Carbonic acid monohydrate

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Abstract

In the water-carbon dioxide system, above a pressure of 4.4 GPa, a crystalline phase consisting of an adduct of the two substances can be observed to exist in equilibrium with the aqueous fluid. The phase had been found to be triclinic, and its unit-cell parameters determined, but the full crystalline and even molecular structure remained undetermined. Here, we report new diamond-anvil cell, X-ray diffraction data of a quality sufficient to allow us to propose a full structure. The crystal exists in the P̅T space group. Unit-cell parameters (at 6.5 GPa and 140 °C) are a = 5.8508(14), b = 6.557(5), c = 6.9513(6) Å, α = 88.59(2)°, β = 79.597(13)°, and γ = 67.69(4)°. Direct solution for the heavy atoms (carbon and oxygen) revealed CO3 units, with co-planar, but isolated, O units. Construction of a hydrogen network, in accordance with the requirements of hydrogen bonding and with minimum allowed distances between non-bonded atoms, indicates that the phase consists of a monohydrate of carbonic acid (H2CO3·H2O) with the carbonic acid molecule in the cis-trans configuration. This is the first experimental determination of the crystalline structure of a H2CO3 compound. The structure serves as a guide for ab initio calculations that have until now explored only anhydrous H2CO3 solids, while validating calculations that indicated that high pressures should stabilize H2CO3 in the solid state. If 4.4 GPa is the lowest pressure at which the phase is thermodynamically stable, this probably precludes its existence in our solar system, although it may exist on larger, volatile-rich exoplanets. If, however, its range of stability extends to lower pressures at lower temperatures (which possibility has not yet been adequately explored), then it might have been be a stable form of CO2 within the water-rich moons and dwarf planets prior to differentiation and might still exist on an undifferentiated Callisto.

Keywords: Carbonic acid, CO2, hydrate, high pressure, single-crystal X-ray diffraction, exoplanets

Introduction

Water and carbon dioxide are ubiquitous compounds in the biological and geological sciences. Their 1:1 adduct, carbonic acid (H2CO3), and its two anions, bicarbonate (HCO3−) and carbonate (CO32−), engage in an important set of reactions governing the solubility of CO2 and the pH of systems critical to life and planetary processes. However, owing to unfavorable kinetics and equilibrium constants at ambient conditions (Loerting et al. 2000), molecular carbonic acid has long eluded detailed experimental observation and, as described below, a crystalline structure had not previously been determined. Recently, Wang et al. (2016) claimed to have observed the formation of solid carbonic acid at high pressures, and Abramson et al. (2017) demonstrated that the observed phase can exist in thermodynamic equilibrium with the aqueous fluid for pressures beyond a quadruple point at 4.4 GPa. Preliminary X-ray results indicated that the new phase was triclinic, but their quality did not allow a refinement of the crystal structure. Here, new X-ray diffraction data of the high-pressure phase provide further insight into its structure. Despite remaining uncertainties pertaining to the hydrogen network, the results confirm the presence of H2CO3 molecules and indicate that the crystal consists of a monohydrate of the acid. Our results complete the initial experimental reports describing that phase, validate calculations that indicated that high pressures should stabilize H2CO3 in the solid state, and offer a structure for an H2CO3 hydrate as a guide to further calculations.

Prior Studies

Over the past three decades, attempts to synthesize H2CO3 have led to the development of numerous protocols divided among four main strategies. (1) The vacuum thermolysis of carbonates led to the first reported synthesis of H2CO3, in the vapor phase; originally using ammonium bicarbonate (Terlouw et al. 1987), the process was more recently accomplished with di-tert-butyl carbonate (Reisenauer et al. 2014). (2) The irradiation of CO2 and H2O ices produced the first H2CO3 solid; the initial experiment involved the proton irradiation of CO2·H2O mixtures (Moore and Khanna 1991), but both UV photolysis (Gerakines et al. 2000; Wu et al. 2003) and electron irradiation of the mixtures (Zheng and Kaiser 2007), as well as the proton irradiation of pure CO2 ice (Brucato et al. 1997; Garozzo et al. 2008) have also been successful. (3) The ionization of CO2 and H2O gases has been used to produce radicals for recombination into H2CO3, either directly in the gas phase (Mori et al. 2009, 2011), or in the solid state by deposition of OH radicals onto CO ice (Oba et al. 2010). (4) Finally, the protonation of carbonates...