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Communication

Ethynylhydroxycarbene (H−C≡C−C̈−OH)

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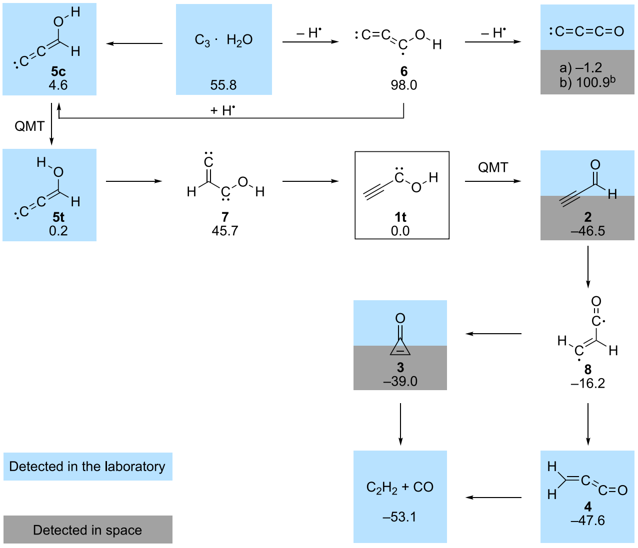
ABSTRACT: The species on the C_3H_2O potential energy surface have long been known to play a vital role in extraterrestrial chemistry. Here we report on the hitherto uncharacterized isomer ethynylhydroxycarbene (H−C≡C−C̈−OH, **1**) generated by high-vacuum flash pyrolysis of ethynylglyoxylic acid ethyl ester and trapped in solid argon matrices at 3 and 20 K. Upon irradiation at 436 nm *trans*-**1** rearranges to its higher lying *cis*-conformer. Prolonged irradiation leads to the formation of propynal. When the matrix is kept in the dark, **1** reacts within a half-life of ca. 70 h to propynal in a conformer-specific [1,2]H-tunneling process. Our results are fully consistent with computations at the CCSD(T)/cc-pVTZ and the B3LYP/def2-QZVPP levels of theory.

Reactions of complexes of small carbon clusters with water resemble conceivable entrance channels for the formation of small oxygenated organic molecules in interstellar media.[1−3] It has been shown that carbon atoms in their triplet ground state are unreactive toward water,[4] and only for $C_n{\cdot}H_2O$ with $n \geq 3$ these complexes exist and show photoreactivity under laboratory conditions.[5,6] Hence, the simplest conceivable addition products all bear the formula C_3H_2O. Among these, readily prepared propynal (**2**, propiolaldehyde)[7,8] and cyclopropenone (**3**)[9−11] have been also detected in space, while propadienone (**4**),[12,13] which lies comparably low in energy (Scheme 1),[14] has only been detected under cryogenic laboratory conditions.[15] Herein, we characterize a hitherto unreported species on the C_3H_2O potential energy surface (PES), namely ethynylhydroxycarbene (H−C≡C−C̈−OH, **1**).

The C_3H_2O PES has been subject to computational and experimental research during the past four decades.[14] In 1990 Ortman et al. conducted photolysis of matrix-isolated carbon clusters complexed with water and found the reaction $C_3{\cdot}H_2O \rightarrow$ **2** + C_3O.[5] A reactive intermediate detected by IR spectroscopy was assigned to the title compound **1**. Only two years later, however, Liu et al. suggested that the observed reactive intermediate is actually 3-hydroxypropadienylidene (**5**) according to computed IR spectral data.[16] Eventually, Szczepanski et al. repeated the experiments of Ortman et al. and confirmed this computational conclusion.[17] The controversial IR bands were assigned to *cis*-3-hydroxypropadienylidene (**5c**) and its *trans*-conformer (**5t**). Additionally, the **5c** → **5t** interconversion in the absence of external stimuli was observed, which was interpreted on the basis of quantum mechanical tunneling (QMT). While the reaction sequence shown in Scheme 1 was later proposed on the basis of experimental and computational results,[18,19] **1** remains elusive.

In recent years we isolated and characterized several members of the hydroxycarbene family using high-vacuum flash pyrolysis (HVFP) of α-keto acids and esters in conjunction with matrix isolation techniques.[20−22] Most

Scheme 1. Proposed Mechanism[18,19] of the Observed Photoinduced Reactions of $C_3{\cdot}H_2O$ to C_3O, 2, and Acetylene + CO[17a]



[a]Ethynylhydroxycarbene (**1**) has not been detected; **2** and **3** are commodity chemicals. All compounds that have been found in space have as well been characterized under cryogenic laboratory conditions. Relative energies in kcal mol^{-1} of singlet geometries were computed at the CCSD(T)/cc-pVTZ level of theory. [b]The relative energy of **6** is corrected for loss of H·: a) refers to $C_3O + H_2$ and b) refers to C_3O + 2 H·.

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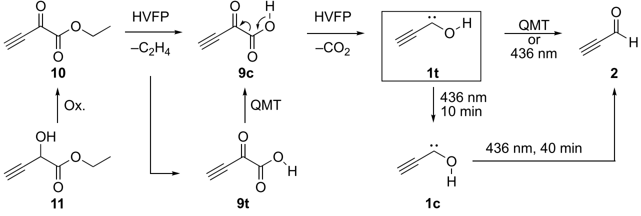
hydroxycarbenes display QMT to the corresponding aldehyde. The tunneling half-life depends on the substituent R, which in the case of R = OH, OMe, and NH_2 inhibits QMT.

In general, ethynylcarbenes are relevant in astrochemical processes[23,24] and can even be used synthetically.[25−29] The electronic structure of parent ground-state triplet propynylidene (HCCCH) has been explored in numerous experimental and computational studies with the result that both terminal carbons are equivalent in terms of their reactivity.[30−32] The photoreaction of propynylidene with triplet dioxygen provides another entrance channel to the C_3H_2O PES as shown in a study by Wierlacher et al., who observed **2** besides the corresponding dioxirane and carbonyl oxide.[33] Other triplet ground-state derivatives of propynylidene have been investigated spectroscopically and they display similarly delocalized electronic structures.[34−36] In contrast, singlet ethynylcarbenes (such as **1**) can best be represented by a localized carbene center in α-position to a localized C≡C bond.[37]

Herein we answer the following questions: (1) Can **1** be generated via pyrolysis of ethynylglyoxylic acid ethyl ester (**10**, Scheme 2) and (2) if so, does **1** undergo [1,2]H-tunneling to **2**? We support our experiments with computations at the CCSD(T)/cc-pVTZ and B3LYP/def2-QZVPP levels of theory and discuss our findings in the context of previous studies.

Scheme 2. High-Vacuum Flash Pyrolysis (HVFP) of 10 Yields 1 *via* 9[a]



[a] **1t** undergoes QMT to **2**. There is a second tunneling reaction from **9t** to **9c**, both of which are present after pyrolysis. Irradiation of the matrix at 436 nm leads to an increase of the concentrations of **1c** and **2** while **1t** vanishes nearly completely over the course of 40 min. Carbene **1c** is not photostable and vanishes after prolonged irradiation to form **2**.

We synthesized ethynylglyoxylic acid ethyl ester (**10**) via oxidation of 2-hydroxybut-3-ynoic acid ethyl ester (**11**) with Dess-Martin periodinane (see the Supporting Information for details). Precursor **10** was obtained as a yellow to brown liquid, which was stable for several weeks in a Schlenk tube connected to the matrix apparatus under reduced pressure (ca. 3 × 10^{-6} mbar). Gaseous **10** was pyrolyzed at 900 °C, and all pyrolysis products were co-condensed with an excess of argon onto the cold matrix window for IR measurements.

Mid-IR measurements of the resulting matrix revealed the formation of CO_2 and ethylene[38] during the pyrolysis. Additionally, we detected **2**, acetylene,[39] CO, and unreacted **10**. Bands from hitherto unreported species are discussed below. Conceivable species that are literature known (Scheme 1) like **3**,[40,41] **4**,[15] and C_3O[42] were not observed based on comparison with published data.

After pyrolysis, a strong band at 1249.4 cm^{-1} coincides well with the strongest band of **1t** computed at 1238.4 cm^{-1} (determined anharmonically at B3LYP/def2-QZVPP). When irradiating the matrix at 436 nm for 40 min (Figure 1A) this band vanishes almost completely along with bands at 3545.0 (theor. 3563.1), 3306.9 (3333.6), 2036.2 (2069.9), 1327.1 (1335.2), 797.7 (806.3), and 539.0 (533.2) cm^{-1} all of which can be assigned to **1t**. Concomitantly, bands that can be assigned to **2** in accordance with literature data[5,17] at 2868.0 (theor. 2833.4), 2107.5 (2160.5), 1688.5 (1720.0), and 940.1 (940.9) cm^{-1} increase in intensity.

Shorter irradiation times at 436 nm led to an increase of three bands that cannot be assigned to propynal (**2**). These bands at 2029.1, 1263.0, and 792.1 cm^{-1} are barely visible after pyrolysis, reach a maximum after 10 min of irradiation at 436 nm, and decrease before they finally vanish completely after prolonged irradiation times (40 min). We assign these bands to *cis*-ethynylhydroxycarbene (**1c**) based on computed bands at 2064.3, 1265.9, and 796.8 cm^{-1} (Figure 1B). This result is in analogy to previous studies on *trans*-trifluoromethylhydroxycarbene ($F_3C-\ddot{C}-OH$, **12**) and *trans*-cyanohydroxycarbene ($NC-\ddot{C}-OH$, **13**), which undergo photoinduced rotamerizations to their corresponding *cis*-conformers.[43,44] Both *cis*-hydroxycarbenes also vanish after prolonged irradiation.

In order to complement our photochemical experiments we checked for QMT reactivity by keeping the as-deposited matrix in the dark and measuring IR spectra in intervals of 1 h. We performed three such experiments: (1) at 3 K, (2) at 20 K, and (3) at 3 K and a 4.5 μm cutoff filter installed between the spectrometer's light source and the matrix window. In all three experiments we observed a slow decay of the bands of **1t** and a simultaneous increase of those of **2** (Figure 1C). Additionally, another such set of bands is apparent, which we assign to *trans*-ethynylglyoxylic acid (**9t**) and its more stable *cis*-conformer (**9c**; Figure 1D), both of which are present due to incomplete pyrolysis of **10**. Both **9c** and **9t** can be assigned in a spectrum measured directly after pyrolysis as minor components (see the Supporting Information for complete band assignments).

We evaluated the kinetics of both QMT reactions by integrating over the strongest IR bands of all four species (**1t**, **2**, **9t**, and **9c**) and following their increase (decrease) over time. The obtained curves were fitted to monoexponential functions (first-order rate law) from which tunneling half-lives were calculated (Figure 2); see the Supporting Information for details, error estimates, and the data for **9t** → **9c**. The kinetic profile of the reaction **1t** → **2** is not temperature dependent, and the spectrometer beam does not seem to have a significant impact on the associated tunneling half-life of ca. 70 h taking the estimated relative error of ca. 12% into account. This result clearly points toward a QMT reaction from **1t** to **2**, which is further supported by CVT/SCT computations (*vide infra*).

We computed the potential energy surface around **1** at the CCSD(T)/cc-pVTZ level of theory (Figure 3). Similar to other hydroxycarbenes the **1t** → **2** reaction is associated with a substantial barrier of 31.8 kcal mol^{-1} and, hence, cannot be initiated solely by excitation from the IR spectrometer in a single photon process. IR spectra were recorded up to 7000 cm^{-1} corresponding to a maximum energy output of only 20.0 kcal mol^{-1}.

Tunneling computations using canonical variational theory in conjunction with small curvature tunneling (CVT/SCT) at the B3LYP/def2-QZVPP level of theory yield a QMT half-life of 62.1 h for **1t** → **2** in excellent agreement with our experiment. The QMT half-life of **1t** nicely fits in the series of hydroxycarbenes (Figure 4). Ethynyl (sp hybridized) as a moderate σ acceptor (−I)[45,46] is expected to captodatively

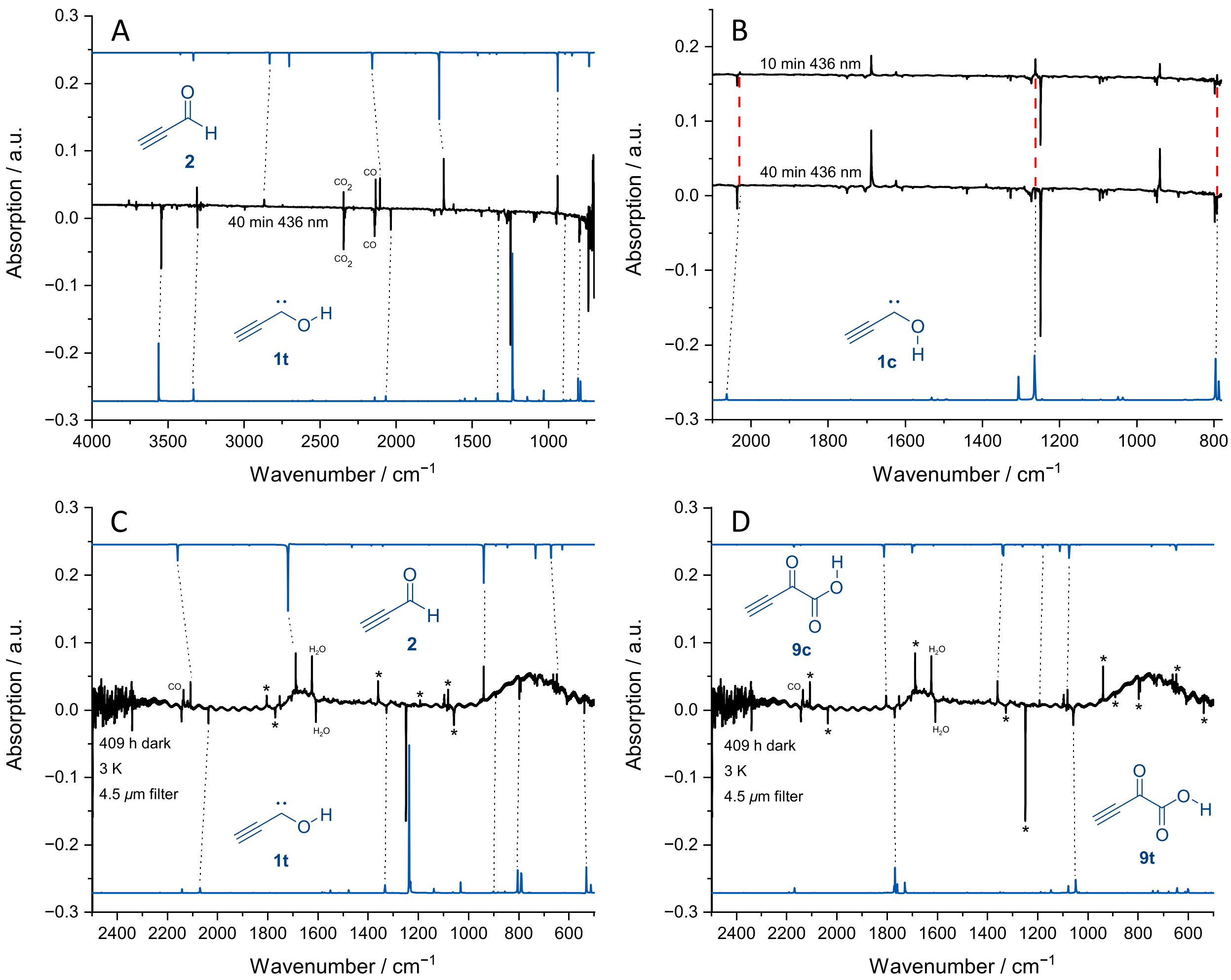


Figure 1. Experimental matrix IR difference spectra (black) and anharmonic spectra computed at the B3LYP/def2-QZVPP level of theory (blue). (A) After 40 min of irradiation at 436 nm bands of **1t** decrease while those of **2** increase in intensity. (B) Three bands that increase after 10 min irradiation at 436 nm and decrease after prolonged irradiation (red dashed lines) are assigned to **1c**. (C and D) By keeping the matrix in the dark for 409 h at 3 K using a 4.5 μm cutoff filter the reactions **1t** → **2** (C) and **9t** → **9c** (D) were observed. Note that C and D display the same experimental difference spectrum. Bands that are assigned in C are marked with an asterisk in D and *vice versa*.

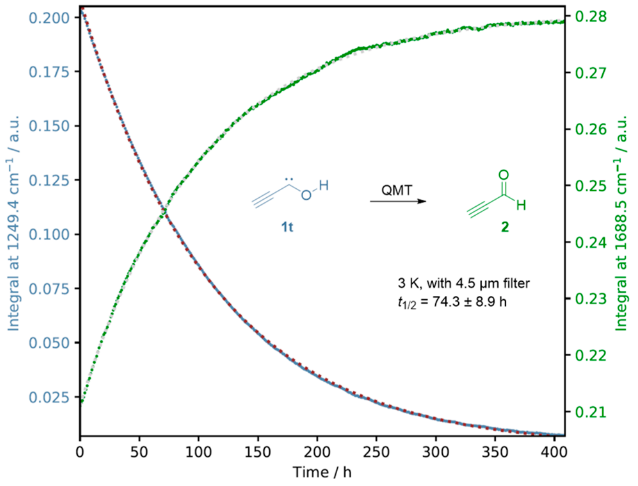


Figure 2. Evaluation of the tunneling half-life of the reaction from **1t** (blue data points, red fit) to **2** (green, gray) at 3 K using a 4.5 μm cutoff filter.

stabilize the carbene center (sp^2) in **1**, resulting in its longer half-life compared to parent hydroxymethylene (**16**).[47] As expected, the effect of the substituent in **1** is smaller than in trifluoromethylhydroxycarbene (**12**)[43] and cyanohydroxycarbene (**13**),[44] both of which also resemble cases of captodatively stabilized hydroxycarbenes. However, the effect is stronger than in cyclopropylhydroxycarbene (**18**),[48] in which the carbene center is stabilized by π donation (+M). The natural bond orbitals (NBO; Figure 3) of **1** support its carbene character (HOMO) and show the stabilizing effect of the adjacent oxygen lone pairs (HOMO−3). The NBOs do not provide hints for the ethynyl's π system to interact with the carbene center (see the SI for details).

Carbene **1** is the only hydroxycarbene without further heteroatom substituents for which the higher lying *cis*-conformer (**1c**) could be observed, which is another sign of its increased stability. According to CCSD(T)/cc-pVTZ computations **1c** lies 2.3 kcal mol^{-1} above **1t**. Recently, we reported the spontaneous rotamerization of *cis-cis*-dihydroxycarbene to its *cis-trans*-conformer, resembling the first tunneling rotamerization in a hydroxycarbene.[49] However, here we could not observe the analogous reaction **1c** → **1t**.

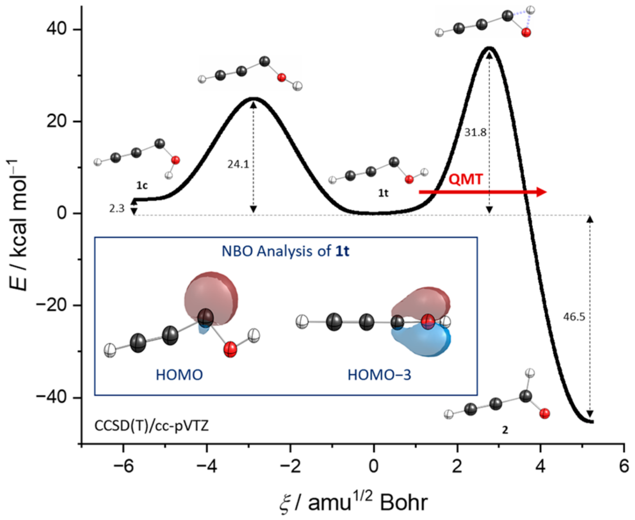


Figure 3. Intrinsic reaction coordinates (IRC) of **1t** → **2** and **1c** → **1t**. The IRC curve was determined at B3LYP/def2-QZVPP, and the relative energies of the stationary points are given at the CCSD(T)/cc-pVTZ level of theory. Inset: Highest occupied molecular orbital (HOMO) and HOMO−3 of **1t** obtained at B3LYP/def2-QZVPP. The HOMO−1 and HOMO−2 (Supporting Information) resemble the π-system at the alkyne moiety. Color code: Carbon, black; hydrogen, white; oxygen, red.

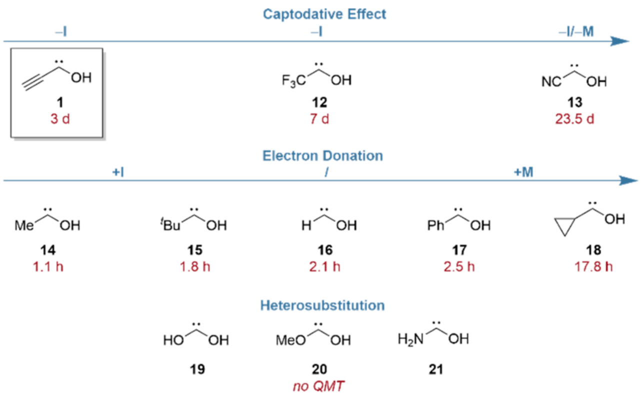


Figure 4. Comparison of experimental QMT half-lives of matrix isolated hydroxycarbenes.[44]

This is in line with the computed tunneling half-life of 60.8 d (CVT/SCT//B3LYP/def2-QZVPP) for this reaction. Note that the **1c** → **1t** activation barrier amounts to 21.8 kcal mol^{-1} at the CCSD(T)/cc-pVTZ level of theory (Figure 3) while the corresponding barrier of *cis-cis*-dihydroxycarbene is only 9.4 kcal mol^{-1}. As only **1t** undergoes QMT to **2** while **1c** is persistent under cryogenic conditions, the Curtin−Hammett principle is not applicable here. Similar cases of conformer-specific QMT have been reported for **12**[43] and **13**.[44]

The feasibility of **1t** → **2** supports the mechanism of the astrochemical formation of small organic molecules from $C_3{\cdot}H_2O$ in Scheme 1.[18] Additionally, the intermediacy of **1** might open a channel for the generation of more complex sugar-like molecules via carbonyl ene reactions with carbonyls, as has been demonstrated for other hydroxycarbenes.[50] As noted before,[17] QMT is a crucial element on the C_3H_2O PES and astrochemical reactions in general, as they usually occur at diluted and low temperature (matrix isolation-like) conditions.

We isolated, characterized, and investigated the reactivity of **1** in argon matrices at 3 and 20 K. This complements and expands previous studies on the C_3H_2O potential energy surface and ethynylcarbenes in general. Carbene **1** is a viable intermediate in astrochemistry (Scheme 1). Upon irradiation at 436 nm **1t** reacts to afford **2**; **1c** forms as well, but vanishes upon prolonged irradiation. The **1t** → **2** reaction also occurs spontaneously when keeping the matrix in the dark via QMT with a tunneling half-life of ca. 70 h in accord with theory and the general trend of hydroxycarbene QMT half-lives. Exploiting substituent effects to influence QMT reactivity and half-lives in a predictable fashion is therefore possible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00897.

Synthetic details, matrix IR and UV/Vis spectra, matrix IR band assignments, details on the kinetic analyses, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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