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In Spite of the Chemist's Belief: Carbonic Acid Is Surprisingly Stable

Ralf Ludwig* and Andreas Kornath*

It is conventional wisdom in any chemistry textbook that carbonic acid is kinetically unstable. Accordingly, the recently published Encyclopedia of Inorganic Chemistry[1] still claims: "Pure carbonic acid, H_2CO_3, cannot be isolated because of its ready dehydration to carbon dioxide, CO_2." Despite belief in the nonexistence of carbonic acid, chemists succeeded in recognizing its stability in the last few years. They were able to synthesize carbonic acid at low temperatures by high-energy irradiation of cryogenic carbon dioxide/water ice mixtures[2, 3], proton-irradiation of pure solid CO_2[4] and by protonation of bicarbonate[5, 6]. The resulting carbonic acid was characterised by IR spectroscopy and mass spectrometry. Recently Liedl and coworkers[7] explained in a beautiful theoretical work why carbonic acid can exist in its free form and why chemists thought and taught for so long that this compound is unstable.

Carbonic acid is of special importance in biological and geochemical carbonate-containing systems. The equilibrium of carbonic acid with carbon dioxide and water and its significance are well recognized and carefully studied. Despite the reaction [Eq. (1)] making carbonates the most abundant minerals on earth, carbonic acid is difficult to observe spectroscopically in its free state.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (1)$$

Carbonic acid is known to be present to the extent of about 0.003 % in water containing dissolved CO_2. The dissociation constant of carbonic acid is large in comparison with those of other hydrates. This has been understood as a result of the high stability of the unhydrated species, CO_2. However, an activation energy of 15.5 $\text{kcal}\,\text{mol}^{-1}$[8] for the dissociation reaction of carbonic acid to water and carbon dioxide suggested that it should be possible to observe carbonic acid in its free state.

In fact, there had been two claims of the preparation of free carbonic acid as an etherate, but no spectral evidence was provided. Isolation of such an ether complex was achieved by the addition of an etheral solution of anhydrous hydrogen chloride to a suspension of finely crushed sodium bicarbonate in ether at 243 K.[9] Cooling the solution to 195 K resulted in the precipitation of a white crystalline etherate. In a similar procedure Gattow and Gerwath[10] used dimethyl ether and sodium carbonate at 238 K to prepare the dimethyl ether complex of carbonic acid. They obtained a solid which decomposed violently above 278 K, yielding water, carbon dioxide and ether. For both studies NMR and IR spectra were not obtained.

For a long period, carbonic acid had not been detected by any spectroscopic means; its formation was only inferred from kinetic data. Schwarz et al.[11] first demonstrated the existence of carbonic acid as a stable, discrete species. Thermal decomposition of NH_4HCO_3 gave carbonic acid in the gas phase which was detected by neutralization–reionization mass spectroscopic (NR-MS) techniques. Olah et al.[12] found spectral evidence for carbonic acid by calculating ^{13}C chemical shifts and comparing them with those obtained from NMR measurements under superacidic conditions. In this environment, the carbonic acid and its protonated species is present in an equilibrium [Eq. (2)].

$$C(OH)_3^+ + HF \rightleftharpoons H_2CO_3 + H_2F^+ \qquad (2)$$

Recently, the protonated carbonic acid was prepared in superacids (HF/AsF_6, HF/SbF_6) from carbonic acid bis(trimethylsilyl)ester.[13] The salts have been characterized with vibrational spectroscopy and X-ray analysis. Obviously, the protonated carbonic acid is formed under these conditions in situ by cleavage of the silyl ester.

The analysis of the IR and mass spectral data by Moore and Khanna[2] gave strong evidence for the formation of carbonic

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[*] Dr. R. Ludwig
Physikalische Chemie
Fachbereich Chemie der Universität Dortmund
Otto-Hahn-Strasse 6, 44221 Dortmund (Germany)
Fax: (+49) 231-755-3937
E-mail: ludwig@pc2a.chemie.uni-dortmund.de

Dr. A. Kornath
Anorganische Chemie
Fachbereich Chemie der Universität Dortmund
Otto-Hahn-Strasse 6, 44221 Dortmund (Germany)
Fax: (+49) 231-755-3797
E-mail: kornath@citrin.chemie.uni-dortmund.de

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acid on irradiating a water/carbon dioxide ice mixture at 20 K. Upon warming the sample to 210 K, the residual film appeared to be principally hydrogen-bonded carbonic acid. Hage et al.[6] synthesized carbonic acid by a different method: They obtained carbonic acid by protonating bicarbonate and characterized it in vitreous methanol films at low temperatures (150 K) by infrared spectroscopy. The authors could demonstrate that their polymorph of carbonic acid was the same than that of Moore and Khanna[2] obtained by proton irradiation. Further, Hage et al.[6] sublimated and recondensed solid carbonic acid without its decomposition into carbon dioxide and water. This study proved the stability of carbonic acid in the gas phase. The vapor pressure estimates were consistent with an equilibrium mixture of monomers and dimers, similar to that of formic acid (Figure 1).

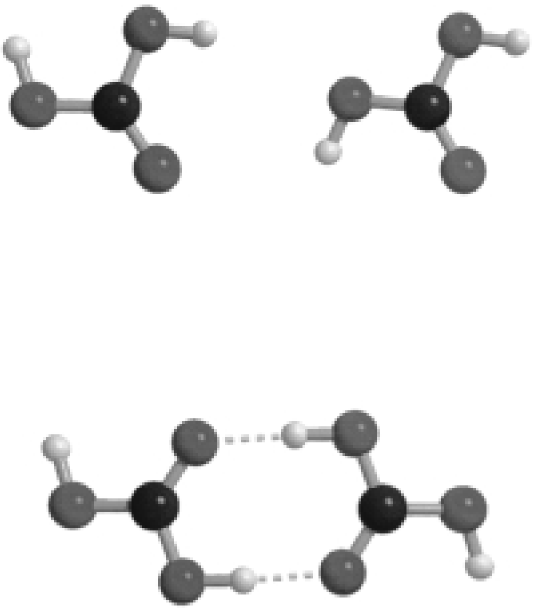

Figure 1. Representitive monomers and dimer of carbonic acid proposed by quantum mechanical calculations. Experimental studies[5] suggest a mixture of monomers and dimers in the gas phase, similar to that for formic acid.

Thus far, it has been proved that carbonic acid can be synthesized and that it is stable in the solid and the gas phase. But there still remain questions: Why is carbon acid surprisingly stable? And why does it decompose so quickly in aqueous solution?

A satisfactory answer is now given by Liedl and co-workers,[7] who studied the influence of water on the decomposition rate of carbonic acid. Using quantum mechanical Transition State Theory (TST), they calculated accurate reaction rates. This method requires exact calculations of energy differences of reactants, transitions states, and products, a multidimensional description of reaction paths, and quantum effects such as tunneling and zero-point energies. That this method generates chemically meaningful results has been proved by benchmark studies of the double proton transfer reaction in carboxylic acid dimers. The calculated reaction barriers for the decomposition of isolated carbonic acid referred to its stability. Successive addition of two water molecules decreased the reaction barrier of about 44 kcal mol^{-1} for pure carbonic acid to 27 kcal mol^{-1} then 24 kcal mol^{-1}, respectively

The calculated half-lives were even more convincing. A half-life of 65.7 million days indicated that carbonic acid is still stable at room temperature (300 K). Even at 400 K, carbonic acid has a half-life of about eight days. This behavior changed drastically in aqueous solution. Adding water decomposed the carbonic acid quickly. At 300 K, the half-life of about 65.7 million days for pure carbonic acid decreased to ten hours and two minutes when catalyzed by one and two water molecules, respectively (Figure 2). Two water molecules shorten the half-life of carbonic acid by a factor of about 50 billion.

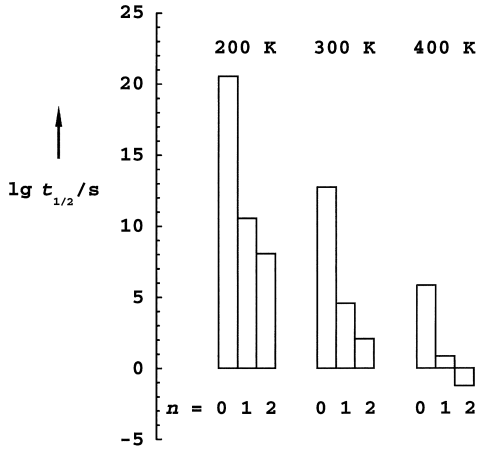

Figure 2. Half-lives of carbonic acid in the framework of Transition State Theory in the absence ($n = 0$) and in the presence of one ($n = 1$) and two ($n = 2$) water molecules at three temperatures (data taken from ref. [7]). At 300 K it can be seen that the half-life of about 65.7 million days for the pure carbonic acid decreased to ten hours and then to two minutes.

This is—according to the authors—the reason why most chemists believe carbon acid is instable. When chemists speak of carbonic acid, they have in mind carbon dioxide dissolved in water and not H_2CO_3. The latter contains, at standard state conditions, 1.6 g carbon dioxide per liter of water. Since 99.8 % of the carbon dioxide molecules are weakly hydrated, only 0.2 % forms carbonic acid and thus the solution shows acidic behavior because of the H_2CO_3/HCO_3^- equilibrium.

The calculations of Liedl and co-workers proved that pure carbonic acid shows a surprisingly kinetic stability whereas in aqueous solution it decomposes quickly. The calculated half-lives could support previous experimental results: Measuring the kinetic stability of crystalline and amorphous carbonic acid in an ice matrix, the experimental decomposition rate was about 18 ± 7 s^{-1} which is only 3000 times faster than the calculated value.

Why is information about the stability of carbonic acid so important? Carbonic acid, the short-lived intermediate in CO_2-HCO_3^-/CO_3^{2-} proton-transfer reactions, is a key compound in biological and geochemical carbonate-containing systems.

We have seen that the hydration of carbon dioxide is a slow reaction, too slow for physiological needs. In blood, the reversible combination of CO_2 and H_2O to form H_2CO_3 is catalyzed by the enzyme carbonic anhydrase.[14] The non-catalyzed reaction would not permit CO_2 to interchange between the blood and the tissues or between the blood and the lungs at rates sufficient for physiological requirements. The activity of carbonic anhydrase is remarkable. It has been estimated that one molecule of this enzyme can catalyze the hydration of about 36 million CO_2 molecules per minute.

The significance and implications of solid and gaseous H_2CO_3 for our upper atmosphere in polar stratospheric clouds, Mars, comets, interstellar icy grains, and outer solar bodies is clear.[5] For example, a comparison between the IR laboratory spectrum of carbonic acid with some spectra of Mars suggests that it could be present on the surface and/or atmosphere of the red planet.[15] It is therefore of primary relevance for understanding both the organic and inorganic chemistry taking place on Mars.

The surprising stability of H_2CO_3 should encourage experimental chemists to synthesize the compound on a preparative scale. It is also wise to look out for other candidates such as H_2SO_3 which might be more stable that we currently believe.

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