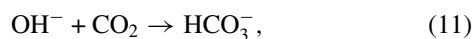
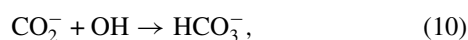


Reactions (5)–(7) have been theoretically investigated in the gas phase (e.g., Yu et al. 2001; Senosiain et al. 2003; Varelo et al. 2004; Song et al. 2006) and are expected to occur at very low temperatures without any external energetic sources inside dense clouds (Oba et al. 2010), although cosmic-ray-induced photons may still be effective for triggering reactions (5)–(7) that occur there (Garrod et al. 2007).

Carbonic acid (H₂CO₃) is a CO-bearing molecule with one carbonyl (C=O) and two hydroxyls (OH) in its structure; it may have a role in acid–base chemistry, such as in reactions with NH₃ to yield NH₄⁺ in astrophysical environments (Brucato et al. 1997; Hage et al. 1998; Gerakines et al. 2000; Schutte & Khanna 2003). The formation of H₂CO₃ on a cold surface has been experimentally demonstrated through energetic processes such as UV irradiation (Gerakines et al. 2000; Wu et al. 2003), ion irradiation (Moore et al. 1991; Moore & Khanna 1991; DelloRusso et al. 1993; Brucato et al. 1997; Gerakines et al. 2000), and electron irradiation (Zheng & Kaiser 2007) of H₂O/CO₂ binary ices and proton (50 keV) irradiation of pure CO₂ ice (Garozzo et al. 2008). These results imply that H₂CO₃ may be formed not only in the interstellar medium (ISM) but also in the outer solar system where H₂O and CO₂ are present (Brucato et al. 1997; Zheng & Kaiser 2007).

Gerakines et al. (2000) proposed a possible formation pathway of H₂CO₃ through proton or UV irradiation of H₂O/CO₂ binary ices as follows:





where p^+ and e^- denote protons and electrons, respectively. However, Zheng & Kaiser (2007) pointed out that reactions (8)–(12) were less likely to occur because reaction intermediates such as ions and radicals were not detected in the experiments by Gerakines et al. (2000). Instead, Zheng & Kaiser (2007) proposed an electron-induced formation pathway of H_2CO_3 from $\text{H}_2\text{O}/\text{CO}_2$ binary ices, which is initiated by an electron-induced O–H bond rupture within the H_2O molecule:



Although reactions (13)–(16) are endothermic by approximately 3800 K, they proceed even at 10 K because of the energy inputs from 5 keV electrons (Zheng & Kaiser 2007). They also showed that intermediate HOCO radicals were observed in the IR spectrum of the products. Because reaction (14) has a significant barrier of more than 12,000 K (e.g., Yu et al. 2001; Zheng & Kaiser 2007), H_2CO_3 is not formed at temperatures as low as 10 K without energy inputs from external sources such as electrons, UV, and ions. In contrast, we recently showed that both HOCO radicals and H_2CO_3 , as well as CO_2 , are formed by surface reactions of CO with non-energetic OH radicals even at 10 K (Oba et al. 2010), indicating that the formation of H_2CO_3 may occur in dense molecular clouds without energy inputs. Elucidating the formation pathways of H_2CO_3 and its astrophysical significance is necessary for understanding chemical reaction networks related to the presence of CO in molecular clouds. In this paper, we report further experimental results of the formation of H_2CO_3 through the OH addition of CO molecules on a cold surface and discuss its astrophysical implications.

2. EXPERIMENTAL

Experiments were performed using the ASURA (Apparatus for Surface Reaction in Astrophysics) system. ASURA consists of a main chamber, an atomic source, and a Fourier transform infrared spectrometer. Details on this apparatus have been described previously (Watanabe et al. 2006; Nagaoka et al. 2007). At the center of the main chamber, a mirror-finished aluminum (Al) substrate is mounted on the cold head of a He refrigerator. The base pressure of the main chamber is $\sim 10^{-10}$ torr, but it reaches $(1\text{--}2) \times 10^{-7}$ torr during the operation of the atomic source. Hydroxyl radicals (OH), together with atomic hydrogen (H) and oxygen (O), were dissociated from H_2O molecules by microwave-induced plasma (Timmermans et al. 1998) in a Pyrex tube. H_2O dissociation may also lead to the direct formation of H_2 and O. The H_2O fragments (H, O, OH, and H_2) were transferred via a series of poly(tetrafluoroethylene) and aluminum tubes to the substrate and then cooled to 100 K in

an aluminum tube that was connected to another He refrigerator. OH radicals obtained by dissociating H_2O are thought to be rovibrationally excited upon formation but after many collisions with the cold aluminum pipe they should already be in the ground state before reacting with other species on the cold substrate (10–40 K) as explained previously (Oba et al. 2010). The deposition rate of OH radicals could not be directly measured in the present experiment; however, it can be estimated from the rate of H_2O_2 formation on the assumption that it is formed via $\text{OH} + \text{OH}$ reaction and from the rate of H_2O deposition when the microwave source is turned off, and it was found to be approximately 1.2×10^{13} radicals $\text{cm}^{-2} \text{ s}^{-1}$. CO molecules were introduced into the main chamber through a capillary plate located at approximately 5 cm from the substrate, with an incidence angle of 30° to the normal of the substrate surface. The deposition rate of CO molecules ranges from 0.3 to 2.8×10^{13} molecules $\text{cm}^{-2} \text{ s}^{-1}$. The reaction products were monitored in situ by infrared reflection–absorption spectroscopy with a resolution of 4 cm^{-1} in the spectral range between 700 and 4000 cm^{-1} . Species desorbing from the substrate were monitored using a quadrupole mass spectrometer (QMS). The temperature of the Al substrate was maintained at 10–40 K during each experiment. Each experiment was performed for a total duration of 60 or 240 minutes, depending on the experiment. After co-deposition of the H_2O fragments and CO molecules, temperature-programmed desorption (TPD) spectra were obtained by the QMS at a heating rate of 4 K minute^{-1} .

3. RESULTS AND DISCUSSION

3.1. Formation of Carbonic Acid

When only H_2O fragments were deposited on the substrate (hereafter referred to as the blank experiment), typical bands of H_2O , H_2O_2 , and O_3 molecules were identified in the IR spectrum of the product at 1649, 1403, and 1039 cm^{-1} , respectively. Opposite to H_2O , H_2O_2 , and O_3 , the O_2 and H_2 molecules are infrared inactive; therefore, they were not observed in the IR spectrum. The QMS revealed that H_2 and O_2 were contained in gases from the source. Trace amounts of CO_2 were detected in the IR spectrum (2344 cm^{-1}) even before any reactive partners were admitted in the chamber. This CO_2 may originate from CO_2 adsorbed on the inner wall of the main chamber. It was found that CO_2 can desorb from the wall during radical beam operation probably due to sputtering by the H_2O fragments.

When CO molecules were introduced together with the H_2O fragments onto the substrate at 40 K, new peaks were observed at around 1750 cm^{-1} as well as significant growth of the CO_2 peak at 2344 cm^{-1} (Figure 1(a)). It should be noted that at temperatures lower than 30 K, two small peaks were observed at 1774 and 1812 cm^{-1} ; these peaks may be attributed to cis- and trans-HOCO radicals, respectively (see Figure 1(b) in Oba et al. 2010). In contrast, cis- and trans-HOCO radicals were not observed at 40 K (Figure 1(a)). Milligan & Jacox (1971) demonstrated that these radicals disappeared as the sample was warmed, which was consistent with our observations. Figure 1(b) shows an IR spectrum of the product formed at 40 K followed by warming up to 220 K. The spectrum shows that most volatile species such as CO_2 , H_2O , H_2O_2 , and O_3 were desorbed from the substrate, and three intense peaks clearly appeared at 1300, 1500, and 1750 cm^{-1} . A weak, broad absorption observed at $3000\text{--}3500 \text{ cm}^{-1}$ implies that small amounts of H_2O and H_2O_2 may have still remained on the substrate. By comparing the spectrum in Figure 1(b) with that

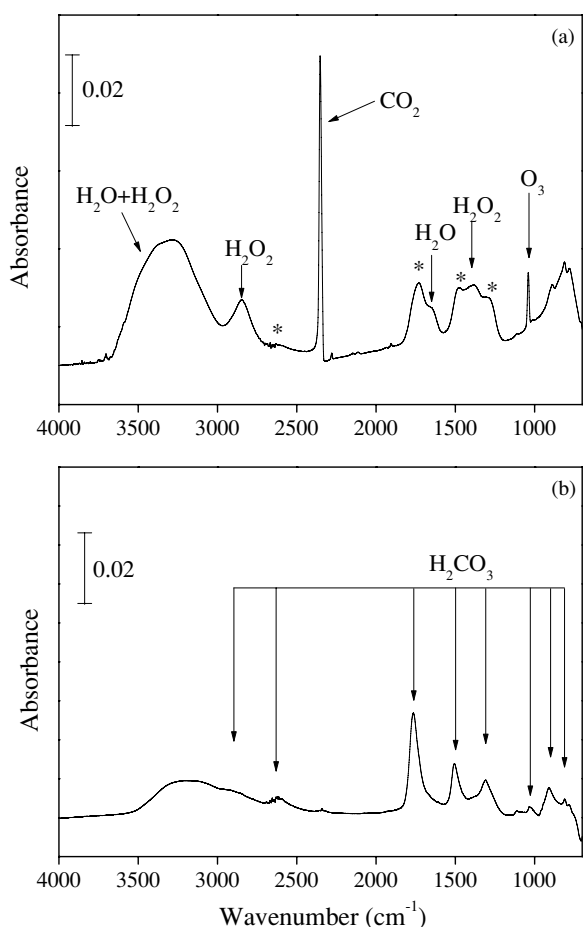


Figure 1. (a) IR spectrum of the product for OH/CO of 0.84 at 40 K after 240 minutes. (b) IR spectrum of the products after warming up to 220 K. Peaks with asterisks in (a) are assigned to be H_2CO_3 .

of H_2CO_3 formed after energetic irradiation of $\text{H}_2\text{O}/\text{CO}_2$ binary ices (DelloRusso et al. 1993; Gerakines et al. 2000; Zheng & Kaiser 2007), it is found that the observed peaks are well consistent with those of H_2CO_3 in terms of their positions and shapes. The most pronounced peak was observed at 1750 cm^{-1} , which can be assigned to the C=O stretch of H_2CO_3 (Gerakines et al. 2000; Zheng & Kaiser 2007), although the peak position differs by approximately 50 cm^{-1} as compared to the previous studies (Table 1). Peaks derived from the O–H stretch were less intense as compared to those of H_2CO_3 formed after energetic irradiation (e.g., Gerakines et al. 2000; Zheng & Kaiser 2007); only small absorption was observed at the region (Figure 1(b)). Hage et al. (1995) experimentally demonstrated that solid H_2CO_3 has at least two polymorphs (i.e., a solid material that exists in more than one form or crystal structure): one, defined as $\alpha\text{-H}_2\text{CO}_3$, is formed by reactions of HCO_3^- with HCl in methanol-rich solutions, the other, $\beta\text{-H}_2\text{CO}_3$ is similarly formed in aqueous solutions. The O–H stretch of $\alpha\text{-H}_2\text{CO}_3$ shows very weak absorptions at these regions (Hage et al. 1996a), which is consistent with the H_2CO_3 formed in this study (Figure 1(b)). In contrast, the H_2CO_3 formed after energetic irradiation of $\text{H}_2\text{O}/\text{CO}_2$ binary ices has been proposed to be $\beta\text{-H}_2\text{CO}_3$ (Hage et al. 1995), which has the most intense absorption at $\sim 2600\text{ cm}^{-1}$ (Hage et al. 1996b). The structure of H_2CO_3 in this study is not strictly equal to but very similar to that of $\alpha\text{-H}_2\text{CO}_3$ (see descriptions about D_2CO_3 below for more details).

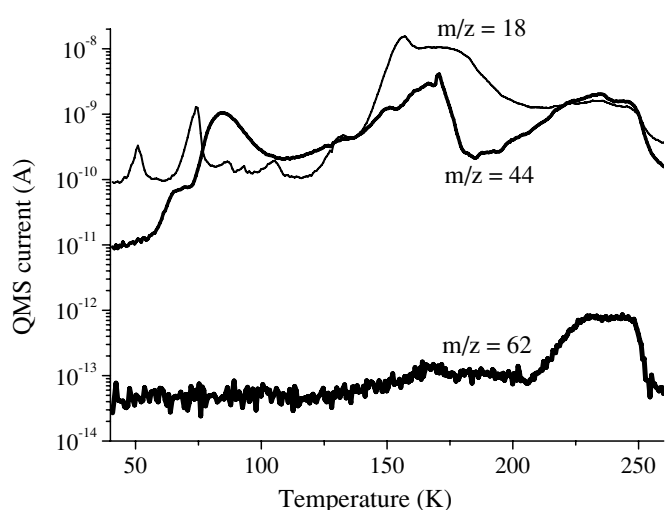


Figure 2. TPD spectra of the products shown in Figure 1 during warming up from 40 K to 260 K. Mass signals of 18, 44, and 62 represent H_2O , CO_2 , and H_2CO_3 , respectively.

The TPD spectrum of mass 62 increased clearly in the temperature range of 200–250 K (Figure 2). This indicates that H_2CO_3 was at least partly released into the gas phase without decomposition at $T > 200\text{ K}$. The mass signals of 18 (H_2O) and 44 (CO_2) appeared significantly even after the temperature exceeded 200 K. Since CO_2 and H_2O originally present on the substrate should have already sublimed below 200 K, the increases in the mass signals 18 and 44 at $T > 200\text{ K}$ in the TPD spectra imply that most of the H_2CO_3 was dissociated into H_2O and CO_2 . This observation is consistent with the experiment by Moore et al. (1991) in which they observed only masses 18 and 44 in the TPD spectra although H_2CO_3 was detected by an infrared spectroscopy. It is probably due to the presence of H_2O near H_2CO_3 , which significantly lowers the barrier height for H_2CO_3 dissociation (Loerting et al. 2000). It has been reported that the signal of mass 62 was detected during warming up of electron-irradiated $\text{H}_2\text{O}/\text{CO}_2$ ices (Zheng & Kaiser 2007), while it was not in proton-irradiated $\text{H}_2\text{O}/\text{CO}_2$ ices (Moore et al. 1991). This difference in observations may be caused by differences in the H_2CO_3 abundances formed in each experiment. The column density of H_2CO_3 after electron irradiation of $\text{H}_2\text{O}/\text{CO}_2$ ices for 180 minutes at 40 K reached approximately $2.0 \times 10^{15}\text{ molecules cm}^{-2}$ (Zheng & Kaiser 2007), which is almost the same as the value obtained after 240 minutes of co-deposition at 40 K in this study (see Section 3.2 for H_2CO_3 quantification). Although Moore et al. (1991) did not quantify H_2CO_3 in their experiment, the quantity of H_2CO_3 in their experiment was assumed to be very small. The products and yields would be different between electron and proton bombardments because electrons lose energy by interacting with the electron cloud (ionization, excitation), while protons up to 200 KeV lose their energy by a cascade of elastic collisions. This difference in the energy deposit and in the mobility of atoms and radicals in the energized regions may produce different products.

As explained above, although the peak shapes of H_2CO_3 formed in this study are very similar to those of $\alpha\text{-H}_2\text{CO}_3$, the peak position derived from C=O stretch differs significantly by 50 cm^{-1} (Table 1), which implies that the formed H_2CO_3 has a structure different from that of the α -polymorph. Then, to further investigate the structure of carbonic acid formed by the non-energetic process, we performed another set of experiments by

Table 1
Infrared Frequencies (cm^{-1}) of the Observed Absorptions of H_2CO_3 Formed in the Present Study

$\text{H}_2\text{CO}_3^{\text{a}}$	Rel. Int. ^b	$\text{H}_2\text{CO}_3^{\text{c}}$	Rel. Int. ^b	$\alpha\text{-H}_2\text{CO}_3^{\text{d}}$	Rel. Int. ^b	$\beta\text{-H}_2\text{CO}_3^{\text{e}}$	Rel. Int. ^b	Assignment
2853, 2610	w	2840+2761, 2626	s	2694, 2585	w	3500-2500	s	O–H stretch
1766	s	1719	s	1715	s	1698	s	C=O stretch
1505	s	1508	s	1477	s	1504	s	C–OH asym stretch
1309	m	1307	s	1304	s	1302	s	C–OH in-plane bend
1111	w							? ^f
1030	w	1038	w	1084	m	1038	w	C–OH sym stretch
908	m	908	w	920	w	910, 881	m	C–OH out-of-plane bend
809	w	813	w	801	w	813	w	CO_3 out-of-plane bend
783	w							? ^f

Notes.^a This study (220 K).^b Relative intensity; s: strong, m: moderate, w: weak.^c Gerakines et al. (2000).^d Hage et al. (1996a).^e Hage et al. (1996b).^f Unable to determine.

Table 2
Infrared Frequencies (cm^{-1}) of the Observed Absorptions of D_2CO_3 Formed in the Present Study

$\text{D}_2\text{CO}_3^{\text{a}}$	Rel. Int. ^b	$\text{D}_2\text{CO}_3^{\text{c}}$	Rel. Int. ^b	$\alpha\text{-D}_2\text{CO}_3^{\text{d}}$	Rel. Int. ^b	$\beta\text{-D}_2\text{CO}_3^{\text{e}}$	Rel. Int. ^b	Assignment
2123, 2008	m	2400-2000	s	2213, 2115	w	2600-1900	s	O–D stretch
1734	s	1677	s	1713	s	1678	s	C = O stretch
1497,1373	s	1463	s	1472, 1373	s	1472	s	C–OD asym stretch
1100	w	997	w	1085, 1075	w	1102, 1096	w	C–OD sym stretch
1071	w							? ^f
1030	m	1021	m	1065	m	1025	m	C–OD in-plane-bend
881	w							? ^f
816	m	812	m	803	m	814	m	CO_3 out-of-plane bend
783	w							? ^f

Notes.^a This study (220 K).^b Relative intensity; s: strong, m: moderate, w: weak.^c DelloRusso et al. (1993).^d Hage et al. (1996a).^e Hage et al. (1996b).^f Unable to determine.

using OD instead of OH. Figure 3(a) shows an IR spectrum of the product upon reactions of CO with OD at 40 K. The formations of D_2O_2 (~ 2400 , 2114, and 1067 cm^{-1}), D_2O (~ 2400 and 1208 cm^{-1}), O_3 (1040 cm^{-1}), and CO_2 (2356 cm^{-1}) were clearly observed in the spectrum. In addition, several intense absorptions were observed at $1300\text{--}1800\text{ cm}^{-1}$ and $700\text{--}1000\text{ cm}^{-1}$. After warming up to 220 K, several peaks were still observed in the IR spectrum (Figure 3(b)) that were consistent with those of D_2CO_3 in terms of their shapes and positions (Hage et al. 1996a, 1996b). The TPD spectra of the reaction products showed an increase in the mass signals of 20, 44, and 64 at $200\text{--}260\text{ K}$ (data not shown); these may correspond to D_2O , CO_2 , and D_2CO_3 , respectively. The IR peak positions of D_2CO_3 are listed in Table 2, together with the reference data of D_2CO_3 formed by ion irradiation of $\text{D}_2\text{O}/\text{CO}_2$ binary ices (DelloRusso et al. 1993) and α - and β - D_2CO_3 (Hage et al. 1996a, 1996b). The most distinctive way to discriminate whether it is α - or β - D_2CO_3 is to confirm the presence or the absence of absorption at 1370 cm^{-1} in the IR spectrum, respectively (Hage et al. 1996a, 1996b). D_2CO_3 formed by ion irradiation of $\text{D}_2\text{O}/\text{CO}_2$ ices does not show such an absorption (DelloRusso et al. 1993), indicating that carbonic acid formed by energetic irradiation is a β -polymorph, as proposed previously

(Hage et al. 1995). In contrast, D_2CO_3 formed in this study had a strong absorption at 1370 cm^{-1} when the substrate was warmed up to 220 K (Figure 3(b)), while it disappeared at 240 K (Figure 3(c)). Therefore, it is assumed that carbonic acid formed in this study may have either an intermediate structure between α - and β -polymorphs, or a distinctive structure previously unreported. In the former case, the IR spectrum of products might have a contribution from each amorphous form, which has a broad absorption at $3000\text{--}3500\text{ cm}^{-1}$ (Winkel et al. 2007). In the latter case, it is reasonable that the peak position derived from the C=O stretch of H_2CO_3 differs by approximately 50 cm^{-1} as compared to previous studies (Table 1).

To confirm that H_2CO_3 was not formed by surface reactions of CO_2 with H_2O fragments such as H and OH, we performed additional experiments in which OH and CO_2 were co-deposited onto the Al surface at 10 K, followed by warming up of the substrate to 250 K. No peaks were observed at around 1750 cm^{-1} after co-deposition, indicating that also in our previous experiments CO_2 was not used for any other reactions once formed. Furthermore, no products were observed during warming up, indicating that H_2CO_3 was formed only when CO and OH were co-deposited onto the Al substrate at low temperatures.

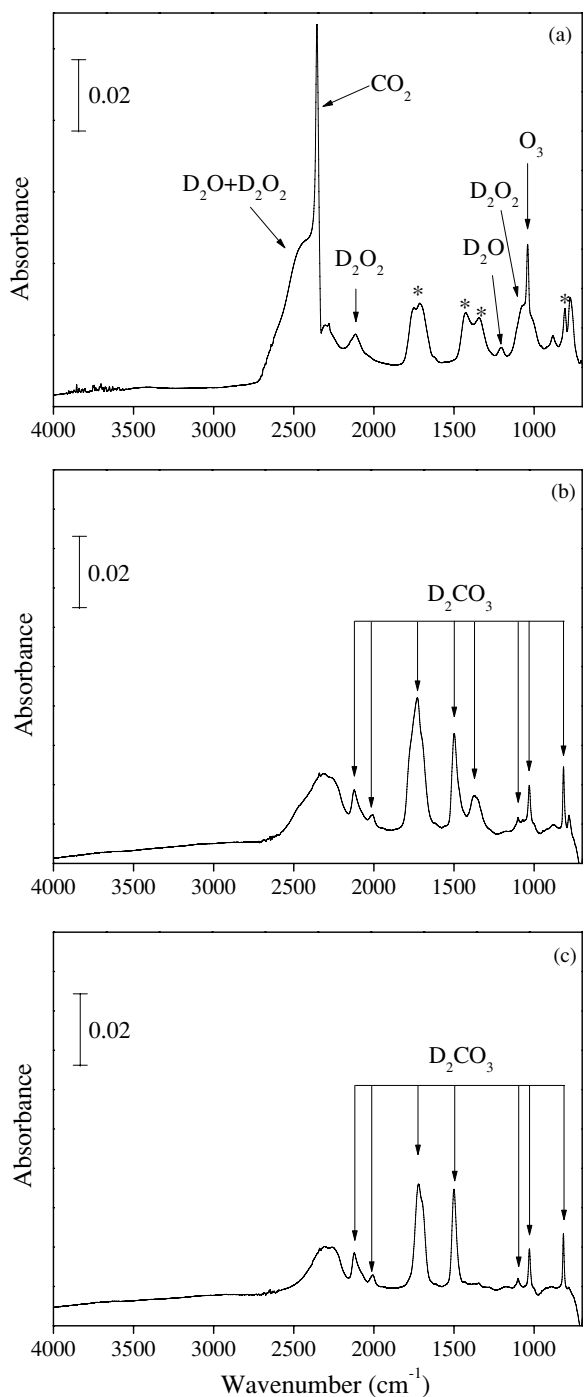


Figure 3. (a) IR spectrum of the product for OD/CO of 0.84 at 40 K after 240 minutes. (b) IR spectrum of the product warmed up to 220 K. (c) IR spectrum of the product warmed up to 240 K. Peaks with asterisks in (a) are assigned to be D_2CO_3 .

Because the intermediate product HOCO has two stereoisomers (cis- and trans-HOCO), it is therefore conceivable that two possible routes exist to the formation of H_2CO_3 : the reaction of OH either with cis- or trans-HOCO (Figure 4). Zheng & Kaiser (2007) proposed that H_2CO_3 is formed through reaction (16), i.e., the reaction of OH with trans-HOCO; this is probably because they identified only trans-HOCO in their products. In their experiment, cis-HOCO was formed by the reaction of energetic H with CO_2 , quickly followed by isomerization to trans-HOCO with the activation barrier at approximately 26,000 and 4500 K,

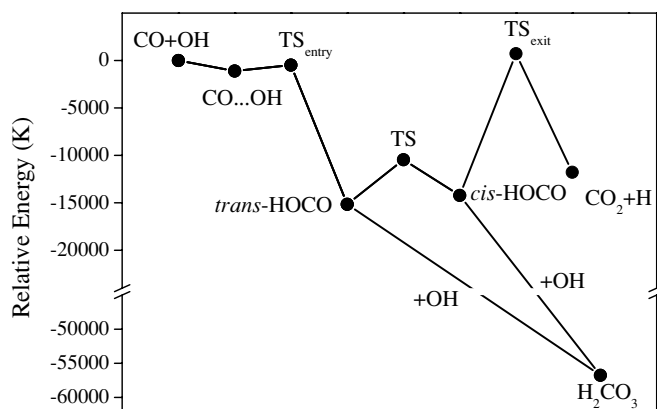
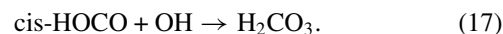


Figure 4. Possible pathways to the formation of CO_2 and H_2CO_3 initiated by reactions of CO with OH. All energies are relative to $CO + OH$, which are derived from theoretical calculations by Yu et al. (2001) for CO_2 formation in the gas phase and by Zheng & Kaiser (2007) for H_2CO_3 formation in ice. TS: transition state.

respectively (Zheng & Kaiser 2007). In contrast, cis-HOCO was already observed as well as trans-HOCO in the IR spectrum of the product at 10 K (Oba et al. 2010). On this basis, we here propose that H_2CO_3 may also be formed by reactions of cis-HOCO with OH as follows:



To summarize we may therefore say (as already announced in Oba et al. 2010 and here supported by a more detailed analysis) that the present experiment shows for the first time that carbonic acid may be formed in astrophysically relevant conditions by the interaction of non-energetic OH radicals and CO molecules. We believe that such synthesis may occur first via the formation of trans-HOCO (reaction (5)) and cis-HOCO radicals (reaction (6)), followed by their subsequent reactions with OH (reactions (16) and (17), respectively; Figure 4). Further theoretical and experimental work is necessary to prove the H_2CO_3 formation pathways envisaged above and in particular to prove whether both cis- and trans-HOCO radicals participate (and to which extent) in the formation of carbonic acid. There is no doubt in any case that in regions in which UV photons are abundant it is likely that H_2CO_3 is formed in photolyzed H_2O/CO binary ices because photolysis of H_2O/CO binary ices can easily yield CO_2 (e.g., Watanabe & Kouchi 2002b), which can be further photolyzed to yield H_2CO_3 in H_2O ices (Gerakines et al. 2000).

3.2. Quantification of Carbonic Acid Production

The column density of H_2CO_3 was calculated from peak areas of the C=O stretch ($\sim 1750 \text{ cm}^{-1}$) and the previously reported integrated band strength, as described in Hidaka et al. (2007). A correction for the light path with an IR incident angle of approximately 83° was made for this calculation. The band strength used was $1.1 \times 10^{-16} \text{ cm molecules}^{-1}$, which was obtained from transmission absorption spectroscopy of H_2CO_3 formed by UV photolysis of H_2O/CO_2 binary ices (Gerakines et al. 2000). Our estimates of column densities using reflection absorption spectroscopy may contain some errors due to the use of band strength obtained by transmission spectroscopy (Oba et al. 2009). Nevertheless, the difference in the H_2CO_3 band strength and the different IR methods should not be so critical to influence our interpretation of our results because our discussion in this study is mainly based on relative column densities. We quantified H_2CO_3 at 200 K where there was no contribution to

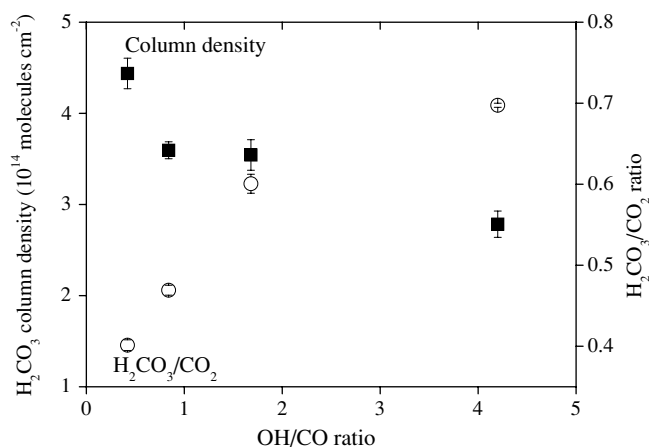


Figure 5. Variations in H₂CO₃ column density (filled square) and H₂CO₃/CO₂ ratio of the product (open circle) formed after 60 minutes at 10 K with OH/CO ratio. Symbols include statistical error.

absorption at around 1750 cm⁻¹ from other molecules present on the surface, and we do not need to consider the effect of H₂CO₃ desorption at this temperature (Figure 2).

The column density of H₂CO₃ after co-deposition of OH and CO (with OH/CO ratio of approximately 0.42) for 60 minutes at 10 K was 4.4×10^{14} molecules cm⁻²; it tended to decrease with increasing OH/CO ratio (Figure 5), where variations in the OH/CO ratio were obtained by changing the deposition rate of CO while keeping the OH deposition rate constant. The conversion factor of CO into H₂CO₃ (H₂CO₃/CO) after 60 minute co-deposition was 0.004 for OH/CO of 0.42, and it increased with increasing OH/CO up to 0.028 (OH/CO = 4.2). The conversion factor after 60 minutes may not be the maximum attainable value because the abundance of H₂CO₃ is not expected to linearly increase with time due to surface morphologies, as seen in the case of CO₂ formation through reactions (5)–(7) (Oba et al. 2010).

Next we show the relative quantities of H₂CO₃ and CO₂ (H₂CO₃/CO₂) in products, because they should be less affected by the changes in the surface morphology. Figure 5 also plots the values of H₂CO₃/CO₂ after 60 minutes at 10 K versus OH/CO. The value of the abundance ratio H₂CO₃/CO₂ increased with OH/CO, ranging from 0.40 (OH/CO = 0.42) to 0.70 (4.2). H₂CO₃ formation was assumed to occur only when the incoming OH radicals encountered thermally relaxed trans- or cis-HOCO radicals on the surface. In this case, the surface density of CO may further constrain the relative abundance of CO₂ and H₂CO₃. As the deposition rate of CO increases, i.e., the OH/CO ratio decreases, HOCO radicals were further buried with additional CO, resulting in a lower accessibility of OH to HOCO radicals. In contrast, CO₂ can still be easily produced unless intermediate HOCO is thermally relaxed in the ice because the initial reactants (CO and OH) have enough excess energy to overcome the barrier for reaction (15) and the barrier height for reaction (7) is expected to be reduced when H₂O is present (Y. Osamura 2008, private communication). Therefore, H₂CO₃ formation was inhibited and that of CO₂ was promoted, which resulted in the lower H₂CO₃/CO₂ ratio of the product (Figure 5).

Under the conditions in which OH/CO = 0.84, the column density of H₂CO₃ after 60 minute co-deposition of CO and OH was 3.6×10^{14} molecules cm⁻² at 10 K and varied with temperature (Figure 6). As for the H₂CO₃/CO₂ ratio of products,

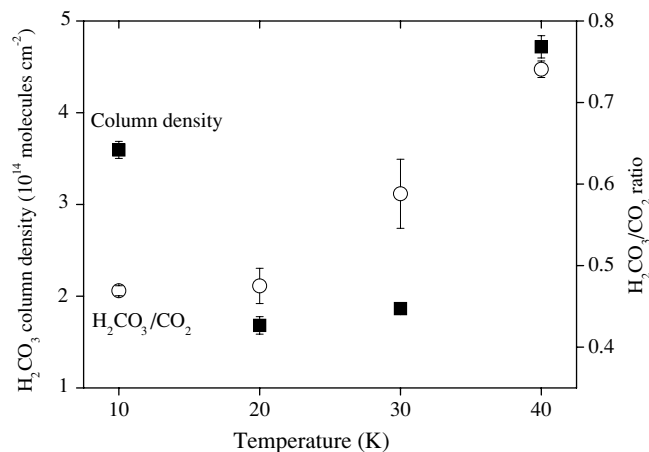


Figure 6. Variations in H₂CO₃ column density (filled square) and H₂CO₃/CO₂ ratio of the product (open circle) formed after 60 minutes at the OH/CO of 0.84 with temperature. Symbols include statistical error.

it was almost the same at approximately 0.47 at 10 and 20 K. At higher temperatures, the ratio increased with temperature to up to 0.74 at 40 K. Although the H₂CO₃/CO₂ ratio did not differ between 10 and 20 K, the column density of H₂CO₃ at 10 K was almost twice as large as that at 20 K (Figure 6). This may be related to the OH-consumption pathways at each temperature. One representative pathway for OH radicals consumption under the present experimental conditions is the reaction of two OH radicals to yield H₂O₂. OH radicals should also react with atomic O without barriers to yield O₂ and atomic H. The formed O₂ may be further used for the formation of O₃ through reactions with atomic O. In blank experiments, the yield of H₂O₂ at 20 K was approximately 15% less abundant than that at 10 K, while the yield of O₃ at 20 K was approximately four times larger than that at 10 K. This can be explained as follows: at 20 K, atomic O may be more mobile than 10 K, which increases the frequency of encountering OH on the surface. If this is the case, fewer OH radicals are available for reactions with CO and HOCO at 20 K. Therefore, the column density of H₂CO₃ at 20 K was assumed to be smaller than that at 10 K, which is consistent with the variations in the CO₂ column density formed at 10 and 20 K (Oba et al. 2010). The most abundant formation of H₂CO₃ at 40 K (Figure 6) within the temperature range (10–40 K) we studied may be partly due to the high mobility of OH radicals at that temperature. Variations in the H₂CO₃/CO₂ ratio with temperature may also imply the dependence of H₂CO₃/CO₂ on the surface density of CO. At 10 and 20 K, the H₂CO₃/CO₂ ratio of products was almost the same (~0.47; Figure 6). Because the sticking probability of CO was assumed to be unity at both temperatures, the surface density of CO should be similar at both temperatures. In contrast, at temperatures higher than 30 K, a large part of adsorbed CO should quickly desorb from the substrate, which would enable additional OH radicals to react more with trans-HOCO. Therefore, the H₂CO₃/CO₂ ratio increased with temperature under constant OH/CO conditions (Figure 6).

It should be noted that the H₂CO₃/CO₂ ratio of products under the experimental conditions of this study was always quite high (>0.4; Figures 5 and 6), although the H₂CO₃/CO ratio was low (0.004–0.028 at 10 K). These results indicate that the consumption of CO is not rapid but once HOCO is produced from CO + thermal OH, roughly half of the HOCO radicals can stabilize in ice without leading to CO₂ and react with another

OH. In contrast, HOCO formed by energetic processes such as UV irradiation of H₂O/CO binary ices should have considerable excess energy to overcome barriers for reactions (6) and (7), which results in the almost complete conversion to CO₂ + H (e.g., Watanabe & Kouchi 2002b).

4. ASTROPHYSICAL IMPLICATIONS

Carbonic acid has not been detected yet in interstellar clouds either in the solid or in the gas phase. This is certainly not due to a scarce production; in fact, even not considering the gas phase production, which has never been investigated in astrophysical conditions, several experimental studies (e.g., Moore & Khanna 1991; Gerakines et al. 2000; Zheng & Kaiser 2007, and this study) show that it is quite abundantly produced in the solid phase and therefore should exist in grain mantles. Gerakines et al. (2000) estimated the upper limit of H₂CO₃ column density formed by energetic processes toward Elias 16 to be 4.6×10^{16} molecules cm⁻², which is approximately 0.2% of the total H₂O in this line of sight. In order to estimate the H₂CO₃ abundance formed by non-energetic processes in molecular clouds, we need to know the OH/CO ratio in those environments. At the OH/CO of 0.42–4.2, the H₂CO₃ abundance relative to H₂O in molecular clouds can roughly be estimated from the H₂CO₃/CO₂–OH/CO correlation in Figure 5 and from the CO₂ abundance relative to H₂O. However, under the actual ISM conditions, the OH/CO could be lower than the lowest OH/CO achieved in the present experiment (0.42). Then, by simply assuming that the H₂CO₃/CO₂ ratio decreases linearly toward zero as OH/CO approaches to 0 from 0.42 (Figure 5), we can roughly estimate the value of H₂CO₃/CO₂ at lower OH/CO. For example, at the OH/CO ratio of 0.1, the estimated abundance of H₂CO₃ formed by non-energetic processes in Elias 16, where the CO₂ abundance is 24% relative to H₂O (Knez et al. 2005), is 2.3% relative to H₂O. This value is about 1 order of magnitude higher than that estimated to be obtainable by energetic processes. Assuming that laboratory and interstellar fluences directly scale and that laboratory conditions can be directly translated to interstellar conditions, the studied non-energetic reactions are effective pathways to the formation of H₂CO₃ in molecular clouds.

We explained that the surface density of CO may partly constrain the relative abundance of H₂CO₃ under the present experimental conditions. In the ISM, however, whether H₂CO₃ is formed or not may also depend on the abundance and stability of HOCO radicals in those environments. The existence of HOCO radicals in ice mantles on interstellar grains has never been reported, while protonated carbon dioxide or HOCO⁺ has been positively identified toward protostar IRAS 04368+2557 in L1527 (Sakai et al. 2008). The stability of HOCO radicals against photons, ions, and electrons is not yet well understood; however, the detections of HOCO radicals in photolyzed (Milligan & Jacox 1971) and electron-irradiated (Zheng & Kaiser 2007; Bennett et al. 2010) ices imply that they can partly survive against energetic irradiation in solids. Once formed by reaction (5), a portion of HOCO radicals should yield CO₂ + H, as experimentally demonstrated previously (Oba et al. 2010). As for the unreacted HOCO radicals, a part of the excess energy is transferred to the grain surface, and the radicals thus become stabilized (Goumans et al. 2008). If this is the case, the reaction of HOCO radicals with OH may be possible on grain surfaces in molecular clouds. Goumans et al. (2008) proposed that HOCO radicals can react with atomic H to yield HCOOH, CO₂ + H₂, or H₂O + CO without a barrier. Because H atoms are more abun-

dant than OH radicals in dense molecular clouds, HOCO will react more with atomic H rather than OH radicals. However, at temperatures higher than the desorption temperature of atomic H (>20 K), reactions with atomic H are not expected to occur. On the other hand, H₂CO₃ formation becomes more effective at temperatures higher than 30 K (Figure 6). Therefore, the formation of HOCO as well as H₂CO₃ may occur in relatively warm environments, as demonstrated in this study.

The reason why H₂CO₃ has not yet been detected is probably due to multiple effects like the superposition of its spectral feature with those of more abundant species; its high destruction rate, due to reactions in which it contributes as a partner to the chemical enrichment of ice mantles; and furthermore because carbonic acid is more refractory than water and to be released in the gas phase energetic processes induced by fast ions (sputtering) or UV photons (photosputtering) are needed.

Certainly the first and probably most important reason for the non-detection of carbonic acid in interstellar environments is that even if H₂CO₃ does exist in the solid phase, it is not easy to be detected in astronomical observations because its most pronounced spectral feature at ~ 1700 cm⁻¹ (C=O stretching) is obscured by strong absorptions from abundant H₂O.

H₂CO₃ is easily destroyed by UV irradiation (Gerakines et al. 2000), but another relevant reason for its non-detection is that carbonic acid may be consumed in chemical reactions in the icy mantle. As a matter of fact, H₂CO₃ might yield to the formation of NH₄⁺ through an acid–base reaction with NH₃. Novozamsky et al. (2001) reported that NH₄⁺ is formed by acid–base reactions of HNCO with NH₃ even at 12 K, indicating that proton transfer can occur in molecular clouds. H₂CO₃ is known to be an acid molecule with an acid dissociation constant (pK_{a1}) of approximately 1–6 at 298 K (Wang et al. 2008), which is similar to that of HNCO (pK_a = 3.85 at 298 K; Krejzle & Siekierski 1995); thus, H₂CO₃ may have a role as a proton donor in molecular clouds. In fact, Schutte & Khanna (2003) suggested that the formation of NH₄⁺ in photolyzed H₂O/CO₂/NH₃/O₂ ice mixtures was partly due to proton transfer to NH₃ from H₂CO₃ which is also formed during irradiation. Based on the results of this study, we further propose that NH₄⁺ formation can occur through acid–base reactions between H₂CO₃ and NH₃ without photons if both species do exist in molecular clouds.

If H₂CO₃ does exist in molecular clouds, the absorption at ~ 1500 cm⁻¹ (~ 6.7 μm) may contribute to the unidentified 6.8 μm band observed in various lines of sight (e.g., Gibb et al. 2004), as proposed by Hage et al. (1998). Many studies have proposed that various classes of compounds such as saturated hydrocarbons (Tielens et al. 1984), methanol (Allamandola et al. 1992), formaldehyde (Schutte et al. 1996), ammonium ion (NH₄⁺; Grim et al. 1989; Schutte & Khanna 2003; Moon et al. 2010), and inorganic compounds such as carbonate (Sandoford & Walker 1985) and calcium oxide (Kimura & Nuth 2005) may contribute to the interstellar 6.8 μm band. Furthermore, hydrogen peroxide (H₂O₂) may contribute as well (Y. Oba et al. 2010, in preparation) because it is a stable intermediate product of H₂O formation through hydrogenation to O₂ molecules (Tielens & Hagen 1982; Miyachi et al. 2008; Ioppolo et al. 2008; Oba et al. 2009) and has absorptions at around 7 μm. In addition, recent observations by *Spitzer* support the possibility that the 6.8 μm band has one or two carriers and at least one of them is less volatile than H₂O (Boogert et al. 2008), which agrees very well with the property of H₂CO₃.

The IR spectrum toward Elias 16 has absorptions at ~ 5.9 μm (~ 1700 cm⁻¹), ~ 6.8 μm (~ 1470 cm⁻¹), and 7.5 μm

(1330 cm^{-1}), even after removing silicate and H_2O contributions (Knez et al. 2005), which resemble the band positions for the C=O stretch, C–OH asymmetric stretch, and C–OH in-plane bend of H_2CO_3 , respectively (Table 1). Therefore, we believe that if H_2CO_3 does exist in molecular clouds, it is a possible carrier of the unidentified 6.8 μm band. More exactly, H_2CO_3 may not only contribute to the 6.8 μm band directly but also indirectly by producing NH_4^+ through acid–base reactions in molecular clouds. In the latter case, an astronomical detection of HCO_3^- may support the existence of H_2CO_3 in molecular clouds.

In this case, it would be possible in the future to observe with a high enough resolution the peak shape of H_2CO_3 ; it might prove to be a useful tool for discriminating whether carbonic acid has been formed by energetic or non-energetic processes because it varies with the formation process.

Finally, some considerations regarding the release in the gas phase of carbonic acid are suitable. H_2CO_3 is more refractory than water ice and in addition, the release of H_2CO_3 to the gas phase from icy mantles is unlikely because it readily decomposes during desorption if H_2O is present near H_2CO_3 (Loerting et al. 2000). Therefore, desorption induced by thermal spikes suffered, even locally, by the grains due to the impulsive release of energy by UV photons and the light component of cosmic rays (protons and helium nuclei), the most abundant, is ruled out as a possible mechanism to release intact carbonic acid molecules in the gas phase.

Another mechanism, further, may assure restoration in the gas phase of H_2CO_3 . On the basis of the experimental results by Hedin et al. (1987), Johnson et al. (1991) proposed that the heavy component of cosmic rays may explain the abundance of the longest molecules in the ISM—molecules like HC_{11}N that would take too long to be formed by gas phase reaction schemes. Hedin et al.'s (1987) results showed that entire molecules of leucine (together with several fragments) are released from a layer of condensed leucine irradiated by about 0.6 MeV amu^{-1} ions (^{32}S , ^{58}Ni , ^{79}Br , ^{127}I). These thermally labile molecules were not all fragmented because a volume of material larger than the single molecules was impulsively (in a timescale lower than 10^{-11} s) ejected. Molecular dynamics calculations (Fenyo et al. 1990) showed a roughly cubic dependence of the volume of the material ejected on the energy per unit path length (dE/dx) deposited by the heavy ions. Such energy, before being thermalized, sets up a large pressure gradient in the solid component leading to a removal of a roughly hemispherical chunk of the material having radius proportional to dE/dx . The same mechanism might be responsible for the ejection of entire H_2CO_3 molecules present in the ice mantle. Naturally the disruption of the mantle by the arrival of a heavy ion is a rare but effective event that would involve both sides of the grain along the ion track. Clearly the actual efficiency of the mechanism will depend on the actual concentration of carbonic acid in the ice, due to both formation and destruction processes.

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