

IR Spectra of Protonated Carbonic Acid and Its Isomeric $\text{H}_3\text{O}^+\cdot\text{CO}_2$ Complex**

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Carbonic acid, H_2CO_3 , and its isomeric weakly bound $\text{H}_2\text{O}\cdot\text{CO}_2$ complex are short-lived intermediates in the hydrolysis of CO_2 , a process of fundamental importance in geochemistry and biology.^[1–5] Whereas $\text{H}_2\text{O}\cdot\text{CO}_2$ has been characterized by spectroscopy,^[6,7] there is only indirect experimental evidence for the existence of H_2CO_3 in the gas phase.^[1,3] Theoretical calculations predict that isolated H_2CO_3 should be stable but that it decomposes into H_2O and CO_2 in the presence of water.^[2,8–11] There have been several unsuccessful attempts to generate and characterize gas-phase H_2CO_3 by heating solid H_2CO_3 ^[3] or NH_4HCO_3 .^[12] Herein we describe the properties of gas-phase protonated H_2CO_3 and report the first spectroscopic identification of the fundamental $\text{C}(\text{OH})_3^+$ carbocation and its $\text{H}_3\text{O}^+\cdot\text{CO}_2$ isomer by argon-tagging photodissociation spectroscopy.

Quantum chemical calculations demonstrate that there are several isomers on the $[\text{C}_3\text{H}_3\text{O}_3]^+$ potential-energy surface (**1–4**, Figure 1).^[13,14] The most stable structure corresponds to the hydrogen-bonded $\text{H}_3\text{O}^+\cdot\text{CO}_2$ 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_2CO_3 at the carbonyl group results in two planar isomers of the trihydroxycarbenium ion, *anti*- and *syn*- $\text{C}(\text{OH})_3^+$. The *anti* structure (**1**, C_{3h} , $E_{\text{rel}} = 18 \text{ kJ mol}^{-1}$) is separated by a barrier of 50 kJ mol^{-1} from the less stable *syn* structure (**2**, C_s , $E_{\text{rel}} = 47 \text{ kJ mol}^{-1}$). Conversion between the $\text{C}(\text{OH})_3^+$ 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 $\text{C}(\text{OH})_3^+$ in superacid solutions or corresponding salts only the *anti* isomer was observed.^[18,19] Finally, a fourth nonplanar $[\text{C}_3\text{H}_3\text{O}_3]^+$ isomer can be generated by protonation of H_2CO_3 at a hydroxyl group (**3**, C_1 ,

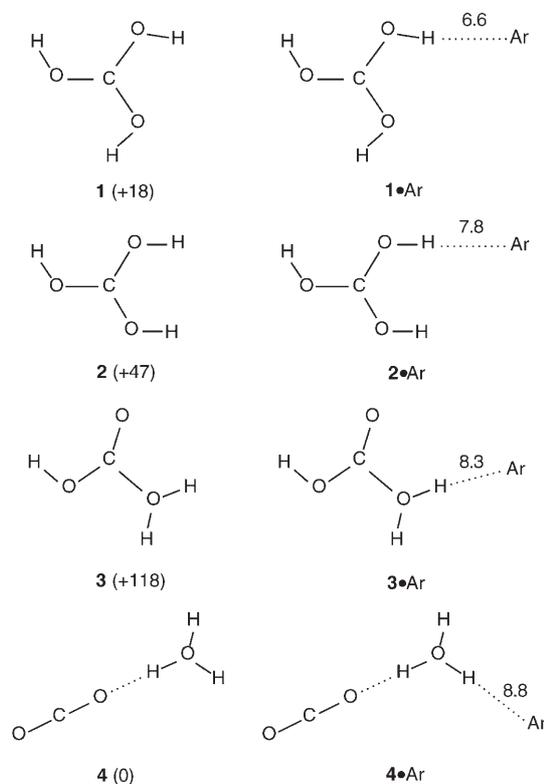


Figure 1. Structures, relative energies (left, in kJ mol^{-1}), and intermolecular binding energies (right, in kJ mol^{-1}) of various isomers of $[\text{C}_3\text{H}_3\text{O}_3]^+$ and $[\text{C}_3\text{H}_3\text{O}_3]^+\cdot\text{Ar}$ calculated at the B3LYP/6-311G** level. The positive charge has been omitted in each structure for clarity.

$E_{\text{rel}} = 118 \text{ kJ mol}^{-1}$), leading to a hitherto undetected complex of H_2O and OCOH^+ ^[14] with a binding energy of 105 kJ mol^{-1} .

Electron ionization (EI) of diethyl carbonate is known to selectively produce $\text{C}(\text{OH})_3^+$ ions through consecutive elimination of a vinyl radical and ethene.^[13,14] They could be distinguished from $\text{H}_3\text{O}^+\cdot\text{CO}_2$ complexes made by EI of a $\text{H}_2\text{O}/\text{CO}_2$ 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 $\text{C}(\text{OH})_3^+$ and $\text{H}_3\text{O}^+\cdot\text{CO}_2$ correspond to OCOH^+ and H_3O^+ , respectively (Figure 2). Experimental conditions can be optimized to favor exclusive production of either $\text{C}(\text{OH})_3^+$ or $\text{H}_3\text{O}^+\cdot\text{CO}_2$ isomers.

Although mass spectrometry experiments can distinguish between different isomers, they do not provide direct structural information. Therefore, the highly sensitive

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[**] This study was supported by the Deutsche Forschungsgemeinschaft (DO 729/2), the Fonds der Chemischen Industrie, and the Bavaria-California Technology Center (BaCaTeC).

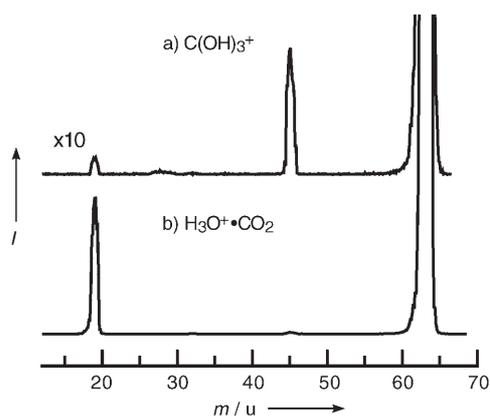
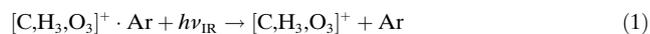


Figure 2. CID spectra of mass-selected $[\text{C},\text{H}_3,\text{O}_3]^+$ ions (63 u) prepared by EI of diethyl carbonate (a) and by EI of a $\text{H}_2\text{O}/\text{CO}_2$ mixture (b). Major fragment ions correspond to H_3O^+ (19 u) and OCOH^+ (45 u). Both spectra are normalized with respect to the parent-ion intensity. Spectrum (a) is vertically expanded by a factor of 10.

method of single-photon IR photodissociation (IRPD) spectroscopy of mass-selected ions^[15] was employed here to determine the structures of the $[\text{C},\text{H}_3,\text{O}_3]^+$ 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 $\nu_{\text{IR}} = 3500 \text{ cm}^{-1}$) surpasses the lowest dissociation energy of the ion. As the calculated dissociation energies of all four $[\text{C},\text{H}_3,\text{O}_3]^+$ isomers exceed typical IR photon energies, Ar atoms are attached to the ions to facilitate resonant single-photon fragmentation [Eq. (1); Ar tagging].^[20,21]



To investigate the effect of Ar on the spectroscopic properties of $[\text{C},\text{H}_3,\text{O}_3]^+$, the minimum-energy structures and IR spectra of the relevant $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ 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 kJ mol^{-1}). The major effects of the complexation on the $[\text{C},\text{H}_3,\text{O}_3]^+$ 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 OH 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 $[\text{C},\text{H}_3,\text{O}_3]^+$ isomers through their Ar complexes.

The IRPD spectrum of $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ 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 $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ 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.

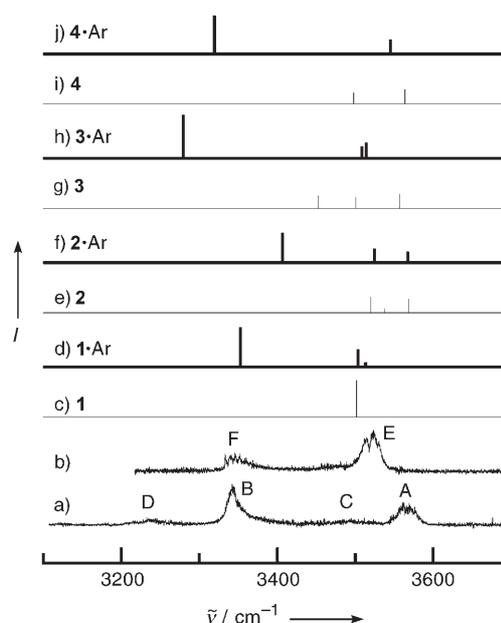


Figure 3. IR absorption stick spectra of $[\text{C},\text{H}_3,\text{O}_3]^+$ and $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ isomers calculated at the B3LYP/6-311G** level (c–j; scaling factor of 0.95) compared to experimental IRPD spectra of $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ complexes prepared from the Ar/ $\text{H}_2\text{O}/\text{CO}_2$ mixture (a) and the Ar/diethyl carbonate mixture (b).

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.^[15] The 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 H_2O and OCOH^+ are present in the $\text{H}_2\text{O}/\text{CO}_2/\text{Ar}$ ion-source plasma.

Comparison of the IRPD spectrum of $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ 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 $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$ 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 $\text{C}(\text{OH})_3^+$. No features attributable to **3**·Ar were observed in the experimental spectra, in agreement with the much higher energy of isomer **3**.

The ν_{OH} wavenumber in isolated *anti*- $\text{C}(\text{OH})_3^+$ 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 ν_{OH} absorptions of **1** in its salts with $[\text{SbF}_6]^-$ (3457 and 3390 cm^{-1}) or $[\text{AsF}_6]^-$ (3409 cm^{-1})^[13] are

strongly red-shifted, reflective of the large impact of the counterions on the O–H bonds. The ν_{OH} wavenumber and its complexation shifts provide an indirect measure of the OH bond strength and the acidity of the OH protons, respectively. Comparison of the ν_{OH} value of **1** (ca. 3520 cm^{-1}) with the ν_{OH} value of H_3O^+ (av. 3499 cm^{-1})^[22] demonstrates that the O–H bonds in **1** are slightly stronger and shorter than those in H_3O^+ ($d(\text{O–H}) = 0.9757$ vs. 0.9797 Å). On the other hand, the O–H bonds in H_3O^+ are significantly more acidic than those in **1**, leading to stronger and shorter hydrogen bonds with Ar ($D_0 = 13.2$ vs. 6.6 kJ mol^{-1} , $d(\text{H–Ar}) = 2.086$ vs. 2.275 Å) and correspondingly larger ν_{OH} red shifts upon complexation. The latter observation is consistent with a proton affinity value for H_2CO_3 (predicted as 769 kJ mol^{-1})^[14] that is larger than that for H_2O (691 kJ mol^{-1})^[23]. As expected, the O–H bonds in the cation **1** are much weaker than those in the isoelectronic neutral compound $\text{B}(\text{OH})_3$ ($\nu_{\text{OH}} \approx 3520$ vs. 3705 cm^{-1})^[24].

It is instructive to contrast the binding of Ar to **1** and to the simplest carbenium ion, CH_3^+ . IR spectra and calculations demonstrate that the positive charge in the CH_3^+ ion is localized on the C atom, and as a result, Ar binds to the vacant electrophilic $2p_z$ orbital of CH_3^+ , leading to a C_{3v} -symmetrical structure of $\text{CH}_3^+\cdot\text{Ar}$ with a strong charge-transfer bond (binding energy 56.8 kJ mol^{-1})^[25–28]. The hydrogen-bonded $\text{CH}_3^+\cdot\text{Ar}$ structure has a far lower binding energy (3.6 kJ mol^{-1}). In contrast, the IR spectra and calculations for $\text{C}(\text{OH})_3^+\cdot\text{Ar}$ confirm previous conclusions^[18,19] that the charge in $\text{C}(\text{OH})_3^+$ is largely delocalized, and as a result, the hydrogen-bonded complex is more stable (6.6 kJ mol^{-1}) than the C-bound one (0.8 kJ mol^{-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_2 , N_2 , and most importantly, H_2O . Characterization of protonated carbonic acid with different degrees of solvation will improve our understanding of processes occurring during CO_2 hydrolysis and chemical reactions involving simple carbocations.

Experimental and Theoretical Methods

IRPD spectra of $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$ complexes were recorded in a tandem quadrupole mass spectrometer (QMS1 + 2) coupled to an ion source and an octopole ion trap.^[25] The ion source combines a pulsed supersonic beam expansion with EI. For Ar complexes of $\text{C}(\text{OH})_3^+$, 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 $\text{H}_3\text{O}^+\cdot\text{CO}_2$, the gas mixture was Ar and CO_2 (ratio > 20:1) at $p = 3$ bar passing over ice ($T = 260$ K). The $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$ ions were mass selected by QMS1 and irradiated in the octopole ion guide with a tunable IR laser pulse (ν_{IR}) generated by an optical parametric oscillator laser. Vibrational excitation led to the loss of Ar from $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$ [Eq. (1)]. The resulting $[\text{C}_2\text{H}_3\text{O}_3]^+$ fragment ions were selected by QMS2 and monitored as a function of ν_{IR} to obtain

the IRPD spectrum. CID spectra of mass-selected $[\text{C}_2\text{H}_3\text{O}_3]^+$ ions with a laboratory kinetic energy of 8 eV were obtained by introducing air into the octopole region ($p = 10^{-5}$ 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: carbenium ions · carbonic acid · IR spectroscopy · noncovalent interactions · protonation

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