Carbonic acid, H$_2$CO$_3$, and its isomeric weakly bound H$_2$O·CO$_2$ complex are short-lived intermediates in the hydrolysis of CO$_2$, a process of fundamental importance in geochemistry and biology.\[1,3\] Whereas H$_2$O·CO$_2$ has been characterized by spectroscopy,\[6,7\] there is only indirect experimental evidence for the existence of H$_2$CO$_3$ in the gas phase.\[1,3\] Theoretical calculations predict that isolated H$_2$CO$_3$ should be stable but that it decomposes into H$_2$O and CO$_2$ in the presence of water.\[2,8–11\] There have been several unsuccessful attempts to generate and characterize gas-phase H$_2$CO$_3$ by heating solid H$_2$CO$_3$\[3\] or NH$_4$HCO$_3$.\[12\] Herein we describe the properties of gas-phase protonated H$_2$CO$_3$ and report the first spectroscopic identification of the fundamental C(OH)$_3$ carbocation and its H$_3$O$^+$·CO$_2$ isomer by argon-tagging photodissociation spectroscopy.

Quantum chemical calculations demonstrate that there are several isomers on the [C,H$_3$,O$_3$] potential-energy surface (1–4, Figure 1).\[13,14\] The most stable structure corresponds to the hydrogen-bonded H$_2$O$^+$·CO$_2$ complex (4, $E_{\text{rel}}$ = 0). The attraction is dominated by charge-induced dipole and charge–quadrupole interaction leading to nearly linear hydrogen bonding.\[15,16\] The predicted dissociation energy of 62 kJ mol$^{-1}$ is in good agreement with the binding enthalpy of 64 kJ mol$^{-1}$ measured by high-pressure mass spectrometry.\[17\]

Protonation of H$_2$CO$_3$ at the carbonyl group results in two planar isomers of the trihydroxycarbenium ion, anti- and syn-C(OH)$_3$$. The anti structure (1, $C_{\text{anti}}$, $E_{\text{rel}}$ = 18 kJ mol$^{-1}$) is separated by a barrier of 50 kJ mol$^{-1}$ from the less stable syn structure (2, $C_{\text{syn}}$, $E_{\text{rel}}$ = 47 kJ mol$^{-1}$). Conversion between the C(OH)$_3$$^+$ isomers and 4 is suppressed by a high isomerization barrier (214 kJ mol$^{-1}$). In the NMR, IR, Raman, and X-ray crystallography spectra of C(OH)$_3$$^+$ in superacid solutions or in superacidic salts only the anti isomer was observed.\[18,19\] Finally, a fourth nonplanar [C,H$_3$,O$_3$]$^+$ isomer can be generated by protonation of H$_2$CO$_3$ at a hydroxyl group (3, $C_{\text{3}}$, $E_{\text{rel}}$ = 118 kJ mol$^{-1}$), leading to a hitherto undetected complex of H$_2$O and OCOH\[14\] with a binding energy of 105 kJ mol$^{-1}$.

Electron ionization (EI) of diethyl carbonate is known to selectively produce C(OH)$_3$$^+$ ions through consecutive elimination of a vinyl radical and ethene.\[13,14\] They could be distinguished from H$_2$O$^+$·CO$_2$ complexes made by EI of a H$_2$O/CO$_2$ mixture by their different fragmentation patterns in metastable decay (MD) and high-energy (8 keV) collision-induced dissociation (CID).\[13,14\] This work takes advantage of low-energy (8 eV) CID spectra for the assignments of isomers. Specifically, the major collision fragments of C(OH)$_3$$^+$ and H$_2$O$^+$·CO$_2$ correspond to OCOH$^+$ and H$_2$O$^+$, respectively (Figure 2). Experimental conditions can be optimized to favor exclusive production of either C(OH)$_3$$^+$ or H$_2$O$^+$·CO$_2$ isomers.

Although mass spectrometry experiments can distinguish between different isomers, they do not provide direct structural information. Therefore, the highly sensitive $E_{\text{rel}}$ = 118 kJ mol$^{-1}$, leading to a hitherto undetected complex of H$_2$O and OCOH\[14\] with a binding energy of 105 kJ mol$^{-1}$.

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Although mass spectrometry experiments can distinguish between different isomers, they do not provide direct structural information. Therefore, the highly sensitive
method of single-photon IR photodissociation (IRPD) spectroscopy of mass-selected ions was employed here to determine the structures of the \([\text{C}_4\text{H}_3\text{O}_3]^+\) ions and to directly probe the acidities of their \(O-H\) bonds. IRPD spectra of cold ions can be recorded with this approach only if the IR photon energy \((E = 42 \text{ kJ mol}^{-1}\) for \(v_{\text{IR}} = 3500 \text{ cm}^{-1}\)) surpasses the lowest dissociation energy of the ion. As the calculated dissociation energies of all four \([\text{C}_4\text{H}_3\text{O}_3]^+\) isomers exceed typical IR photon energies, Ar atoms are attached to the ions to facilitate resonant single-photon fragmentation [Eq. (1); Ar tagging].

\[
[\text{C}_4\text{H}_3\text{O}_3]^+ \cdot \text{Ar} + h\nu_{\text{IR}} \rightarrow [\text{C}_4\text{H}_3\text{O}_3]^+ + \text{Ar}
\]  

(1)

To investigate the effect of Ar on the spectroscopic properties of \([\text{C}_4\text{H}_3\text{O}_3]^+\), the minimum-energy structures and IR spectra of the relevant \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar isomers were calculated. For all of them, Ar forms a nearly linear hydrogen bond to one of the available acidic OH protons (Figure 1) with comparable binding energies \((6.6-8.8 \text{ kJ mol}^{-1}\)). The major effects of the complexation on the \([\text{C}_4\text{H}_3\text{O}_3]^+\) ions are an elongation of the \(O-H\) donor bond, a reduction in the wavenumber and an enhancement in the IR intensity of the corresponding \(O-H\) stretch vibration, and shifts and splittings arising from reducing the symmetry. Figure 3 compares computed IR spectra of 1-4 with those of their Ar complexes in the OH stretch range. The IR spectra of 1-4 show pronounced differences in the positions and intensities of the OH stretch bands, and these differences are amplified by Ar complexation, thus making IRPD spectroscopy a suitable tool for identifying the \([\text{C}_4\text{H}_3\text{O}_3]^+\) isomers through their Ar complexes.

The IRPD spectrum of \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar generated by EI of the \(\text{H}_2\text{O}/\text{CO}_2/\text{Ar}\) mixture is shown in Figure 3a. Comparison with the calculated stick spectra of the \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar isomers immediately suggests that 4-Ar is the dominant carrier for these bands. Bands A and B observed at 3566 and 3343 cm\(^{-1}\) can be assigned to the free and Ar-bound OH stretch vibrations predicted at 3545 and 3319 cm\(^{-1}\), respectively.

The nearly symmetric shape of band A and blue shading of band B are consistent with the assignments to free and hydrogen-bonded OH stretch modes. The \(\text{CO}_2\)-bonded OH stretch mode of 4-Ar is predicted to occur outside the scanned range (at 2869 cm\(^{-1}\)). The two much weaker bands D and C near 3237 and 3493 cm\(^{-1}\) in the IRPD spectrum may tentatively be attributed to the Ar-bound and free OH stretch modes of 3-Ar, which are predicted to be near 3279 and 3511 cm\(^{-1}\), respectively. It is conceivable that a small amount of 3 may be produced in the ion source, because both \(\text{H}_2\text{O}\) and \(\text{O}_{\text{CO}}\) are present in the \(\text{H}_2\text{O}/\text{CO}_2/\text{Ar}\) ion-source plasma.

Comparison of the IRPD spectrum of \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar generated by EI of the diethyl carbonate/Ar mixture shown in Figure 3b with the simulated spectra clearly demonstrates that 1-Ar is the primary absorber. The bands F and E at 3343 and 3519 cm\(^{-1}\) are attributed to the Ar-bound and free OH stretch modes of 1-Ar, which are predicted to be at 3352 and 3508 cm\(^{-1}\), respectively. The spectrum lacks any noticeable contributions from other \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar isomers, in particular from 2-Ar. On the basis of the similar Ar binding energies and calculated IR intensities, 2 must be less abundant than 1 by at least one order of magnitude, in agreement with the predicted lower stability of the syn versus the anti structure of \(\text{C(OH)}_3^+\).

No features attributable to 3-Ar were observed in the experimental spectra, in agreement with the much higher energy of isomer 3.

The \(v_{\text{OH}}\) wavenumber in isolated anti-\(\text{C(OH)}_3^+\) can be estimated from the 1-Ar spectrum to be about 3520 cm\(^{-1}\) (band E, 3519 cm\(^{-1}\)) because the shifts and splittings induced by Ar complexation are predicted to be small for the free OH modes. In contrast, the \(v_{\text{OH}}\) absorptions of 1 in its salts with \([\text{SbF}_6]^+\) (3457 and 3390 cm\(^{-1}\)) or \([\text{AsF}_6]^+\) (3409 cm\(^{-1}\)) are

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**Figure 2.** CID spectra of mass-selected \([\text{C}_4\text{H}_3\text{O}_3]^+\) ions (63 u) prepared by EI of diethyl carbonate (a) and by EI of a \(\text{H}_2\text{O}/\text{CO}_2\) mixture (b). Major fragment ions correspond to \(\text{H}_3\text{O}^+\) (19 u) and \(\text{OCOH}^+\) (45 u). Both spectra are normalized with respect to the parent-ion intensity. Spectrum (a) is vertically expanded by a factor of 10.

**Figure 3.** IR absorption stick spectra of \([\text{C}_4\text{H}_3\text{O}_3]^+\) and \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar isomers calculated at the B3LYP/6-311G** basis set (c–j; scaling factor of 0.95) compared to experimental IRPD spectra of \([\text{C}_4\text{H}_3\text{O}_3]^+\)-Ar complexes prepared from the Ar/\(\text{H}_2\text{O}/\text{CO}_2\) mixture (a) and the Ar/diethyl carbonate mixture (b).
strongly red-shifted, reflective of the large impact of the counterions on the O–H bonds. The ν\textsubscript{OH} wavenumber and its complication shifts provide an indirect measure of the OH bond strength and the acidity of the OH protons, respectively. Comparison of the ν\textsubscript{OH} value of 1 (ca. 3520 cm\textsuperscript{-1}) with the ν\textsubscript{OH} value of H\textsubscript{2}O (av. 3499 cm\textsuperscript{-1})\textsuperscript{[22]} demonstrates that the O–H bonds in 1 are slightly stronger and shorter than those in H\textsubscript{2}O (d(\text{OH}) = 0.9757 vs. 0.9797 Å). On the other hand, the O–H bonds in H\textsubscript{2}O are significantly more acidic than those in 1, leading to stronger and shorter hydrogen bonds with Ar (D\textsubscript{A} = 13.2 vs. 6.6 kJ mol\textsuperscript{-1}, d(H–Ar) = 2.086 vs. 2.275 Å) and correspondingly larger ν\textsubscript{OH} red shifts upon complexation.

The latter observation is consistent with a proton affinity value for H\textsubscript{2}CO\textsubscript{3} (predicted as 769 kJ mol\textsuperscript{-1})\textsuperscript{[14]} that is larger than that for H\textsubscript{2}O (691 kJ mol\textsuperscript{-1}).\textsuperscript{[23]} As expected, the O–H bonds in the cation 1 are much weaker than those in the isoelectronic neutral compound B(OH)\textsubscript{3} (ν\textsubscript{OH} = 3520 vs. 3705 cm\textsuperscript{-1}).\textsuperscript{[24]}

It is instructive to contrast the binding of Ar to 1 and to the simplest carbonium ion, CH\textsubscript{3}+. IR spectra and calculations demonstrate that the positive charge in the CH\textsubscript{3}+ ion is localized on the C atom, and as a result, Ar binds to the vacant electrophilic 2p\textsubscript{o} orbital of CH\textsubscript{3}+. Leading to a C–OH symmetrical structure of CH\textsubscript{3}+:Ar with a stronger charge-transfer bond (binding energy 56.8 kJ mol\textsuperscript{-1}).\textsuperscript{[25–28]} The hydrogen-bonded CH\textsubscript{3}+:Ar structure has a far lower binding energy (3.6 kJ mol\textsuperscript{-1}). In contrast, the IR spectra and calculations for C(OH)\textsubscript{3}:Ar confirm previous conclusions:\textsuperscript{[18,19]} that the charge in C(OH)\textsubscript{3} is largely delocalized, and as a result, the hydrogen-bonded complex is more stable (6.6 kJ mol\textsuperscript{-1}) than the C-bound one (0.8 kJ mol\textsuperscript{-1}).

The results presented herein characterize isomers of protonated carbonic acid and provide a glimpse of the properties of carbonic acid itself. Future research in this area will focus on studying protonated carbonic acid with variable degrees of solvation by Ar, CO\textsubscript{2}, N\textsubscript{2}, and most importantly, H\textsubscript{2}O. Characterization of protonated carbonic acid with different degrees of solvation will improve our understanding of processes occurring during CO\textsubscript{2} hydrolysis and chemical reactions involving simple carbocations.

**Experimental and Theoretical Methods**

IRPD spectra of [\text{CH}_\text{3}\text{H}O\text{3}]\textsuperscript{-}Ar complexes were recorded in a tandem quadrupole mass spectrometer (QMS1+2) coupled to an ion source and an octopole ion trap.\textsuperscript{[25]} The ion source combines a pulsed supersonic beam expansion with EI. For Ar complexes of C(OH)\textsubscript{3}\textsuperscript{-}, the gas mixture was obtained by passing Ar at a pressure of p = 7 bar through a reservoir filled with diethyl carbonate (T = 300 K). For Ar complexes of H\textsubscript{2}O–CO\textsubscript{2}, the gas mixture was Ar and CO\textsubscript{2} (ratio > 20:1) at p = 3 bar passing over ice (T = 260 K). The [\text{CH}_\text{3}\text{H}O\text{3}]\textsuperscript{-}Ar ions were mass selected by QMS1 and irradiated in the octopole ion guide with a tunable IR laser pulse (ν\textsubscript{IR}) generated by an optical parametric oscillator laser. Vibrational excitation led to the loss of Ar from [\text{CH}_\text{3}\text{H}O\text{3}]\textsuperscript{-}Ar [Eq. (1)]. The resulting [\text{CH}_\text{3}\text{H}O\text{3}]\textsuperscript{-} fragments ions were selected by QMS2 and monitored as a function of ν\textsubscript{IR} to obtain the IRPD spectrum. CID spectra of mass-selected [\text{CH}_\text{3}\text{H}O\text{3}]\textsuperscript{-} ions with a laboratory kinetic energy of 8 eV were obtained by introducing air into the octopole region (p = 10\textsuperscript{-}\textsuperscript{1} mbar). Quantum chemical calculations were carried out at the B3LYP/6-311G** level of theory. Minima were located on the potential-energy surface corrected for basis-set superposition error. Harmonic vibrational wavenumbers were scaled by a factor of 0.95 and all energies were corrected for harmonic zero-point energies.

Received: February 19, 2007
Published online: May 8, 2007

**Keywords:** carbonium ions · carbonic acid · IR spectroscopy · noncovalent interactions · protonation

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