

Ultrafast generation of aqueous carbonic acid

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Exploring the acid-base chemistry of bicarbonate, HCO_3^- , in aqueous solution, and the conversion to aqueous carbon dioxide, CO_2 , is of utmost importance in understanding the chemical reactivity of these molecular species in contexts as diverse as blood physiology, chemical weathering, ocean acidification, and carbon dioxide sequestration strategies. Under conditions of $\text{pH} < 8.5$ it is assumed that CO_2 first becomes hydrated, forming carbonic acid (H_2CO_3), which subsequently dissociates into HCO_3^- and H_3O^+ . Direct observation of aqueous H_2CO_3 , however, has proven to be elusive. Protonation of HCO_3^- should in principle lead to H_2CO_3 , that, however, generally is assumed to be unstable, as prompt water catalysed decomposition into CO_2 and H_2O is believed to occur. Only recently it has been shown that H_2CO_3 can be detected as isolated molecules in the gas phase [1], or in ice matrices [2]. H_2CO_3 in aqueous solution in contrast has – until now – remained uncharacterized. Rapid mixing techniques have only provided access to the overall time scale for the hydration and subsequent deprotonation (or the reverse protonation/dehydration) kinetics of the reaction [3]. We present femtosecond infrared spectroscopic results showing unequivocal support for the existence of deuterated carbonic acid, D_2CO_3 , under aqueous conditions, formed after ultrafast protonation of DCO_3^- dissolved in D_2O , and its persistence for nanoseconds. Here we photoexcite at 330 nm a photoacid, 2-naphthol-6,8-disulfonate (2N-6,8S), with a 50 fs pump pulse. We follow the aqueous bimolecular deuteron transfer by monitoring IR-active vibrational marker modes of 2N-6,8S with femtosecond time resolution. We use the Szabo-Collins-Kimball approach to describe bimolecular reaction dynamics subject to the Debye-von Smoluchowski diffusional motions, and derive on-contact proton transfer reaction rates between HCO_3^- and 2N-6,8S that follow the Marcus correlation between free energy and the proton transfer rates found for a large class of aqueous proton transfer of photoacid dissociation and photoacid-base neutralization reactions [4]. This Marcus free energy correlation supports an associated pK_a of 3.45 ± 0.15 for carbonic acid (in bulk water at 25°C , zero ionic strength, atmospheric pressure), substantially lower than the value of 6.35 commonly assumed on the basis of the overall CO_2 to bicarbonate equilibrium.

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