Carbonic Acid | Hot Paper

DOI: 10.1002/ange.201406969

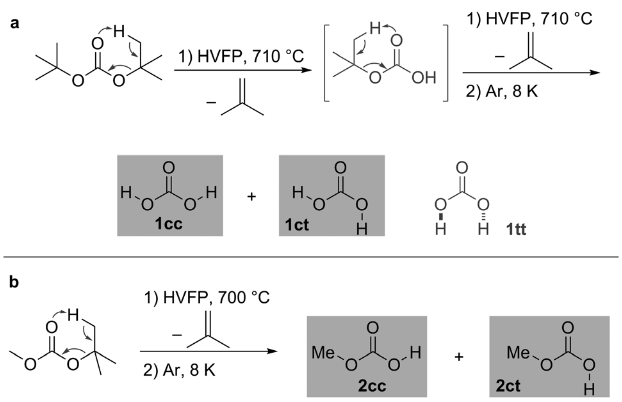
Gas-Phase Preparation of Carbonic Acid and Its Monomethyl Ester**

*Hans Peter Reisenauer, J. Philipp Wagner, and Peter R. Schreiner**

Dedicated to Professor Helmut Schwarz

Abstract: *Carbonic acid (H_2CO_3), an essential molecule of life (e.g., as bicarbonate buffer), has been well characterized in solution and in the solid state, but for a long time, it has eluded its spectral characterization in the gas phase owing to a lack of convenient preparation methods; microwave spectra were recorded only recently. Here we present a novel and general method for the preparation of H_2CO_3 and its monomethyl ester (CH_3OCO_2H) through the gas-phase pyrolysis of di-tert-butyl and tert-butyl methyl carbonate, respectively. H_2CO_3 and CH_3OCO_2H were trapped in noble-gas matrices at 8 K, and their infrared spectra match those computed at high levels of theory [focal point analysis beyond CCSD(T)/cc-pVQZ] very well. Whereas the spectra also perfectly agree with those of the vapor phase above the β-polymorph of H_2CO_3, this is not true for the previously reported α-polymorph. Instead, the vapor phase above α-H_2CO_3 corresponds to CH_3OCO_2H, which sheds new light on the research that has been conducted on molecular H_2CO_3 over the last decades.*

Carbonic acid (H_2CO_3, **1**) is an essential molecule of life, whose mere existence, however, was debated for a long time. It is the key intermediate in the exhalation of CO_2 and part of the natural carbonate buffer, which stabilizes, for instance, the pH value of blood. Similarly, **1** is an intermediate in the acidification of the oceans through the uptake of CO_2 from the atmosphere despite its rapid decomposition into CO_2 and H_2O,[1] in particular, in aqueous solutions.[2] As such, **1** is also likely to be a key species to be considered in CO_2 sequestration technologies. Carbonic acid has been suggested to be present in extraterrestrial ices and interstellar regions, including the surface of Mars,[3] that contain both water and carbon dioxide,[4] and the high-energy irradiation of CO_2/H_2O (ice) mixtures[5] provides access to bulk carbonic acid. Furthermore, **1** has been prepared on cold surfaces, in glasses by protonation of (bi)carbonate salts,[6] and in D_2O solution through ultrafast deuteration of bicarbonate.[7] Yet, isolated **1** was long considered not to be detectable in the gas phase, although the first gas-phase preparation and mass-spectrometric identification of **1** were already achieved in 1987 through the thermal decomposition of ammonium bicarbonate (NH_4HCO_3).[8] This approach, however, could not be successfully adapted to produce a sufficiently high concentration of **1** in the gas phase for spectroscopic characterization. The energetically higher lying *cis–trans* conformer (**1ct**, Scheme 1) was first prepared through an electric



Scheme 1. Proposed mechanism for the high-vacuum flash pyrolysis (HVFP) of di-*tert*-butyl carbonate. a) Trapping of the *cis–cis* (**1cc**) and *cis–trans* (**1ct**) conformers of carbonic acid as the pyrolysis products (isobutene also forms as an extrusion product) in a solid argon matrix at 8 K. b) Analogous preparation of the *cis–cis* (**2cc**) and *cis–trans* (**2ct**) conformers of carbonic acid monomethyl ester from *tert*-butyl methyl carbonate through HVFP and trapping in the matrix.

discharge of a CO_2/Ar mixture, which was then passed through water before injection into a pulsed discharge nozzle, and it was identified by Fourier-transform microwave spectroscopy[9] in 2009. The most favorable conformer, namely **1cc**, was only characterized in 2011 by utilizing a similar technique.[10]

Herein, we present a novel approach for the gas-phase preparation of isolated **1** through unimolecular ester pyrolysis of alkyl carbonates, which had been suggested theoretically,[11] but not practically realized. Our pyrolysis procedure is general and also amenable to the preparation of alkyl monoesters of **1**, for instance, carbonic acid monomethyl ester (methyl hydrogen carbonate, **2**, CH_3OCO_2H), which had not been prepared in the gas phase before. We will also show in the following that the matrix-isolated species derived from

[*] Dr. H. P. Reisenauer, M. Sc. J. P. Wagner, Prof. Dr. P. R. Schreiner
Institute of Organic Chemistry, Justus-Liebig-University
Heinrich-Buff-Ring 58, 35392 Giessen (Germany)
E-mail: prs@uni-giessen.de

[**] This research was supported by the Deutsche Forschungsgemeinschaft (Schr597/18-1). J.P.W. is grateful to the Fonds der Chemischen Industrie for a fellowship. We thank Alexander Vaughn and Wesley D. Allen for sharing their Perl script for the FPA computations. We thank Hinrich Grothe for sending us an electronic version of Jürgen Bernard's PhD thesis,[13] and Hinrich Grothe as well as Thomas Loerting for permission (May 04, 2014) to reproduce Figure S4 of Ref. [16]. This work was first presented at the EUCHEM Conference on Stereochemistry (Bürgenstock) on May 04, 2014.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406969.

the sublimation of the so-called α-polymorph of **1**,[12] which was prepared by protonation of $KHCO_3$ with HCl in methanol,[4a] indeed is not **1**, but rather the monomethyl ester **2**.[13] Although carbonic acid monoalkyl esters were recently suggested to occur in alcoholic beverages,[14] they are uncommon and have only recently come into focus as key intermediates in CO_2 sequestration as they can ideally form from the reactions of alcohols with CO_2.[15]

As we will demonstrate, only the matrix-isolated species derived from the vapor phase above the β-polymorph of **1**[16] is consistent with the spectroscopic and theoretical data for **1** prepared by the alternative route presented here. The present study will aid in the unequivocal identification of **1** and **2** in clouds as well as in extraterrestrial environments, and it will allow further studies on these and closely related species owing to the ease of preparation that is offered by the present experimental procedure (Scheme 1).

Owing to the proposed,[11] yet experimentally unreported route to **1** through ester pyrolysis, we surmised that the previously not considered elimination of isobutene from di-*tert*-butyl carbonate, for example (Scheme 1 a), a starting material that is readily prepared from the 4-dimethylaminopyridine-catalyzed reaction of di-*tert*-butyl dicarbonate (Boc_2O; Boc = *tert*-butoxycarbonyl) with *tert*-butyl alcohol, would be suitable. As documented in the Supporting Information (Figure S1), commercially available Boc_2O can also be used directly for these pyrolyses, but this process requires higher temperatures (850 °C), leading to the formation of somewhat larger amounts of side products. Di-*tert*-butyl carbonate was evaporated from a pre-cooled storage bulb at −45 °C and passed through a quartz pyrolysis tube (710 °C), after which the pyrolysis products were co-condensed with a large excess of argon (introduced by a separate jet) on the surface of the 8 K matrix window; several experiments were performed to determine the optimal pyrolysis temperature. Alternatively, a pre-mixed highly diluted gaseous mixture (dilution in argon 1:1000) was passed directly through the hot pyrolysis tube at 710 °C, and the pyrolysis products were condensed on the surface of the 8 K matrix window. Under these conditions, most of the olefin elimination reactions were not complete, and unreacted precursors were present in the matrices; secondary decomposition reactions to CO_2, H_2O, and *tert*-butyl alcohol were unavoidable (Figure S2). Utilizing density functional theory (DFT) computations at the M06-2X/cc-pVTZ level of theory to study this pyrolysis reaction, we found that the barrier (35.2 kcal mol^{-1}) for the formation of **1** can effectively compete with that for CO_2 extrusion (34.4 kcal mol^{-1}) from the intermediate carbonic acid mono-*tert*-butyl ester (Figure S8) to give *tert*-butyl alcohol. This is not the case for other pyrolytic leaving groups for which alcohol formation dominates (e.g., for carbonic acid diethyl ester, Figure S6).[11]

Thus, **1** can readily be prepared through ester pyrolysis from either carbonic acid di-*tert*-butyl ester (Figure 1) or from

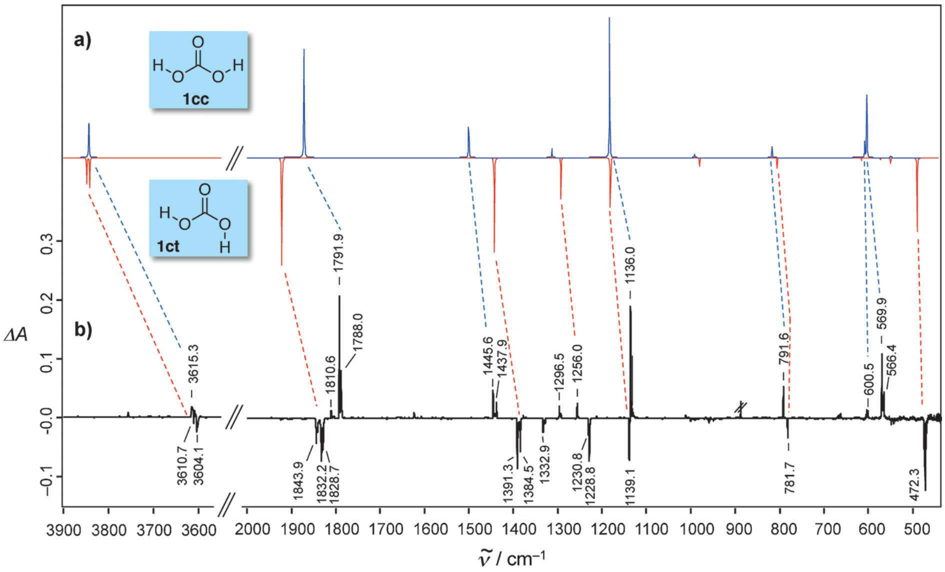


Figure 1. Irradiation-induced isomerization of **1 cc** and **1 ct**, prepared by HVFP of di-*tert*-butyl carbonate. a) CCSD(T)/cc-pVTZ computed spectra of **1 cc** (blue) and **1 ct** (red). b) Difference of the two spectra recorded after 50 min irradiation with l = 2454 nm and after additional 28 min radiation with l = 2108 nm. The splittings of several IR bands are due to matrix effects (multiple sites). For the preparation of **1** from Boc_2O, see Figure S2.

Boc_2O (Figure S2), as evident from the excellent agreement of the experimental and the unscaled CCSD(T)/cc-pVTZ computed infrared bands for the two observed rotamers **1 cc** and **1 ct**, which can be interconverted with monochromatic near infrared (NIR) light from an optical parametric oscillator (OPO) by selective excitation of overtones or combination modes (Figure 1).

Our infrared band positions agree very well with those previously assigned to **1 cc** and **1 ct** of matrix-isolated "β-H_2CO_3"[16] (for detailed comparisons, see Figure 3 as well as Tables S7 and S8). Additionally, we provide several previously unreported IR bands, including the very strong absorptions of the O−H out-of-plane deformation mode at 569.9 cm^{-1} for **1 cc** as well as 472.3 cm^{-1} for **1 ct**, which will aid in the detection of **1** in other environments.

The hitherto unknown isomer **1 tt** cannot be prepared under these conditions as it is much higher in energy (+10.1 kcal mol^{-1}) than the most favorable structure **1 cc** according to our high-level computations (Figure 2); the isomerization barrier to **1 ct** is only +1.8 kcal mol^{-1}. The very good agreement of the geometrical parameters of the computed structures with those determined by microwave spectroscopy[9,10] (the experimental and computed rotational constants agree within 0.5 %, Table S1) lends confidence to

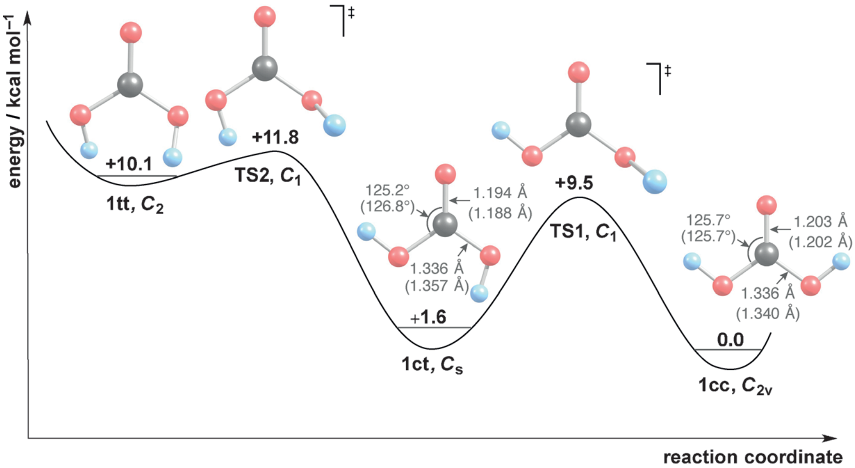


Figure 2. Potential energy hypersurface for the rotational interconversion of the rotamers of **1** with relative energies ΔH_0 (in kcal mol^{-1}) computed from convergent focal-point analyses extrapolated to the basis-set limit. The bond lengths [Å] and angles [°] given for **1** are ground-state optimum geometrical parameters for the CCSD(T)/cc-pVQZ optimized structures in the given symmetries. For comparison, the experimental geometrical parameters determined from Fourier-transform microwave spectroscopy for **1 ct**[9] and **1 cc**[10] are given in parentheses. Carbon dark gray, hydrogen light blue, oxygen red.

the quality of the geometry optimizations. The relative energies (ΔH_0) computed from the convergent focal-point analyses (FPA)[17] and extrapolated to the basis set limit (for details, see the Supporting Information) provide the most accurate assessment of the energies of the stationary points of **1** (Figure 2) to date, and they slightly revise previously published values.[9,10] Hence, we find that **1 tt** displays overall C_2 symmetry, which gives a 0.8 kcal mol^{-1} lower relative energy, and that the previously computed C_{2v} geometry[9,10] is not a minimum. The **1 ct**→**1 cc** isomerization barrier is also reduced from 8.8 to 7.9 kcal mol^{-1}.[9]

Our IR spectral data perfectly agree with the band assignments for **1** generated through vapor deposition from β-H_2CO_3, but they are significantly different to those assigned to α-H_2CO_3;[4a,6,12b,16,18] note that the signal intensities herein reported for **1** are an order of magnitude larger, which simplifies their assignment. Our results shed new light on an earlier report that states "that not only α-H_2CO_3 can sublime and recondense as α-H_2CO_3 but also β-H_2CO_3 can sublime and recondense as β-H_2CO_3".[16] In our view, this astounding feature would imply that the bulk structural information about the polymorphic origin is retained upon sublimation into individual molecules in the gas phase. It is important to note that the α and β polymorphs first introduced were only tentatively assigned;[6] the crystal structures of the two polymorphs remain unsolved, but structural predictions were made for α-H_2CO_3.[1] The IR spectra of matrix-isolated **1** sublimed and re-condensed from α-H_2CO_3 were interpreted as evidence for a 10:1 mixture of the **1 cc** and **1 ct** conformers in addition to small amounts of carbonic acid dimers, CO_2, and H_2O.[12b] At the same time, comparisons of the ν(C=O) region of carbonic acid vapor isolated in argon after sublimation of α- and β-H_2CO_3 (Figure S4 in Ref. [16]) very clearly show two different sets of carbonyl absorptions for the two conformers of the α- and β-polymorphs, respectively (Figure 3, see below).

In our view, the two different sets of carbonyl absorptions in the matrix-isolation IR spectra from sublimation of the α- and β-polymorphs of **1** and the unprecedented behavior upon recondensation can only be due to two different compounds constituting α- and β-H_2CO_3. As α-H_2CO_3 was prepared from a methanolic solution of $KHCO_3$ and HCl,[4a,12b,16] we surmised that carbonic acid monomethyl ester (**2**, Scheme 1b) formed instead of **1** under such typical esterification conditions. This conjecture is supported by the notion that β-H_2CO_3 is transformed into α-H_2CO_3 in acidic methanolic solutions.[4a,19] As there are only very few reports on the preparation of **2** in solution, for example from protonation of $CH_3OCO_2^-Na^+$ with HCl or H_2O,[20] we had to devise a strategy for the preparation of **2** in the gas phase, so that it can be condensed into a noble-gas matrix to allow detailed comparisons of its IR spectrum with that of **1**.

Fortunately, our HVFP protocol for the preparation of **1** is general and thus also applicable to the synthesis of **2** from *tert*-butyl methyl carbonate (Scheme 1 b). Hence, this constitutes the first gas-phase preparation of **2**, allowing a direct comparison with the rotamer spectra of **1**. As found for the parent acid, **2** also displays two readily identifiable rotamers that differ in the position of the OH bond *cis* (**2 cc**) or *trans* (**2 ct**) relative to the C=O moiety. We have not found evidence for the formation of conformers with a *trans* orientation of the methyl group, in line with the facts that **2 tc** and **2 tt** are 3.5 and 10.7 kcal mol^{-1} higher in energy than **2 cc** at the MP2/cc-pVQZ level of theory, and that their barriers for rearrangement to the lower-lying *cis*-methyl isomers are only 7.0 and 2.5 kcal mol^{-1}, respectively. Whereas the acid moieties of the lowest-lying conformers **2 cc** and **1 cc** are structurally very similar, the difference for the C=O IR absorptions amounts to $\Delta\nu = 12.8$ cm^{-1} (Figure 3, Tables S7–S12). This band separation is much too large to be due to experimental errors, it rather is indicative of two different chemical entities.

Visual inspection of the overlaid published spectra[16] of the matrix-isolated condensed vapor phases of the α- and β-H_2CO_3 polymorphs (Figure 3 b) with our individual IR spectra for **1** (Figure 3 a) and **2** (Figure 3 c) indicates that in spectrum (b) in Figure 3 b, for the condensed vapor of α-H_2CO_3, the bands for the *cis–trans* isomers **2 cc** and **2 ct** of the monomethyl ester can be clearly seen (for full spectra, see Figure S4). The agreement of the data of the present work and those of Figure S4 of Ref. [16] for α-H_2CO_3 is within less than 0.5 cm^{-1} (for exact tabulated comparisons, see Tables S9 and S10). The spectral data also agree very well with our unscaled harmonic CCSD(T)/cc-pVTZ computations for **2 ct** and **2 cc** (Tables S7–S12). The difference of only 0.5 cm^{-1} between $\Delta\nu$ (experiment) = 50.3 cm^{-1} and $\Delta\nu$ (theory) =

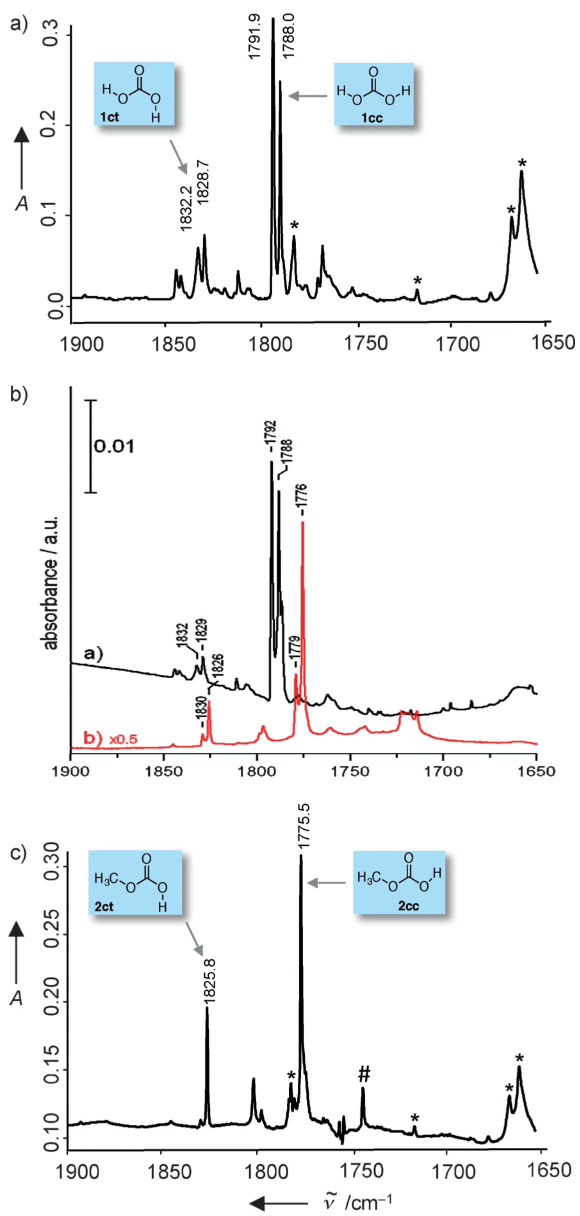


Figure 3. Comparison of the carbonyl region of the FT-IR spectra. a) FT-IR spectrum of the matrix-isolated (Ar, 8 K) pyrolysis products of di-*tert*-butyl-carbonate (deposition time: 2 h, 710 °C, * = co-fragment isobutene). b) Figure S4 of Ref. [16] (reproduced with permission from the authors) with the caption "Comparison of the ν(C=O) region of carbonic acid vapor isolated in argon after sublimation of a) β-H_2CO_3 and b) α-H_2CO_3". c) Matrix-isolated pyrolysis products (Ar, 8 K) of *tert*-butyl methyl carbonate (deposition time: 2 h, 650 °C). * = co-fragment isobutene, # = traces of formaldehyde; IR bands of unreacted starting material have been subtracted for clarity. The carbonyl absorptions are split because of matrix effects.

49.8 cm^{-1} for the carbonyl absorptions of **2ct** and **2cc** underlines our spectral assignments. It is also evident that in spectrum (a) of Figure 3b, the condensed vapor of β-H_2CO_3 corresponds to the bands for **1cc** and **1ct** that agree equally well with our computations.

Our results strongly suggest that the condensed vapors that were thought to be originating from α-H_2CO_3 rather correspond to the monomethyl ester **2**. We found no evidence for the interpretation that "Based on isotopic substitution experiments and the fact that the product from reaction in aqueous solution (β-H_2CO_3) can be converted into the product obtained by reaction in methanolic solution (α-H_2CO_3), we conclude that the two reaction products correspond to two polymorphic modifications of carbonic acid. For both products alternative assignments have been discussed and rejected".[21] As no reagents were added in the sublimation of α-H_2CO_3, we also conclude that all studies[4a,6,12,16,18,19,21] relating to the "α-polymorph" in fact must be assigned to **2** instead. To chemically and spectroscopically unequivocally confirm that we have indeed made **2** and that its spectral identity is significantly different from **1**, we also prepared **2** with a perdeuterated methyl group ([D_3]-**2**) through pyrolysis of di-*tert*-butyl [D_3]-methyl carbonate under otherwise identical conditions to compare the experimental and computed isotopic shifts exerted on the vibrational bands through deuteration of the methyl group (Tables S11–S14). As the agreement of the vibrational shifts is exceptionally good (on average within ±2 cm^{-1}), both in sign (i.e., blue- or red-shift) and relative magnitude (Tables S13 and S14), a methyl group *must* be present, and there is no doubt that we have positively identified **2** and [D_3]-**2**.

In summary, we have presented the first gas-phase preparation of carbonic acid (**1**) and its monoalkyl esters, as exemplified for the monomethyl ester (**2**), through unimolecular ester pyrolysis from readily available dialkyl carbonates. The unequivocal spectral assignments of both **1** and **2**, including isotopic shifts for the deuterated precursor of **2**, and the perfect matching with high-level ab initio computations allowed us to re-interpret the identity of the molecules derived from the vapor phase above the α-polymorph of solid carbonic acid, which must be, as shown in the present work, be re-assigned to the monoester **2**. This casts a new light on the gas-phase chemistry of **1** and will help in its identification in environmental, atmospheric, and astrophysical environments.

Experimental Section

Preparation of di-*tert*-butyl carbonate: In a 100 mL flask with a magnetic stir bar, di-*tert*-butyl dicarbonate (5 g, 0.023 mol), *tert*-butyl alcohol (6.8 g, 0.092 mol), 4-dimethylaminopyridine (1.4 g, 0.011 mol), and triethylamine (4.8 mL, 0.034 mol) were dissolved in dichloromethane (50 mL). Then, sodium hydride (1.10 g, 0.046 mol) was added in portions under intense gas evolution. The mixture was stirred vigorously for two days. Under ice cooling, first water was added to the reaction mixture and then 0.5 M citric acid. The reaction was extracted several times with diethyl ether, and the combined organic layers were washed with 0.5 M citric acid, water, and brine. The organic phase was dried with sodium sulfate, and the solvent was removed by rotary evaporation. The crude product was distilled under vacuum giving 0.48 g (0.003 mol, 12 %) of a colorless oil that crystallized after some time. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43 ppm (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.0, 81.0, 152.2 ppm. ESI microTOF, positive mode: *m/z* calcd for $C_9H_{18}NaO_3$: 197.1154 [M+Na]$^+$; found: 197.1154.

Preparation of *tert*-butyl methyl carbonate: In a 100 mL flask with a magnetic stir bar, di-*tert* butyl dicarbonate (3 g, 0.014 mol), 4-dimethylaminopyridine (0.17 g, 0.001 mol), and triethylamine (5.1 mL, 0.037 mol) were dissolved in methanol (30 mL). The mixture was heated at reflux for 24 h. Then, the reaction was quenched with 0.5 M citric acid. Thereafter, the reaction was extracted several times with dichloromethane, and the combined organic phases were washed with 0.5 M citric acid, water, and brine. The organic phase was dried with sodium sulfate, and the solvent was removed by rotary evaporation. The obtained liquid was distilled under atmospheric pressure to yield 0.73 g (0.005 mol, 39%) of a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.63$ (s, 3H), 1.41 ppm (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 27.9$, 54.0, 82.2, 154.3 ppm. ESI microTOF, positive mode: *m*/*z* calcd for $C_6H_{12}NaO_3$: 155.0684 $[M+Na]^+$; found: 155.0672.

Preparation of *tert*-butyl $[D_3]$-methyl carbonate: In a 100 mL flask with a magnetic stir bar, di-*tert*-butyl dicarbonate (6 g, 0.027 mol), $[D_4]$-methanol (1.97 g, 0.056 mol), 4-dimethylaminopyridine (0.33 g, 0.003 mol), and triethylamine (10.2 mL, 0.074 mol) were dissolved in dichloromethane (60 mL). The mixture was stirred for five days and then heated at reflux for four hours. The reaction was quenched with 0.5 M citric acid. Thereafter, the reaction was extracted several times with dichloromethane, and the combined organic layers were washed with 0.5 M citric acid, water, and brine. The organic phase was dried with sodium sulfate, and the solvent was removed by rotary evaporation. The obtained liquid was distilled under atmospheric pressure to yield 0.33 g (0.002 mol, 9%) of a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.37$ ppm (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 27.6$, 52.9 (sept, $J = 22.3$ Hz), 81.6, 154.0 ppm. ESI microTOF, positive mode: *m*/*z* calcd for $C_6H_9D_3NaO_3$: 158.0872 $[M+Na]^+$; found: 158.0872.

Matrix-isolation studies: The cryostat used for the matrix-isolation studies was a Leybold RDK 10-320/RW-2 closed-cycle refrigerator system, whose temperature was controlled by a Leybold LTC 60 Si-diode temperature controller. The cryostat was equipped with CsI windows for IR and BaF_2 windows for UV/Vis measurements. The noble-gas deposition rates of the matrices were controlled by an MKS 11798 gas-flow controller that was set to 1–2 sccm. IR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}). Whenever necessary to avoid unwanted photochemistry induced by the IR light from the light source of the spectrometer, spectra were recorded using long-pass IR filters ($\lambda > 4.5$ μm). For the combination of high-vacuum flash pyrolysis (HVFP) with matrix isolation, a small home-built water-cooled oven that was directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a resistively heated completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm). The temperature was controlled by a Ni/CrNi thermocouple. The precursors were evaporated from a pre-cooled storage bulb (ethyl methyl carbonate: −70 °C; *tert*-butyl methyl carbonate: −50 °C; di-*tert*-butyl carbonate: −45 °C; di-*tert*-butyl dicarbonate: 10–18 °C) into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of approximately 50 mm, the pyrolysis products were co-condensed with a large excess of argon, which was introduced by a separate jet on the surface of the 8 K matrix window. Alternatively, gaseous mixtures (argon, 1:1000) were prepared for all precursors, except for di-*tert*-butyl dicarbonate, and subjected to pyrolysis. For broad-band NIR irradiation of matrix-isolated samples, light emitted from the IR source (globar) of the FTIR spectrometer or alternatively light from a high-pressure mercury lamp (HBO 200, Osram) filtered by a long-pass filter ($\lambda >$ 1100 nm) was used. An optical parametric oscillator (GWU OPO versaScan 280 MB, pump laser: Spectra-Physics Quanta Ray Nd:YAG LAB-170-10, 355 nm) was used for narrow-band NIR irradiation (line width 4 cm^{-1}). Specific *cis*–*trans* isomerizations were induced by narrow-band NIR irradiation using an OPO laser. Difference spectra of these NIR light-induced isomerization reactions were particularly well suited for the specific elaboration the IR bands of the rotamers of carbonic acid. Several experiments were performed to determine the optimal pyrolysis temperature with respect to the yield of the carbonic acid or the carbonic acid monomethyl ester (ethyl methyl carbonate: 850 °C; *tert*-butyl methyl carbonate: 700–750 °C; di-*tert*-butyl carbonate (bis(2-methyl-2-propanyl) carbonate): 710 °C; di-*tert*-butyl dicarbonate: 850 °C; see also Figure S2). Commercial di-*tert*-butyl dicarbonate (Sigma–Aldrich) was used without further purification.

Electronic structure computations: We utilized single-reference coupled-cluster theory with all single and double excitations (CCSD) and perturbatively treated triple excitations [CCSD(T)] for the benchmarking of the carbonic acid conformer energy landscape.[22] Geometries were optimized at the CCSD(T)/cc-pVQZ level of theory within the frozen core (FC) approximation (no deleted virtual orbitals). We applied the focal-point analysis (FPA) of Allen and co-workers,[17,23] targeting the CCSD(T) complete basis set (CBS) limit. Herein, the treatment of the electron correlation and the quality of the basis set are systematically enlarged and thus improved. To assure smooth convergence towards the CBS limit, we employed Dunning's correlation-consistent basis set families cc-pV*XZ* and cc-pCV*XZ* (with $X = D(2), T(3), Q(4), 5$).[24] The SCF energy was extrapolated with a Feller-type[25] scheme; the dynamic electron correlation energy was extrapolated with a two-point Helgaker[26] power law. As only valence electrons are correlated in the focal point tables, the core correlation was estimated by the following correction:

$$\Delta E_{\text{core}} = E^{\text{cc-pCVTZ}}_{\text{AE-CCSD(T)}} - E^{\text{cc-pCVTZ}}_{\text{FC-CCSD(T)}} \quad (1)$$

Relativistic corrections to the energy, including mass velocity contributions and one-electron Darwin terms (MVD1), were computed at the CCSD(T)/cc-pVTZ level of theory.[27] Additionally, the diagonal Born–Oppenheimer correction (DBOC) was included in the final focal-point energies; the latter one was computed at the HF/cc-pVTZ level of theory.[28] Finally, the CCSD(T)/cc-pVTZ zero-point vibrational energies (ZPVE) were added to the corresponding electronic energies. Vibrational frequency computations were also used to determine the nature of each stationary state (ground or transition structure). All ab initio computations were performed with the CFOUR program package employing analytic first and second derivatives.[29]

For the pyrolyses of the carbonates only a density functional theory (DFT) approach was possible. The M06-2X functional was chosen in combination with a cc-pVTZ basis set.[30] All DFT computations were performed with the Gaussian 09 electronic structure code.[31]

Received: July 7, 2014
Published online: September 3, 2014

Keywords: ab initio calculations · ester pyrolysis · IR spectroscopy · matrix isolation

[1] S. K. Reddy, S. Balasubramanian, *Chem. Commun.* **2014**, *50*, 503.
[2] T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, K. R. Liedl, *Angew. Chem. Int. Ed.* **2000**, *39*, 891; *Angew. Chem.* **2000**, *112*, 919.
[3] G. Strazzulla, J. R. Brucato, G. Cimino, M. E. Palumbo, *Planet. Space Sci.* **1996**, *44*, 1447.
[4] a) W. Hage, K. R. Liedl, A. Hallbrucker, E. Mayer, *Science* **1998**, *279*, 1332; b) Y. Oba, N. Watanabe, A. Kouchi, T. Hama, V. Pirronello, *Astrophys. J.* **2010**, *722*, 1598; c) W. Zheng, R. I. Kaiser, *Chem. Phys. Lett.* **2007**, *450*, 55.
[5] M. H. Moore, R. K. Khanna, *Spectrochim. Acta Part A* **1991**, *47*, 255.
[6] W. Hage, A. Hallbrucker, E. Mayer, *J. Am. Chem. Soc.* **1993**, *115*, 8427.
[7] K. Adamczyk, M. Prémont-Schwarz, D. Pines, E. Pines, E. T. J. Nibbering, *Science* **2009**, *326*, 1690.

[8] J. K. Terlouw, C. B. Lebrilla, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 354; *Angew. Chem.* **1987**, *99*, 352.
[9] T. Mori, K. Suma, Y. Sumiyoshi, Y. Endo, *J. Chem. Phys.* **2009**, *130*, 204308.
[10] T. Mori, K. Suma, Y. Sumiyoshi, Y. Endo, *J. Chem. Phys.* **2011**, *134*, 044319.
[11] G. Bucher, *Eur. J. Org. Chem.* **2010**, 1070.
[12] a) K. Winkel, W. Hage, T. Loerting, S. L. Price, E. Mayer, *J. Am. Chem. Soc.* **2007**, *129*, 13863; b) J. Bernard, M. Seidl, I. Kohl, K. R. Liedl, E. Mayer, Ó. Gálvez, H. Grothe, T. Loerting, *Angew. Chem. Int. Ed.* **2011**, *50*, 1939; *Angew. Chem.* **2011**, *123*, 1981; c) C. Mitterdorfer, J. Bernard, F. Klauser, K. Winkel, I. Kohl, K. R. Liedl, H. Grothe, E. Mayer, T. Loerting, *J. Raman Spectrosc.* **2012**, *43*, 108.
[13] J. Bernard, PhD Thesis, University of Innsbruck (Austria), **2014**. This thesis was sent to the authors on May 9, 2014. J. Barnard concludes "…the formation of the monomethyl carbonic acid appears possible." (p. 106) and "To shed further light on the nature of the different species, more experiments need to be done." (p. 107).
[14] M. R. Rossi, D. T. R. Vidal, C. L. do Lago, *Food Chem.* **2012**, *133*, 352.
[15] a) S. Minakata, I. Sasaki, T. Ide, *Angew. Chem. Int. Ed.* **2010**, *49*, 1309; *Angew. Chem.* **2010**, *122*, 1331; b) K. N. West, C. Wheeler, J. P. McCarney, K. N. Griffith, D. Bush, C. L. Liotta, C. A. Eckert, *J. Phys. Chem. A* **2001**, *105*, 3947.
[16] J. Bernard, R. G. Huber, K. R. Liedl, H. Grothe, T. Loerting, *J. Am. Chem. Soc.* **2013**, *135*, 7732.
[17] A. G. Császár, W. D. Allen, H. F. Schaefer, *J. Chem. Phys.* **1998**, *108*, 9751.
[18] W. Hage, A. Hallbrucker, E. Mayer, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3183.
[19] W. Hage, A. Hallbrucker, E. Mayer, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2823.
[20] a) G. Gattow, W. Behrendt, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 534; *Angew. Chem.* **1972**, *84*, 549; b) A. Dibenedetto, M. Aresta, P. Giannoccaro, C. Pastore, I. Pápai, G. Schubert, *Eur. J. Inorg. Chem.* **2006**, *2006*, 908.
[21] W. Hage, A. Hallbrucker, E. Mayer, *J. Mol. Struct.* **1997**, *408*, 527.
[22] a) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; b) R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *165*, 513; c) R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *167*, 609; d) T. D. Crawford, H. F. Schaefer, in *Reviews in Computational Chemistry*, Wiley, Hoboken, **2007**, p. 33.
[23] A. G. Császár, G. Tarczay, M. L. Leininger, O. L. Polyansky, J. Tennyson, W. D. Allen in *Spectroscopy from Space*, *Vol. 20* (Eds.: J. Demaison, K. Sarka), Kluwer, Dordrecht, **2001**, p. 317.
[24] a) J. T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007; b) D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1995**, *103*, 4572.
[25] D. Feller, *J. Chem. Phys.* **1993**, *98*, 7059.
[26] a) A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.* **1998**, *286*, 243; b) T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.* **1997**, *106*, 9639.
[27] W. Klopper, *J. Comput. Chem.* **1997**, *18*, 20.
[28] N. C. Handy, Y. Yamaguchi, H. F. Schaefer, *J. Chem. Phys.* **1986**, *84*, 4481.
[29] J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay, CFOUR, a quantum chemical program package, with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts, and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen, **2012**.
[30] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.
[31] M. J. T. Frisch et al., Gaussian09, D.01, Wallington CT, **2009**.