Gas-Phase Structure Determination of Dihydroxycarbene, One of the Smallest Stable Singlet Carbenes**

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Abstract: *Carbenes are reactive molecules of the form $R^1-\ddot{C}-R^2$ that play a role in topics ranging from organic synthesis to gas-phase oxidation chemistry. We report the first experimental structure determination of dihydroxycarbene ($HO-\ddot{C}-OH$), one of the smallest stable singlet carbenes, using a combination of microwave rotational spectroscopy and high-level coupled-cluster calculations. The semi-experimental equilibrium structure derived from five isotopic variants of $HO-\ddot{C}-OH$ contains two very short CO single bonds (ca. 1.32 Å). Detection of $HO-\ddot{C}-OH$ in the gas phase firmly establishes that it is stable to isomerization, yet it has been underrepresented in discussions of the CH_2O_2 chemical system and its atmospherically relevant isomers: formic acid and the Criegee intermediate CH_2OO.*

Carbenes ($R^1-\ddot{C}-R^2$) comprise an important class of molecules in chemistry owing to a highly reactive electron-deficient carbon atom. Relatively stable singlet carbenes with bulky electron-donating substituents, such as *N*-heterocyclic carbenes, have long been used in organic synthesis,[1,2] but smaller carbenes are more difficult to isolate and characterize. Numerous studies[3–7] implicate small organic carbenes as intermediates in chemical reactions such as the thermal decomposition of dicarboxylic acids (which are a key component of secondary organic aerosols,[8–10] photochemical smog,[11] and interstellar clouds[12]) and the reactions of carbon dioxide and carbon monoxide with H_2O/H_2, thought to be important in prebiotic chemistry,[12–14] and in reversible hydrogen storage.[15,16] Although triatomic carbenes ($:CX_2$ where $X = H$, F, Cl, Br, or I) and vinylidene ($:C=CH_2$) have been studied extensively,[17–22] fewer experimental studies have examined the properties of small carbenes with sub-stituent groups containing two to three atoms, which have a larger range of possible reaction pathways.[23–29]

It is understood that carbenes are stabilized by nearby electron-donating groups.[1] Several studies have reported the potential energy surface (PES) of one of the smallest carbenes with two electron-donating groups: the singlet ground state of dihydroxycarbene ($HO-\ddot{C}-OH$),[3,4,23] which has been suggested to be an intermediate in the photolysis of oxalic acid.[30,31] The three local minima of the singlet $HO-\ddot{C}-OH$ PES, shown in Figure 1, are some of the most thermodynami-cally stable isomers of the CH_2O_2 family, lying approximately
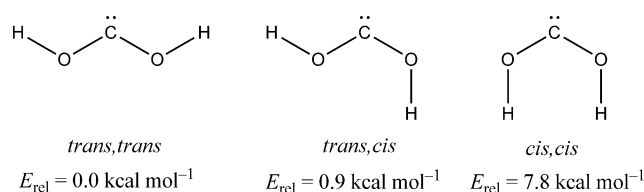

trans,trans	*trans,cis*	*cis,cis*
$E_{rel} = 0.0$ kcal mol^{-1}	$E_{rel} = 0.9$ kcal mol^{-1}	$E_{rel} = 7.8$ kcal mol^{-1}

Figure 1. Three isomers of HO–$\ddot{C}$–OH, with the CCSD(T)/cc-pVTZ relative energies calculated by Schreiner et al.[23]

167 kJ mol^{-1} higher than formic acid, but roughly 335 kJ mol^{-1} lower than the recently detected Criegee intermediate,[32–35] CH_2OO, and 250 kJ mol^{-1} lower than dioxirane,[4] yet are rarely considered in the literature. The stability of singlet $HO-\ddot{C}-OH$ is provided by the overlap between the electrons in the oxygen p orbitals and the empty p orbital on the carbon, leading to much shorter CO bond lengths (1.32 Å)[4,23] than those found in alcohols (such as the 1.42 Å CO bond length in methanol[36]). The triplet state lacks an empty p orbital and is stabilized to a much lesser extent by this overlap and so lies nearly 125 kJ mol^{-1} higher in energy, in contrast to many other carbenes.[3]

The first experimental evidence for the existence of dihydroxycarbene was inferred by neutralization/reionization mass spectroscopy.[24,25] More recently, Schreiner et al. reported the generation of *trans,trans*- and *trans,cis*-HO–$\ddot{C}$–OH by the thermal extrusion of CO_2 from oxalic acid and its subsequent isolation in an argon matrix at 10 K.[23] A similar experiment showed that hydroxycarbene (H–$\ddot{C}$–OH) rapidly isomerizes to formaldehyde (CH_2O) at 10 K, a phenomenon attributed to quantum tunneling through the 125 kJ mol^{-1}

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barrier.[6,26] In contrast, HO−C̈−OH displays no tunneling behavior and is stable under the low-temperature matrix conditions. Subsequent work with several substituted oxycarbenes indicates that the propensity for tunneling is greatly influenced by the identity of the substituent.[7,27,37,38]

We present here the first direct gas-phase evidence for *trans,cis*-HO−C̈−OH, and a precise determination of its rotational spectrum and geometric structure, using a combination of Fourier transform microwave spectroscopy (FTMW), microwave–millimeter-wave double resonance (DR) spectroscopy, and high-level theoretical calculations. The 5–43 GHz Balle–Flygare-type FTMW spectrometer used in these experiments has been described elsewhere,[39–42] so only a brief description is provided here; a more extensive discussion can be found in the Supporting Information. A gaseous mixture of 0.5% CO_2 and 12.5% H_2 in Ne was supersonically expanded into a Fabry–Pérot cavity through a pulsed valve coupled to a direct current electrical discharge source, which produced *trans,cis*-HO−C̈−OH in detectable yield. (The *trans,trans*- and *cis,cis*-isomers may also be present, but both only possess *b*-type rotational transitions, which lie above the frequency ceiling of our spectrometer (see Supporting Information), and were therefore not measured in this work.) Four isotopic variants of HO−C̈−OH were detected under similar conditions using an appropriate isotopically enriched precursor gas ($C^{18}O_2$, $^{13}CO_2$, or an H_2/D_2 mixture). A short microwave pulse (1 µs) excited the rotational transitions that fell within the narrow bandwidth of the cavity (ca. 1 MHz). A Fourier transform of the free induction decay (FID) emitted by the coherently rotating molecules yielded a power spectrum. The lines with frequencies greater than 40 GHz were detected using microwave–millimeter-wave DR spectroscopy, a technique that is used to confirm assignments and extend measurements to higher frequencies.[42–45] Sample FTMW and DR spectra are shown in Figure 2. In total, at least four J_{K_a,K_c}-$J'_{K'_a,K'_c}$ rotational transitions were measured (see Table 1) for HO−C̈−OH and four of its isotopologues: HO−^{13}C̈−OH, H^{18}O−C̈−^{18}OH, HO−C̈−OD$_{cis}$, and D$_{trans}$O−C̈−OH.

The SPFIT/SPCAT suite of programs was used to derive the molecular constants, A_0, B_0, and C_0, from a least squares fit to the experimentally measured transitions.[46] The vibrationally corrected, semi-experimental equilibrium rotational constants, A_e^{SE}, B_e^{SE}, and C_e^{SE}, were determined for each species (see Table 2) and used to determine a semi-experimental equilibrium structure (r_e^{SE}, shown in Figure 3) using the STRFIT program.[47] Several theoretical studies have confirmed a planar structure of dihydroxycarbene[3,4,23] and the derived inertial defects (Δ in Table 2) are uniformly small for all isotopic species, indicating that the molecule is planar and does not undergo large amplitude motions.[48] All structural parameters have estimated 1σ uncertainties less than 0.5% of their respective values, and are in excellent agreement with recent calculations,[4,23] including the CCSD(T)/cc-pCVQZ ab initio structure calculated in this work using the electronic structure package in the CFOUR suite of programs (see Figure 3).[49–51]

The PES calculated by Schreiner et al.[23] suggests that HO−C̈−OH, with sufficient internal energy, may surmount
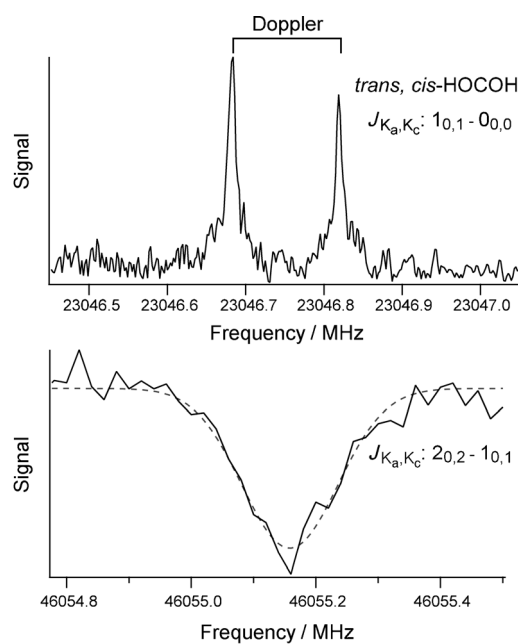

Figure 2. A FTMW spectrum of the $1_{0,1}$–$0_{0,0}$ transition (top frame) and DR spectrum of the $2_{0,2}$–$1_{0,1}$ transition (bottom frame) of *trans,cis*-HO−C̈−OH. Two Doppler-split peaks appear in the FTMW spectrum because the molecular beam is aligned along the Fabry–Pérot cavity axis.[39] The DR spectrum was obtained by monitoring the intensity of the $1_{0,1}$–$0_{0,0}$ spectrum as a second microwave synthesizer is swept in frequency near that predicted for the $2_{0,2}$–$1_{0,1}$ transition. The depletion signal is fit to a Gaussian curve, shown in gray dashed line, to determine the center frequency.
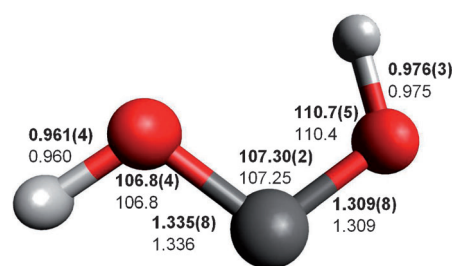

Figure 3. The semi-experimental equilibrium structure, r_e^{SE} of *trans,cis*-HO−C̈−OH. Bold numbers indicate semi-experimental values with estimated 1σ uncertainties given in parentheses in the unit of the last digit. Normal script values show the ab initio structure, calculated at the CCSD(T)/cc-pCVQZ level of theory. The bond lengths are in angstrom and the bond angles are in degrees.

one of the 138 kJ mol^{-1} barriers to form formic acid or dissociate to $CO_2 + H_2$ or $CO + H_2O$.[23] Their measurement of the HO−C̈−OH lifetime at 10 K demonstrates that it is not susceptible to quantum tunneling, unlike H−C̈−OH and CH_3−C̈−OH. From our relative intensity measurements, we conclude that HO−C̈−OH is present at 7% of the level of *trans*-formic acid, indicating that the lifetime of HO−C̈−OH in the gas phase is at least a few milliseconds and that its abundance is sizable. The structure in Figure 3 contains two very short C−O single bonds, lending further credence to the assertion that the substantial overlap between the oxygen and carbon p orbitals is the root cause of the stability of the

Table 1: Measured frequencies for several low-J transitions of isotopologues of HO–C̈–OH. All values are given in MHz, and the estimated 1σ uncertainties are given in parentheses in the unit of the last digit. The signal-to-noise ratio of the $1_{1,1}$–$2_{0,2}$ transitions of the two singly deuterated species was too low to determine an exact frequency.

Transition	HO–C̈–OH	HO–^{13}C̈–OH	H^{18}O–C̈–^{18}OH	HO–C̈–OD$_{cis}$	D$_{trans}$O–C̈–OH
$1_{1,1}$–$2_{0,2}$	16 084.6005 (20)	12 686.6853 (20)	20 151.8988 (20)	–	–
$1_{0,1}$–$0_{0,0}$	23 046.7507 (20)	22 973.2378 (20)	20 832.5530 (20)	22 415.1500 (20)	21 407.0360 (20)
$2_{0,2}$–$1_{0,1}$	46 055.1580 (100)	45 902.3957 (100)	41 638.0770 (100)	44 773.8440 (100)	42 784.8405 (250)
$1_{1,0}$–$1_{0,1}$	63 929.0101 (100)	60 454.4531 (100)	63 285.3450 (100)	53 336.5897 (250)	63 740.3755 (250)
$1_{1,1}$–$0_{0,0}$	85 186.4955 (100)	81 562.2895 (100)	82 622.5246 (100)	73 772.1960 (250)	83 585.1815 (250)

Table 2: A summary of rotational constants derived from the experimental data and theoretical calculations. All values shown in MHz unless otherwise stated. The estimated 1σ uncertainties are given in parentheses in the unit of the last digit. The uncorrected values were derived from a fit to the experimental transitions in Table 1. Additional constants were used in the fitting procedure (see Table S1). The zero-point vibrational corrections were calculated at the CCSD(T)/ANO1 level,[56] and the vibrationally corrected semi-experimental rotational constants were calculated as $A_e^{SE} = A_0 + \Delta A$. The inertial defect is defined as $\Delta = I_C - I_B - I_A$ and has units u·Å^2. The rotational constants of the CCSD(T)/cc-pCVQZ ab initio structure, A_e, B_e and C_e, are shown here for comparison.

Constant	HO–C̈–OH	HO–^{13}C̈–OH	H^{18}O–C̈–^{18}OH	HO–C̈–OD$_{cis}$	D$_{trans}$O–C̈–OH
	Experimental (uncorrected) rotational constants				
A_0	74 559.0428 (34)	71 009.5742 (75)	72 955.1706 (7)	63 555.148 (36)	73 663.9592 (70)
B_0	12 418.0239 (33)	12 419.3332 (73)	11 163.9796 (7)	12 197.379 (35)	11 484.6541 (70)
C_0	10 628.7693 (34)	10 553.9479 (76)	9668.6086 (7)	10 217.807 (35)	9922.4236 (70)
	Zero-point vibrational corrections				
ΔA	341.3648	304.6495	326.3149	374.4679	331.3751
ΔB	114.2458	112.9567	100.6500	103.2054	100.7534
ΔC	107.7056	105.6664	95.5990	98.6285	95.1602
	Semi-experimental rotational constants				
A_e^{SE}	74 900.4076 (34)	71 314.2237 (75)	73 281.4855 (7)	63 929.616 (36)	73 995.3343 (70)
B_e^{SE}	12 532.2697 (33)	12 532.2899 (73)	11 264.6295 (7)	12 300.584 (35)	11 585.4075 (70)
C_e^{SE}	10 736.4749 (34)	10 659.6143 (76)	9764.2077 (7)	10 316.436 (35)	10 017.5838 (70)
Δ	−0.00234	−0.00217	−0.00232	−0.00326	−0.00272
	Ab initio rotational constants				
A_e	74 833.7616	71 247.2243	73 213.5345	63 906.8188	73 931.6234
B_e	12 532.3542	12 532.3303	11 264.3359	12 303.2298	11 586.5264
C_e	10 734.6332	10 657.6569	9762.3418	10 317.0159	10 016.7123

molecule.[3,23] These results illustrate the critical role that the second electron-donating group plays in quenching tunneling to formic acid. Exploring the behavior of other electron-donating substituents (such as nitrogen-containing groups) and performing more detailed lifetime measurements would help to answer questions about how this quenching is achieved.

The close agreement between the theoretical predictions and the experimental results, and the certainty with which the structural parameters are determined leaves little doubt about the identity and structure of *trans,cis*-HO–C̈–OH. Experimental evidence for the apparent gas-phase stability of this carbene indicates that HO–C̈–OH should be included in discussions of the reactivity of the CH$_2$O$_2$ isomeric family, which includes the simplest Criegee intermediate and formic acid. Although CH$_2$OO was not present in our CO$_2$/H$_2$ discharge source, we have recently generated CH$_2$OO in a CH$_4$/O$_2$ mixture[52] in comparable abundance to HO–C̈–OH. One of the established unimolecular reactions of vibrationally excited CH$_2$OO is isomerization to the more stable formic acid isomer;[34] HO–C̈–OH is usually not considered in those discussions despite its relative thermodynamic stability. Taatjes and co-workers found that the Criegee intermediates, CH$_2$OO and CH$_3$CHOO, will readily donate a weakly bound oxygen to the common atmospheric oxides NO$_2$ and SO$_2$ and postulated that Criegee intermediates may play an important role in nitrate and sulfate chemistry.[33,53,54] Given the reactive nature of its carbon atom, yet its relative stability to unimolecular dissociation, HO–C̈–OH formed under atmospheric conditions could play a similarly important role, albeit one involving reactions of the electron-deficient carbon atom (partial charge = +0.036 by Mulliken population analysis) with hydrocarbons. HO–C̈–OH could also be formed by the hydrogenation of HOCO, a radical species with numerous applications in atmospheric and combustion chemistry.[55] However, further study of this molecule must be undertaken to fully understand its reactivity and its role in atmospheric processes.

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