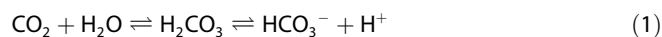


Aqueous Carbonic Acid (H₂CO₃)

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Carbonic acid (H₂CO₃) is a molecule right at the interface between organic and inorganic chemistry. In fact, according to some definitions it is an organic molecule, while according to others it is an inorganic molecule. Its exceptionality can also be recognized from the fact that it formally belongs neither to the mono- nor dicarboxylic acids, even though it is a C1 diprotic acid. The diprotic nature, that is, the ability to react to its conjugate base bicarbonate (HCO₃⁻) and to carbonate (CO₃²⁻), provides a link to geology and mineralogy. Carbonate minerals such as calcite, dolomite or siderite are ubiquitous in sedimentary rock. In addition to the acid–base equilibrium, carbonic acid is in equilibrium with carbon dioxide and water. Both equilibria can be summarized as Equation (1):



In mineralogy, it has long been known that carbonate minerals kept in acidic environments dissolve and release carbon dioxide.^[1,2] This process of weathering impedes efforts to preserve buildings made from carbonates.^[3] Only recently was it recognized that carbonic acid may be a relatively stable intermediate as a surface-adsorbed species in the presence of acidic gases, but only in case of dry conditions near 0% relative humidity.^[4–6] Once the humidity increases to up to 5%, the surface-adsorbed H₂CO₃ immediately decomposes to carbon dioxide, leaving behind a Ca(OH)(CO₃H) surface. In marine science, this link between carbon dioxide and acidic behaviour is of importance in understanding ocean acidification and dissolution of carbonate minerals induced by uptake of anthropogenic carbon dioxide from the atmosphere.^[7–9] In physiology, the kidneys and lungs work together to maintain a blood pH of 7.40 ± 0.05 by balancing carbon dioxide and bicarbonate levels in the bloodstream. In case this balance is disturbed, acidosis (pH < 7.35) or alkalosis (pH > 7.45) can result. For example, when one hyperventilates, carbon dioxide is lost, which shifts the equilibrium to the left (“alkalosis”). The process of converting these species into each other has to be so efficient in all living organisms that one of the enzymes that accelerate the reaction is one of the fastest known by biochemists. This enzyme belongs to the family of carbonic anhydrases and shows turnover rates of up to 10⁶ reactions per second.

Because of the two equilibria in Equation (1), a solution of carbon dioxide in water reacts as an acid. However, the neutralization of carbon dioxide is a slow process compared with

other weak acids.^[10] In 1912 McBain showed in a simple and memorable experiment that the neutralization process of basic solutions with solutions saturated with carbon dioxide progresses rather slowly. He coloured the basic solution with the pH indicator phenolphthalein in pink, and this colour fades away slowly within fifteen seconds, after which neutralization is complete.^[11,12] By contrast the neutralization with, for example, formic acid takes place suddenly at the moment of mixing. The reason for the delay is that only much less than 1% of the solution exists as H₂CO₃. Eigen et al. have even asked the question whether H₂CO₃ is a short-lived intermediate, as implicitly assumed in Equation (1), or rather a transition state, which can not be isolated at all.^[13] The slow kinetics of the first step together with the much faster second step of deprotonation prevent a significant build-up of transient H₂CO₃. This makes observation of carbonic acid in aqueous solution a real challenge, and all researchers failed to observe carbonic acid when walking down the route of hydration of carbon dioxide.

The acid dissociation constant K'_a in the temperature range between 0 °C and 50 °C was determined by a few researchers in the first half of the 20th century.^[14–19] All data are in quite good agreement and show $\text{p}K'_a(\text{CO}_2 \text{ in } \text{H}_2\text{O}, 25^\circ\text{C}) \approx 6.4 \pm 0.1$. This was referred to as the acid dissociation constant of “carbonic acid”, but in fact involves both equilibria, that is, hydrated carbon dioxide is also present in equilibrium. It is, therefore, more appropriate to regard this number as the “apparent” dissociation constant of carbonic acid. We use the notion K'_a in order to indicate that more than one process is involved. The “true” dissociation constant of carbonic acid (defined as $K_a = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$) remained unclear due to the presence of carbon dioxide in the equilibrium. Determining K_a would require dissolving H₂CO₃ in water and measuring the pH or bicarbonate equilibrium concentration. This remained a gedankenexperiment simply because pure H₂CO₃ could not be synthesized and isolated for a long time, and also because it decomposes on the time scale of seconds in aqueous solutions.^[20–22] In some contemporary chemistry textbooks H₂CO₃ is described as an instable species decomposing rapidly to carbon dioxide and water, which can not be isolated in its pure form.^[23] This is no longer correct. Evidence that carbonic acid has enough thermal stability to allow for its characterization using standard techniques accreted in the late 1980s and 1990s, both in the solid phase and in the gas phase.

In 1993 the Innsbruck group succeeded not only in isolating micrometer-thick films of pure H₂CO₃, but also in characterizing this species by FTIR spectroscopy.^[24] This was possible by means of a cryo-technique for isolation of short-lived intermediates in acid–base reactions, in this case the protonation of bicarbonates studied at temperatures ranging from 77 K to

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240 K. The first isolation was performed in methanolic solution,^[24] later on in aqueous solution as well, or, more precisely, in an ice matrix.^[25] In both cases the IR spectra, after removal of the solvent, can be clearly attributed to crystalline H_2CO_3 because of the position and sharpness of the bands as well as several band splittings. Still, the spectra obtained from the two different solvents show some bands at clearly different wavelengths, with different intensities and different band splitting. This implies that carbonic acid crystallizes in (at least) two different polymorphs called $\alpha\text{-H}_2\text{CO}_3$ (from the methanolic solution) and $\beta\text{-H}_2\text{CO}_3$ (from the aqueous solution). The unambiguous assignment of the bands was possible by IR characterization of the D and ^{13}C isotopic forms crystallized both from methanolic^[26] and aqueous solutions.^[27] Lately, it was recognized that immediately after removal of the solvent, two amorphous solids of carbonic acid can be characterized, which develop into crystalline solids upon heating. This transition takes place within hours at ~ 200 K and within minutes at ~ 220 K and was followed by Raman^[28] and IR spectroscopy and powder X-ray diffraction.^[29] The basic structural motif found in the two polymorphs of carbonic acid has already developed in the two amorphous forms. From spectroscopic considerations the building block in the β -polymorph and in the amorphous precursor is a centrosymmetric unit such as the cyclic carbonic acid dimer.^[28] The crystal structure of the two polymorphs is not yet known, though. In a vacuum chamber ($\sim 10^{-7}$ mbar) the two polymorphs are stable up to ~ 210 K (α) and ~ 230 K (β). At these temperatures desorption rates are so high that the sample is pumped off.

In 1991, after irradiation of a 1:1 mixture of solid carbon dioxide and H_2O -ice with 700 keV protons at 20 K, Moore and Khanna obtained a mixture of several radical and molecular product species, and after heating to 215–250 K they observed an unknown species by FT-IR spectroscopy, which they tentatively (and correctly) assigned to crystalline carbonic acid.^[30–32] Besides proton irradiation, UV bombardment^[33] and ion implantation^[34] also have the potential to convert carbon dioxide water ices to carbonic acid, even though this is limited to the near surface area. For instance, 4:1 mixtures of water and carbon dioxide are converted to carbonic acid under high-flux UV radiation at the wavelength of prominent solar lines.^[35] This implies that in outer space cryogenic $\text{CO}_2\text{-H}_2\text{O}$ deposits will possibly be converted to $\beta\text{-H}_2\text{CO}_3$ after irradiation.^[36] Indeed, the 2.4–5.0 μm spectral region of comet Halley shows several bands consistent with the IR-bands found in the laboratory.^[37] The infrared spectra of the Martian surface and of the Galilean satellites of Jupiter^[38–40] are also at wavelengths very similar to that of carbonic acid. Lately, solid carbonic acid has also been discussed as a surface compound on Edgeworth–Kuiper–Belt bodies.^[41] In these environments carbonic acid can occur either as the crystalline β -polymorph or as an amorphous solid.

Observation of carbonic acid in the gas-phase was first claimed by Terlouw et al. after thermolysis of $(\text{NH}_4)\text{HCO}_3$.^[42] They succeeded in observing a weak signal at $m/z=62$ by electron-ionization mass spectroscopy, which they attributed to gas-phase H_2CO_3 .^[42] The intensity of the signal was less than 1% of the signal arising from the decomposition product

carbon dioxide, but could still be selected as parent ion for fragmentation studies. In the gas-phase three possible conformations of carbonic acid are possible, which can be interconverted by rotating around the angles Φ_1 and Φ_2 (see Figure 1).

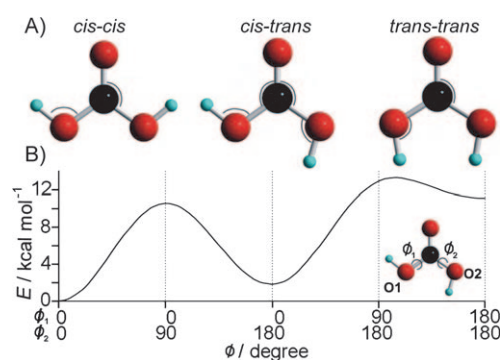


Figure 1. A) Conformational isomerism of the carbonic acid monomer. The isomers can be interconverted by changing either one of the two dihedral angles Φ_1 or Φ_2 (inset). B) Calculated potential energy curve showing that there are two low-energy minima (*cis-cis*, *cis-trans*) and one high-energy minimum (*trans-trans*) in the gas-phase. The curve was obtained from ab initio calculations of the gas-phase molecule at the CCSD(T)/cc-pVQZ level of theory. The potential energy curve for conformational isomerism in aqueous solution is unknown at present. The figure is adapted from ref. [44], with permission.

The three rotamers representing local potential minima are called *cis-cis*, *cis-trans* and *trans-trans*. According to calculations the *cis-cis* conformation is the most stable, mostly because both hydrogen atoms form a weak internal hydrogen bond. The *cis-trans* conformation is less stable by $\sim 1\text{--}2$ kcal mol^{-1} ,^[43,44] that is, in equilibrium at 200 K one would expect the *cis-cis* rotamer to be the main conformer, whereas less than 10% of *cis-trans* monomers are expected. The *trans-trans* conformation is less stable by more than 10 kcal mol^{-1} and is not supposed to appear in experiments (see Figure 1). In some calculations it is even an unstable transition state rather than a metastable equilibrium state. By contrast, the cyclic dimer $(\text{H}_2\text{CO}_3)_2$ is stabilized by two strong hydrogen bonds and, therefore, the enthalpy of decomposition to carbon dioxide and water is astonishingly close to zero.^[45] For this reason, an appreciable fraction of the cyclic dimer $(\text{H}_2\text{CO}_3)_2$ is thought to be present in the gas phase. Higher oligomers such as $(\text{H}_2\text{CO}_3)_3$ are thermodynamically even more stable in the gas phase,^[46] but are not thought to occur because an encounter of three or more carbonic acid molecules in the gas phase is extremely unlikely. On this basis, Tossell has even suggested a strategy for capturing and sequestration of carbon dioxide in the form of solid carbonic acid.^[47]

While *cis-trans* H_2CO_3 could be positively identified in experiments,^[44] a clear spectroscopic proof for the presence of *cis-cis* H_2CO_3 and cyclic $(\text{H}_2\text{CO}_3)_2$ is currently missing. *Cis-trans* H_2CO_3 and three deuterated isotopologues were generated in a supersonic jet within a discharge nozzle by applying a pulsed high voltage of 1.8 kV on a gas mixture saturated with water vapour and containing 5% carbon dioxide and identified from the observation of pure rotational transitions by Fourier-

transform microwave spectroscopy.^[44] It remains unclear why in this experiment the thermodynamically most stable rotamer is not observed, but a metastable one instead. Hage et al. showed that crystalline H_2CO_3 can be sublimed and recondensed without decomposition to CO_2 and H_2O .^[37] After desorption at ~ 220 K and flying for a few centimetres through the gas phase, roughly 50% of the initial amount recondensed as $\alpha\text{-H}_2\text{CO}_3$ on a window kept at ~ 10 K. This is consistent with a high kinetic stability of water-free carbonic acid as inferred from transition state theory considerations.^[48] Once water is present, the half-life with respect to decomposition to carbon dioxide is greatly reduced from 180 000 years (water-free) to roughly a minute in a 1:3 complex of water with carbonic acid.^[49] When hydrated with water carbonic acid decays via thermally easily accessible transition states by a proton-relay mechanism rather than via a highly strained four-membered transition state.^[48,50,51] Kinetic isotope effects and rate constants are in rather good agreement with experiments, which suggests that any attempt of detecting carbonic acid in aqueous solution has to be done on timescales faster than a second.

Some fast techniques were developed more than 50 years ago in order to cope with this challenge, such as rapid mixing or stopped-flow techniques followed by a time-dependent readout of fast high-field conductance,^[52] temperature^[20] or pH.^[53] Using such techniques, the “true ionization constant” was determined to be $\text{p}K_a \approx 3.8$ in the temperature range $5\text{--}45^\circ\text{C}$ at zero ionic strength^[54] and later refined to $\text{p}K_a \approx 3.45 \pm 0.05$.^[53] This renders carbonic acid a stronger acid than for example, acetic acid ($\text{p}K_a \approx 4.7$) and comparable to formic acid ($\text{p}K_a \approx 3.8$). It should therefore not be ignored in discussions of ocean acidification, especially in view of increasing atmospheric CO_2 mixing ratios.

Spectroscopic identification of carbonic acid has remained elusive for quite a long time. The first report in solution was possible by means of a fast technique, namely rapid acquisition of Raman spectra in a continuous flow apparatus.^[55] Rather than walking down the route of carbon dioxide hydration, Falcke and Eberle took the reverse pathway of protonation of bicarbonates, which provides the possibility of a significant buildup of intermediary carbonic acid as a slow second step (decomposition) follows a rapid first step (protonation). After rapid acidification of 1 M NaHCO_3 with 3 M HCl to $\text{pH} \approx 0\text{--}1$ they succeeded to observe a marker band of carbonic acid, namely the C–OH stretching vibration at 1017 cm^{-1} , and followed its time-dependent decay caused by decomposition to carbon dioxide (observed at 1280 cm^{-1} and 1382 cm^{-1}).^[55] The analysis of the kinetics of decomposition has proven to be difficult because bicarbonate in aqueous solution shows a band at 1017 cm^{-1} overlapping with the marker band of carbonic acid.^[56] The rate of decomposition to carbon dioxide by Falcke and Eberle is slightly higher than the earlier literature data.^[20] In the very recent work by Adamczyk et al. the C=O stretching vibration was used for spectroscopic observation of aqueous H_2CO_3 .^[57] The C=O mode has the advantage that there is no overlap between carbonic acid (C=O double bond), bicarbonate (C–O 3/2 bond) or carbonate (C–O 4/3 bond)

[Figure 2]. This mode can be observed only with difficulty by using Raman spectroscopy, but easily using infrared spectroscopy. The work by Adamczyk et al.^[57] goes far beyond what

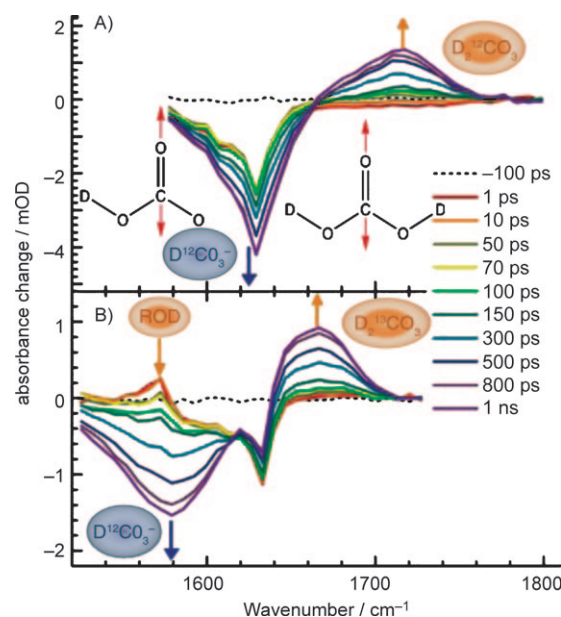


Figure 2. Time-resolved infrared spectra in the $\nu(\text{C}=\text{O})$ range $1520\text{--}1800\text{ cm}^{-1}$. A) The deuteration of aqueous $\text{D}^{12}\text{CO}_3^-$ producing aqueous $\text{D}_2^{12}\text{CO}_3$ is followed. B) The deuteration of aqueous $\text{D}^{13}\text{CO}_3^-$ producing aqueous $\text{D}_2^{13}\text{CO}_3$ is followed. For both C-isotopes a correlated decrease of the bicarbonate marker mode (arrows pointing down) and the rise of the carbonic acid C=O stretching marker band (arrows pointing up) is observed. In case of ^{13}C the bicarbonate mode overlaps with a mode of the photoacid, which triggers the deuteron transfer event at the time of 0 ps. A simplified normal-mode depiction is shown in the inset. The figure is adapted from ref. [57], with permission.

Falcke and Eberle achieved. They used time-resolved femtosecond infrared spectroscopy and even succeeded to monitor the buildup of D_2CO_3 also by walking down the lane of ultrafast protonation of bicarbonate. In a system buffered at $\text{pD} = 8$ they observe the protonation of NaDCO_3 at relatively high ionic strengths ($0.1\text{--}0.8\text{ M}$ solutions) on the fly, which is highly non-trivial because this event takes place within one nanosecond. The most elegant aspect of this study is that the proton transfer reaction can be triggered by a short pulse of light. The source of the proton is a “photoacid”. Typical photoacids suitable for studying proton transfer reactions in aqueous solutions are pyranine (8-hydroxypyrene-1,3,6-trisulfonate, HPTS) or 2-naphthol-6,8-disulfonate (2N-6,8S). For the latter, the dissociation constant in the ground state $\text{p}K_a(S_0) \approx 9.3 \pm 0.1$, while in the excited state $\text{p}K_a(S_1) \approx 1.2 \pm 0.2$. That is, the proton is not donated to water in the ground state, but in the excited state. Thus, the short pulse of light at 330 nm excites the photoacid, weakens its OH-bond and triggers proton transfer. The events following the proton transfer can be followed on a femtosecond time resolution, for example by infrared spectroscopy, which provides the basis for observations of microscopic details of proton transfer events with unprecedented resolution.^[58] For instance, the traditional Eigen–Weller picture of

neutralization reactions between an acid and a base in water has been shown by Rini et al. to need refinement to a three-stage model using this technique.^[59] Also, proton exchange between an acid and a base in aqueous solution has been shown to proceed by a sequential von Grothuss-type proton-hopping mechanism through water bridges involving intermediary H_3O^+ ions stabilized in the Eigen configuration.^[60]

In the case of proton transfer to bicarbonate, or more precisely, deuteron transfer to DCO_3^- , the question to be answered was whether or not carbonic acid D_2CO_3 would form as a transient species, and this can be clearly positively answered now when inspecting the data collected by Adamczyk et al., which is reproduced in Figure 2, where it is shown that the C=O stretching vibration shifts from 1628 cm^{-1} , which is characteristic of DCO_3^- , to 1720 cm^{-1} , which is characteristic of carbonic acid. The process occurs simultaneously, as can be seen from the fact that the increase in peak area below the 1720 cm^{-1} marker band is proportional to the loss below the 1628 cm^{-1} marker mode. The assignment of this band to the C=O stretching band is ascertained by observing the expected $^{12}\text{C}/^{13}\text{C}$ isotope shift, namely to 1579 cm^{-1} for $\text{D}^{13}\text{CO}_3^-$ and to 1666 cm^{-1} for $\text{D}_2^{13}\text{CO}_3$. The shifts of -49 cm^{-1} and -54 cm^{-1} , respectively, are in good agreement with the shifts observed for the C=O stretching mode in crystalline carbonic acid.^[26,27] Together with the simultaneous build-up of the deprotonated photoacid (marker modes at 1410 cm^{-1} and 1510 cm^{-1}) and the simultaneous loss of photoacid (marker mode at 1472 cm^{-1}) this observation eliminates any doubt about the formation of D_2CO_3 in aqueous solution. The formation is complete after a few hundred picoseconds according to the data in Figure 2. On this time scale no decomposition to carbon dioxide is observable, which is monitored by the absence of the CO_2 marker mode at 2364 cm^{-1} . From the kinetic data an on-contact deuteron transfer time of 8 ps is extracted, and a deprotonation rate slower by roughly four orders of magnitude, 280 000 ps, is calculated. The deprotonation is still much faster than decomposition to carbon dioxide, which takes place in the order of seconds. Thus, the lifetime of D_2CO_3 clearly exceeds a few nanoseconds. From a Marcus plot, Adamczyk et al. obtain an acidity constant of $\text{p}K_a = 3.45$ for carbonic acid. Computational predictions on the basis of CBS-QB3 gas phase calculations and a continuous solvation model (CPCM) result in $\text{p}K_a(\text{cis-cis}) = 3.8$, $\text{p}K_a(\text{cis-trans}) = 3.6$ and $\text{p}K_a(\text{trans-trans}) = 2.2$.^[61] Assuming an error of ± 0.5 , the comparison between experiment and calculation suggests that both *cis-cis* and *cis-trans* are species relevant in aqueous solution, but not *trans-trans*. What remains open from this study is whether water molecules act as shuttles to transfer the proton from the photoacid to bicarbonate (or, more unlikely, whether the protonation is direct). It also remains unanswered whether the decomposition reaction depends on specific conformations of the carbonic acid molecule. From theoretical calculations it seems that oligomers such as the dimer^[45] and the most stable monomer conformer (*cis-cis*) have to pass through a high transition state, whereas the less stable *cis-trans* conformer can access a lower transition state, and may be hence of higher importance in understanding decomposition to carbon dioxide.^[48,49] We

hope these issues will be addressed in future studies on much longer time scales than employed in the present meticulous work by Adamczyk et al.^[57] In view of the astrophysical relevance of carbonic acid it would also be of interest to study the rates of protonation/deprotonation in glassy water or ice matrices at low temperatures rather than in aqueous solution.

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Keywords: acidity · carbonic acid · IR spectroscopy · metastable compounds · time-resolved spectroscopy

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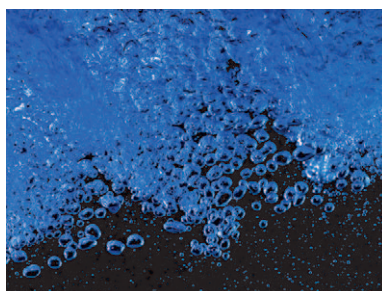
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HIGHLIGHTS

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Aqueous Carbonic Acid (H_2CO_3)



Rewrite the textbooks! Observation of the species H_2CO_3 has remained an elusive goal for a long time. The recent real-time observation of formation kinetics of aqueous carbonic acid highlighted herein follows earlier reports of the observation of pure carbonic acid in the gas-phase and in the solid-phase.