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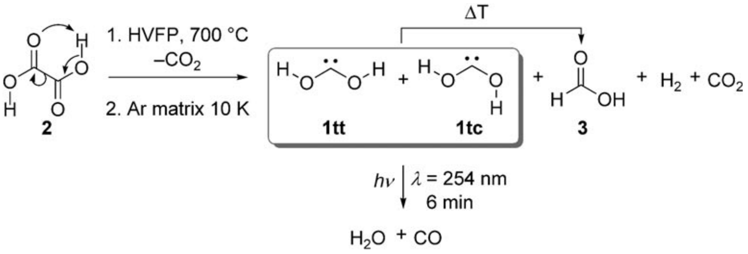
Reactive Intermediates

Spectroscopic Identification of Dihydroxycarbene**

Peter R. Schreiner and Hans Peter Reisenauer*

Dihydroxycarbene (HO-C-OH, **1**, Scheme 1) is a prototypical compound that plays a fundamental role in the class of synthetically valuable heterosubstituted carbenes that act as reagents and metal ligands. In tribute to the discoverer of such metal–carbene complexes, these types of structures are now referred to as Fischer carbenes.[1] However, attempts to prepare free hydroxycarbenes through the thermal decomposition of metal carbenes have failed.[2] Like its smaller cousin hydroxycarbene, **1** also plays an important role in deciphering the organic chemistry of small organic molecules in prebiotic Earth and extraterrestrial environments, since **1** is implied in the thermal decomposition of oxalic acid (**2**), which gives rise to formic acid (**3**), CO, CO_2, H_2, and H_2O.[3–5] Here we show that **1** can be generated thermally through high-vacuum flash pyrolysis (HVFP), subsequently be trapped in an argon matrix at 10 K, and be fully characterized spectroscopically.



Scheme 1. Generation of dihydroxycarbene (**1**; **tt** refers to the *s-trans,s-trans* rotamer, **tc** denotes the *s-trans,s-cis* rotamer) through CO_2 extrusion from oxalic acid (**2**). Irradiation near the absorption maximum of **1** quickly gives water and CO.

The thermal decomposition of **2** is a long-known reaction that has been used to generate CO_2. Wobbe and Noyes apparently presented the first kinetic study of this reaction as early as 1926,[3] and numerous publications followed by Clark[4] in the 1950s as well as by Lapidus et al. in the 1960s.[6] None of these, however, mention the possible involvement of free carbene **1** along the decomposition pathway to give predominantly CO_2 and H_2; the reason for this is that carbenes were just being established as viable chemical entities at that time. Lapidus et al. proposed the direct decomposition of **2** to CO_2 and H_2 by an intramolecular hydrogen transfer that implies the formation of a divalent species, although it was neither drawn nor explicitly stated.[7] The proposed intermediacy of **1** in the thermal decomposition of **2** in the gas phase came in 1985 when Yamamoto and Back noted a marked difference in the rate of formation of CO_2 in the photochemical and thermal reactions of **2**.[8] A subsequent MP2/4-31G//HF/3-21G computational study emphasized the key role **1** plays in the thermal reactions of **2**,[9] and confirms the singlet ground state of **1** predicted earlier by Feller et al.[10] These authors noted that besides the Woodward—Hoffmann-allowed C_{2v}-symmetric decomposition of **1** into CO_2 and H_2, the radical path through $H^\cdot$ + $^\cdot$OCOH and recombination may also be important, and that the hydrogen shift of **1** to give **3** is formally a forbidden process.

Indirect evidence for the successful experimental preparation of **1** through neutralization of the radical cation of **1** ($1^{\cdot+}$, generated from $2^{\cdot+}$) comes from gas-phase studies by Burgers et al., who employed neutralization-reionization mass spectrometry.[11] Wiedmann et al. reported that **1** must survive intact for at least 0.3 μs, and that **1** should indeed possess a singlet ground state.[12] Theoretical studies emphasize that singlet **1** indeed lies in a deep potential well and should therefore be observable.[13,14]

Since we were successful recently in the preparation of hydroxymethylene by the thermal decomposition of glyoxylic acid,[15] we attempted the generation of **1** by thermal extrusion of CO_2 from **2** (Scheme 1) by using HVFP followed by immediate matrix isolation at 10 K in solid argon. The starting material **2** is sufficiently volatile to enable gas-phase decomposition in a heated quartz tube. After several attempts and optimization of the reaction temperature we were successful in the generation and trapping of **1** (see the Experimental Section for details).

We characterized the two populated rotamers **1tt** and **1tc** of **1** (Scheme 1) by their measured difference IR spectra (Figure 1) and by comparison with the spectrum obtained by high-level coupled cluster theory computations including all electrons (AE) at the AE-CCSD(T)/cc-pVTZ level (see the Experimental Section for details). The remarkable agreement between the measured and computed IR absorptions provides convincing evidence for the successful preparation of **1**. The generation of two of the three possible rotamers of **1** (the last one is C_{2v}-symmetric, namely, *s-cis,s-cis*, **1cc**) derives from the mechanism of preparation, as indicated by the arrows in Scheme 1. Although the depicted C_{2h} form of **2** is most stable, less-symmetric forms are close in energy (within several

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[*] Prof. Dr. P. R. Schreiner, Dr. H. P. Reisenauer
Institut für Organische Chemie
Justus-Liebig-Universität
Heinrich-Buff-Ring 58, 35392 Gießen (Germany)
Fax: (+49) 641-99-34309
E-mail: prs@org.chemie.uni-giessen.de
Homepage: http://www.chemie.uni-giessen.de/schreiner

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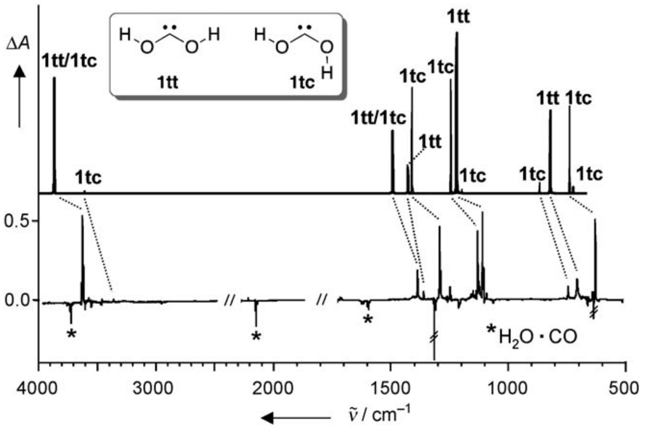


Figure 1. Dihydroxycarbene rotamers **1tt** and **1tc** (see Scheme 1) identified in an argon matrix at 10 K. Lower trace: Difference IR spectrum obtained by subtracting the IR spectrum of the irradiated (6 min, 254 nm) from the un-irradiated matrix-isolated pyrolysis products of oxalic acid (**2**). Upper trace: Computed IR spectrum of a 1:1 mixture of **1tt** and **1ct** at the CCSD(T)/cc-pVTZ level. For the full IR spectrum see the Supporting Information.

kcal mol^{-1}, see below),[14] and can readily be interconverted before CO_2 extrusion in the hot quartz tube. As found for hydroxymethylene, the OH stretching vibrations are highly anharmonic and the quantitative deviation from the computed harmonic absorptions is larger than usual (we have not applied scaling).[15]

To provide further evidence for the successful preparation of **1**, we also studied the deuterated species by thermal decomposition of deuterated oxalic acid [D$_2$]-**2**. The agreement between the computed and measured IR spectra (Figure 2) is again excellent.

We also obtained the UV spectrum of **1** (Figure 3) which showed a maximum absorption at $\lambda = 256$ nm. This absorption maximum essentially coincides with that of dimethoxycarbene ($\lambda_{max} = 257$ nm), and emphasizes the close relationship between the parent and substituted alkyoxycarbenes.[16]

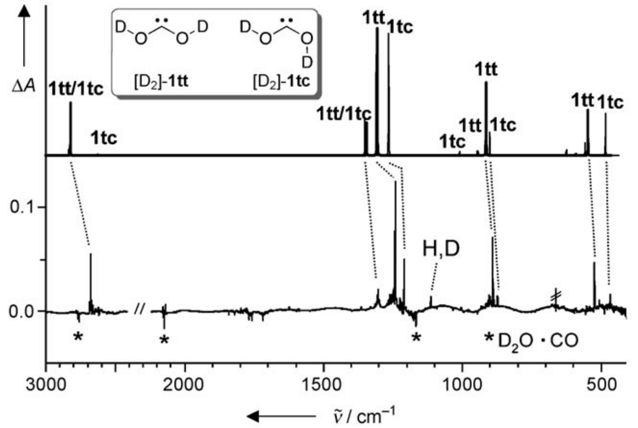


Figure 2. Deuterated dihydroxycarbene rotamers [D$_2$]-**1tt** and [D$_2$]-**1tc** (see Scheme 1) identified in an argon matrix at 10 K. Lower trace: Difference IR spectrum obtained by subtracting the IR spectrum of the irradiated (6 min, 254 nm) from the un-irradiated matrix-isolated pyrolysis products of deuterated oxalic acid ([D$_2$]-**2**). Upper trace: Computed IR spectrum of a 2:1 mixture of [D$_2$]-**1tt** and [D$_2$]-**1ct** at the CCSD(T)/cc-pVTZ level.

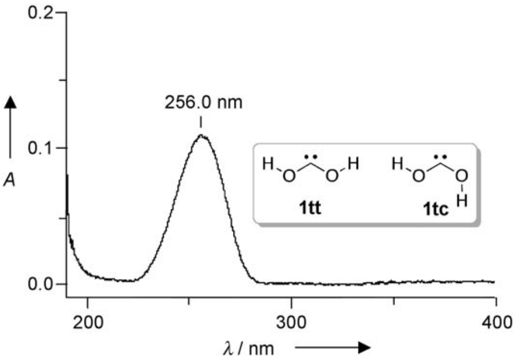


Figure 3. UV spectrum of **1** (argon matrix, 10 K). The spectrum was obtained by subtracting the spectrum of the irradiated (32 min, 254 nm) from that of the un-irradiated matrix-isolated pyrolysis products of **2**.

In marked contrast to hydroxymethylene,[15] which has a half-life of only two hours under comparable conditions (with its isotopologue surviving for at least several days), both **1** and [D$_2$]-**1** are persistent for days in the matrix: while hydrogen tunneling is pronounced for hydroxymethylene, there is no indication for such a process for **1**. This finding may be due to strong π donation of the lone pairs of electrons on the oxygen atoms into the empty p orbital on the carbon atom, which greatly reduces its electron deficit. This proposal is substantiated by the rather short computed C–O bond lengths of 1.325 Å in **1tt**. The three-center-two-electron delocalized nature of the respective molecular orbitals of **1tt** underline this conclusion (Figure 4).

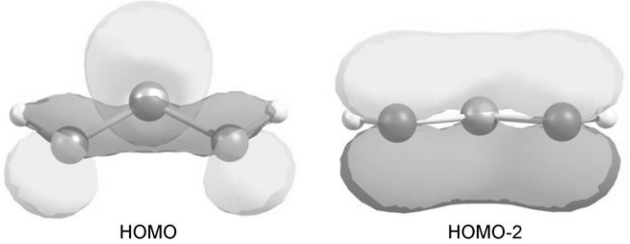


Figure 4. Molecular orbitals of **1tt** involved in the π delocalization and shortening of the C–O bond. HOMO = highest occupied molecular orbital.

Not only the heteroallyl-type HOMO-2 but also the HOMO—formally comprised of the sp^2 lone pair of electrons on the carbon atom and the p in-plane lone pairs of electrons on the oxygen atoms—contribute to the internal stabilization of **1tt**, and this explains the significant shortening of the C–O bond as compared to, for example, that in methanol (1.427 Å).[17] This stabilization results in a rather large rotational barrier for the interconversion of the rotamers of **1** (Figure 5).

To determine the energetics for **1** and its rearrangement products we computed the respective potential energy hypersurface (ΔH_0) at the CCSD(T)/cc-pVTZ + ZPVE level

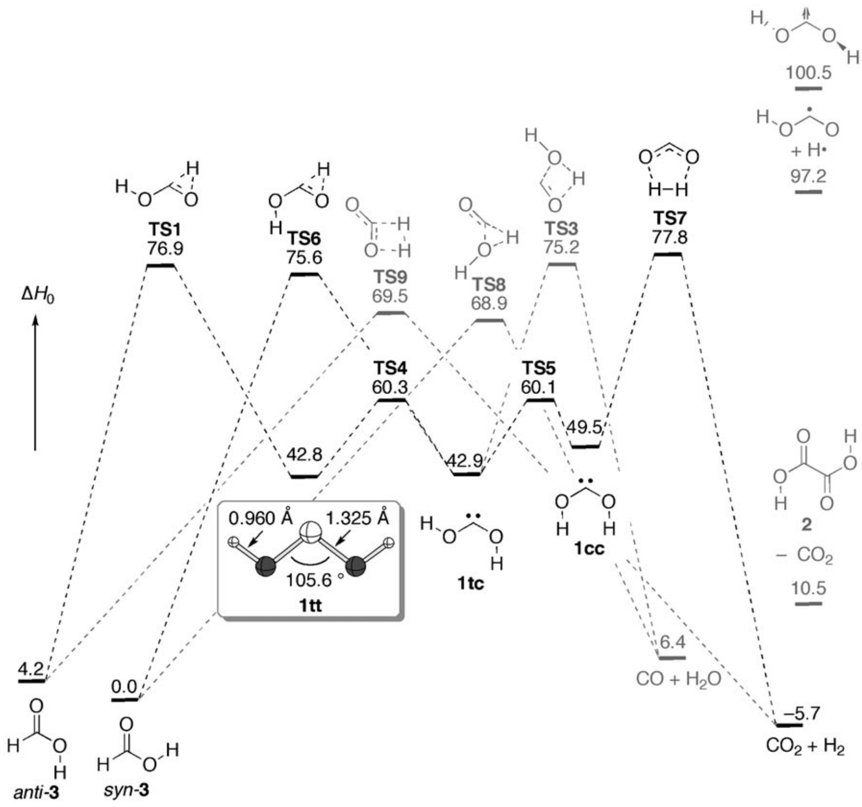


Figure 5. Potential energy hypersurface (ΔH_0) of **1** and related species at the CCSD(T)/cc-pVTZ + ZPVE level in kcal mol^{-1}. The main reaction pathways are highlighted.

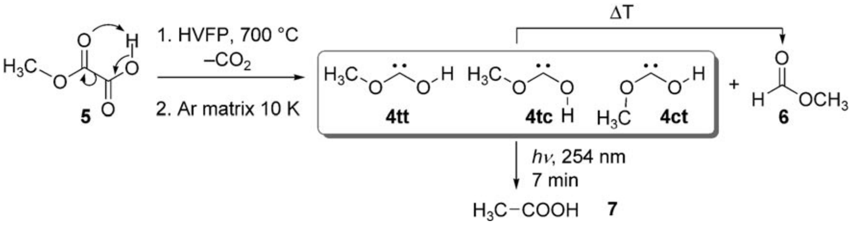
(Figure 5). As predicted,[8,9,13,14] all rotamers of **1** lie in sizeable potential energy wells that cannot be overcome once they are trapped in the matrix at low temperatures. Somewhat surprising are the virtually isoenergetic escape routes for the rotamers of **1**, which lead to the observed rearrangement and decomposition products upon irradiation of the matrix around the UV absorption maximum.

In terms of the conservation of orbital symmetry, we see that there is no dominant energetic preference for the symmetry-allowed H_2 extrusion and the forbidden hydrogen shifts. In marked contrast to earlier (necessarily lower level) theoretical studies,[10,18] the dissociation of **1** to $H^{\bullet}$ + $^{\bullet}$OCOH (+44.4 kcal mol^{-1}) is highly unfavorable because of the high dissociation energy of the O–H bond.[19]

The computational data also allow the derivation of the enthalpy of formation (ΔH_f^0) of **1tt** from either CO_2 ($\Delta H_f^0 = -94.05$ kcal mol^{-1}) and H_2 or from formic acid (**3**, $\Delta H_f^0 = -90.49$); these approaches give a ΔH_f^0(**1tt**) value of −47.26 kcal mol^{-1} and −47.67 kcal mol^{-1}, respectively. To underline the generality of the experimental approach to the preparation of carbenes by CO_2 extrusion from substituted carboxylic acids, we also generated the hitherto unknown hydroxymethoxycarbene (**4**) from oxalic acid monomethyl ester (**5**; Scheme 2); the conditions were virtually the same as before.

The difference IR spectrum of the pyrolysate before and after irradiation (Figure 6) and comparison with CCSD(T)/cc-pVTZ computational data show that the *s-trans,s-trans* form (**4tt**) dominates over the *s-trans,s-cis* (**4tc**) and *s-cis,s-trans* (**4ct**) rotamers. There is no indication of the presence of an *s-cis,s-cis* form, as expected from its lower stability and the mechanism of its generation (see above). Remarkably, the thermal reaction (during HVFP) leads to methyl formate (**6**), while irradiation at 254 nm produces acetic acid (**7**).

Extrusion of CO_2 from α-keto carboxylic acids provides direct access to hydroxycarbenes. This has been shown for hydroxycarbene,[15] dihydroxycarbene, and hydroxymethoxycarbene, and is likely to be of broad general utility. Given that the energies required are around 30 kcal mol^{-1} (Figure 5), this approach may in the future also be amenable to preparative chemistry involving some metal-free Fischer carbenes.



Scheme 2. Generation of hydroxymethoxycarbene (**4**, *s-trans,s-trans* (**4tt**), *s-trans,s-cis* (**4tc**), and *s-cis,s-trans* (**4ct**)) through CO_2 extrusion from oxalic acid monomethyl ester (**5**). The rearrangement product methyl formate (**6**) also forms in the reaction.

Experimental Section

Matrix isolation experiments: Anhydrous oxalic acid (**2**) was prepared by heating the dihydrate under vacuum to 90 °C. Monomethyl oxalate (**5**) was prepared by reaction of equimolar amounts of anhydrous oxalic acid with anhydrous methanol, and was purified by fractional trap to trap distillation under vacuum. The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR spectroscopic measurements and BaF_2 windows for UV/Vis measurements. The IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}), and UV/Vis spectra with an Agilent HP 8453 Diode-Array spectrometer and a JASCO V-670 spectrophotometer. For the combination of HVFP with matrix isolation we employed a small water-cooled oven directly connected to the vacuum shroud of the cryostat. The pyrolysis zone consisted of an empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax wire. The temperature was controlled by a Ni/CrNi thermocouple. The

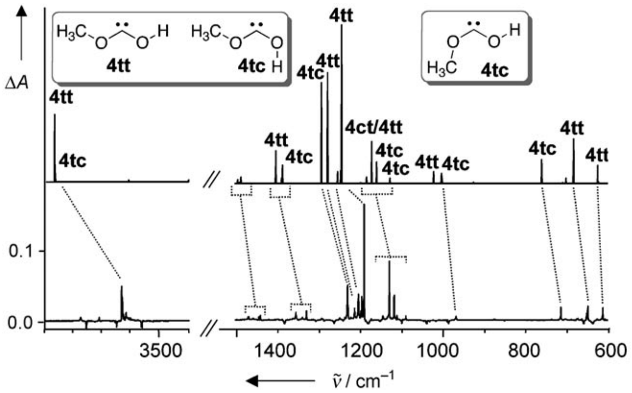


Figure 6. Hydroxymethoxycarbene (**4**) rotamers *s-trans,s-trans* (**4tt**), *s-trans,s-cis* (**4tc**), and *s-cis,s-trans* (**4ct**) in an argon matrix 10 K. Lower trace: Difference IR spectrum obtained by subtracting the IR spectrum of the irradiated (6 min, 254 nm) from the un-irradiated matrix-isolated pyrolysis products of monomethyl oxalate. Upper trace: Computed IR spectrum of a 8:4:1 mixture of the **4tt**, **4tc**, and **4ct** rotamers at the CCSD(T)/cc-pVTZ level, respectively.

precursors were evaporated from a precooled or heated storage bulb (**2**: 30–40 °C, **5**: −15 °C) into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, the pyrolysis products were co-condensed with a large excess of argon on the surface of the 10 K matrix window. Either a low-pressure mercury spiral lamp (Gräntzel) with an interference filter (254 nm) or a high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used for irradiation.

Several experiments were performed to determine the optimal reaction temperature, which turned out to be 700 °C for both **2** and **5**. Under these conditions the decarboxylation reactions were not complete, starting materials were also present in the matrix and the yields of the matrix-isolated carbenes were low. The main reaction products in the matrix were the more-stable tautomers formic acid (**3**) and methyl formate (**6**). Subsequent photolysis of the matrix with a low-pressure mercury lamp at a wavelength of 254 nm (which corresponds to the absorption wavelengths of **1**) for 4 min induced specific photochemical transformations. By calculating the differences in the spectra of the irradiated and un-irradiated matrices, it was possible to determine the IR and UV/Vis properties of the carbenes **1** and **4**, despite their low concentrations in the reaction mixture.

Computations: Computations of the electronic structure were carried out using the correlation-consistent triple-ζ atomic-orbital basis set cc-pVTZ.[20] All geometries were optimized with single-reference all-electron coupled-cluster theory, incorporating all single and double excitations, and with perturbative inclusion of connected triple excitations [AE-CCSD(T)]. All structures were characterized as minima or transition structures by computing harmonic vibrational frequencies.[21]

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