Heats of Formation and Singlet−Triplet Separations of Hydroxymethylene and 1-Hydroxyethylidene

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Thermochemical parameters of hydroxymethylene (HC:OH) and 1-hydroxyethylidene (CH_3C:OH) were evaluated by using coupled-cluster, CCSD(T), theory, in conjunction with the augmented correlation consistent, aug-cc-pV*n*Z, basis sets, with n = D, T, Q, and 5, extrapolated to the complete basis set limit. The predicted value at 298 K for $\Delta H_f(CH_2O)$ is −26.0 ± 1 kcal/mol, as compared to an experimental value of −25.98 ± 0.01 kcal/mol, and for ΔH_f(CH:OH) it is 26.1 ± 1 kcal/mol. The hydroxymethylene−formaldehyde energy gap is 52.1 ± 0.5 kcal/mol, the singlet−triplet separation of hydroxymethylene is ΔE_{ST}(HC:OH) = 25.3 ± 0.5 kcal/mol, the proton affinity is PA(HC:OH) = 222.5 ± 0.5 kcal/mol, and the ionization energy is IE_a(HC:OH) = 8.91 ± 0.04 eV. The predicted value at 298 K for $\Delta H_f(CH_3CHO)$ is −39.1 ± 1 kcal/mol as compared to an experimental value of −40.80 ± 0.35 kcal/mol, and for $\Delta H_f(CH_3C$:OH) it is 11.2 ± 1 kcal/mol. The hydroxyethylidene−acetaldehyde energy gap is 50.6 ± 0.5 kcal/mol, the singlet−triplet separation of 1-hydroxyethylidene is $\Delta E_{ST}(CH_3C$:OH) = 30.5 ± 0.5 kcal/mol, the proton affinity is PA(CH_3C:OH) = 234.7 ± 0.5 kcal/mol, and the ionization energy is $IE_a(CH_3C$:OH) = 8.18 ± 0.04 eV. The calculated energy differences between the carbene and aldehyde isomers, and, thus, the heats of formation of the carbenes, differ from the experimental values by 2.5 kcal/mol.

Introduction

Carbenes, R_1CR_2, contain two substituents and two nonbonding electrons at the divalent, dicoordinate carbon. They form a diverse class of reactive intermediates and play an important role in many areas of chemistry from combustion, to organic synthesis, to ligands in metal complexes to photochemistry.[1] Stable carbenes have been prepared,[2] but most of the simpler carbenes with small substituents R_1 and R_2 are short-lived transient and highly reactive species. Thus, the experimental determination of the thermochemical properties of carbenes is challenging and, when available, experimental results have often been the subject of much debate.

After decades of work, the heat of formation and singlet−triplet separation of methylene (:CH_2, the parent carbene) have now been well established.[3,4] Recently, work on the halogenated carbenes, in particular dichlorocarbene (:CCl_2) with an experimental singlet−triplet separation[5] of 3 ± 3 kcal/mol, determined from photoelectron spectroscopy (PES) study of the corresponding anion, has been challenged by theory.[6−17] Indeed, high-level quantum chemical calculations agree with each other, yielding a much larger value ranging from 19 to 23 kcal/mol for this quantity. A difference of 16−20 kcal/mol between experiment and theory is indeed too large by the current standards of computational thermochemistry. More importantly, whereas available experiment[5] suggested a nearly degenerate ground state for :CCl_2, theory consistently demonstrates that it is a singlet. The involvement of excited electronic states in the starting anions used in the reported PES experiment has been suggested to be responsible for the discrepancy.[16] For phenylcarbene (PhC:H), the difference between the experimental standard heat of formation[18] of 103.8 ± 2.2 kcal/mol and the corresponding theoretical result[19] of 111.0 ± 2 kcal/mol is less severe, but still substantial although the computational level does not rival that used for :CCl_2.

For the hydroxyl-substituted carbenes (HOC:R) in which the π-electron donor hydroxyl group is expected to strongly stabilize the closed-shell singlet state, a few thermochemical parameters have been reported. The formation enthalpy of hydroxymethylene (HC:OH) was reported[20] in 1982 based on proton affinity (PA) bracketing measurements with deuterated D_2COH^+. Observation of the deuteron abstraction reactions from the latter ion by different abstracting bases (giving two distinct isomers) indicated that hydoxymethylene is 54.2 ± 2 kcal/mol higher in energy than its formaldehyde isomer. Adopting the recent revision of the PA scale,[21] a larger value of 60 ± 2 kcal/mol has been derived for this gap.[22] However, quantum chemical calculations provided a smaller value for the HC:OH−H_2CO energy difference ranging from 50 to 55 kcal/mol.[22−24]

1-Hydroxyethylidene (CH_3C:OH, the methyl substituted homologue of HC:OH), has been estimated from neutralization−reionization mass spectrometry (NRMS) experiments[25] to be about 60 and 50 kcal/mol less stable than its isomers acetaldehyde and vinyl alcohol, respectively. However the role played by the carbene in the unimolecular rearrangements between lower-lying C_2H_4O species put forward by the NRMS study was not supported by a subsequent quantum chemical study.[26] More recent measurements of the threshold energy for collision-induced dissociation (CID) of protonated 2,3-butanedione in a quadrupole mass spectrometer led to a value of 16 ± 4 kcal/mol for the enthalpy of formation of 1-hydroxyethylidene.[22] Given the heat for formation of acetaldehyde as −40.8 ± 0.35 kcal/mol,[21] 1-hydroxyethylidene lies 57 ± 4 kcal/mol above

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acetaldehyde. Such a value is close to the earlier NRMS estimate of 60 kcal/mol,[24] but is significantly larger than the available theoretical results of about 51 kcal/mol obtained at the G1,[26] G2,[22] and CBS-Q[22] levels. A singlet−triplet separation of ∼28 kcal/mol has been measured for CH_3C:OH in the latest MS study[22] using the difference in the first and second C−H bond dissociation energies of ethanol. Earlier theoretical results for this gap range from 23 (CISD/3-21G),[27] to 30.5 (CBS-Q)[22] to 33.0 (G2)[22] kcal/mol.

Other simple substituted hydroxycarbenes including FC:OH,[28] HOC:OH,[29] H_2NC:OH,[30] HCC−C:OH,[31] and HSC:OH,[32] exist and some thermochemical data have been reported for these species. In view of the relatively large uncertainties on the available quantitative results for hydroxycarbenes, we have calculated their heats of formation and singlet−triplet energy gaps using high level molecular orbital theory based calculations on the basis of a method that has been developed over the past few years of extrapolating valence shell CCSD(T) calculations to the complete basis set limit using the correlation-consistent basis sets and including other smaller corrections to the total atomization energy.[33−39] In the present work, our focus is on the simplest parent HC:OH and CH_3C:OH species, and we have used our composite approach to predict their heats of formation and singlet−triplet gaps. The present study thus constitutes a benchmark for further theoretical studies of larger carbenes.

Computational Methods

The calculations were performed by using the Gaussian-03 suite of programs.[40] and MOLPRO.[41] The geometries of singlet and triplet :CH_2 were optimized at the CCSD(T) level with the aug-cc-pV*n*Z basis sets for $n = $ D, T, Q, and 5. We abbreviate the basis set label to aVnZ below. The frequencies for singlet and triplet :CH_2 were calculated at the CCSDT/aug-ccpTZ level. The geometries for ^{1}HC:OH, ^{3}HC:OH, H_2CO, H_2COH^+, H_2CO^+, and $HC{:}OH^+$ were calculated at the CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels and the frequencies were calculated at the CCSDT/aug-cc-pVDZ level. The geometries obtained at the CCSD(T)/aug-cc-pVTZ level were used for the single point energy calculations at the CCSD(T)/aug-cc-pVQZ level. The geometries for $^1CH_3C$:OH, $^3CH_3C$:OH, CH_3CHO, $CH_3C(OH)H^+$, $CH_3C{:}OH^+$ and CH_3CHO^+ were calculated at the CCSD(T)/6-311++G** level and used in single point CCSD(T) calculations with the aug-cc-pV*n*Z, $n = $ D, T, Q, basis sets. The geometries were reoptimized and frequencies were calculated at the MP2/aug-cc-pVDZ level. We used the fully unrestricted formalism U/UCCSD(T) for the open-shell valence correlation energy calculations done with Gaussian (some geometry optimizations). All of the final energies were calculated with the R/UCCSD(T) formalism. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[42−44] The CCSD(T) energies were extrapolated to the complete basis set (CBS) limit CBS energies using the following expressions,[45]

$$E(x) = A_{CBS} + B \exp[-(x-1)] + C \exp[-(x-1)^2] \quad (1)$$

where $x = 2$, 3, and 4 for the aug-cc-pV*n*Z basis, D, T, and Q, respectively, and[46]

$$E(x) = E_{CBS} + B/x^3 \quad (2)$$

where $x = 4$ and 5 for aug-cc-pVQZ and aug-cc-pV5Z, respectively.

Smaller corrections are also required for high accuracy calculations and include core-valence corrections and relativistic corrections. Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[47] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI−SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass−velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[48] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. The spin−orbit corrections are 0.08 kcal/mol for C and 0.22 kcal/mol for O, both from the excitation energies of Moore.[49]

As there are not good anharmonic force fields available for all of the molecules of interest, we had to scale the frequencies to obtain the zero point energies. For methylene, we took the average of CCSD(T)/aug-cc-pVTZ harmonic frequency values and the experimental values for the singlet state following the recommendations of Grev et al.[50] This yields a factor of 0.983 (ZPE(best estimate)/ZPE(CCSD(T)/aug-cc-pVTZ)) for scaling the CCSD(T) ZPE's of :CH_2 ($^3B_1$), :CH_2^-, :CH_2^+, and CH_3^+. As there are no experimental values for HC:OH, we used a similar procedure to obtain a scale factor of 0.985 (ZPE(best estimate)/ZPE(CCSD(T)/aug-cc-pVDZ)) for the CCSD(T) ZPE of *cis*- and *trans*-^{1}HC:OH, ^{3}HC:OH, and $^2HC{:}OH^+$, where the best estimate value is taken from the average of the experimental and CCSD(T)/aug-cc-pVDZ ZPEs for CH_3OH. We calculated a scaling factor of 0.976 for formaldehyde (H_2CO) and applied it to ^3H_2CO, $^2H_2CO^+$, and H_2COH^+, For $^1CH_3CO$:H, $^3CH_3C$:OH, $^2CH_3C{:}OH^+$, $^3CH_3CHO$, $^2CH_3CHO^+$, and CH_3CHOH^+, we scaled the MP2/ aug-cc-pVDZ frequencies by a factor of 0.981 based on the average of the experimental and MP2 values for acetaldehyde (CH_3CHO). We note that the scaling factors are quite similar to each other. The calculated vibrational frequencies are given as Supporting Information.

By combining our computed $\sum D_0$ values with the known heats of formation at 0 K for the elements[51] ($\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal mol^{-1}, $\Delta H_f^0(O) = 58.98 \pm 0.02$ kcal mol^{-1}, and $\Delta H_f^0(H) = 51.63 \pm 0.001$ kcal mol^{-1}), we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[52]

Results and Discussion

Methylene. The :CH_2 singlet−triplet energy gap has been extensively studied theoretically since the advent of computational quantum chemistry.[53] The ground state $^3B_1$ electronic configuration is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$ and can be qualitatively described by an ROHF or UHF determinant, whereas wave functions including two reference configurations are required to represent the closed-shell singlet state $^1A_1$ at the Hartree−Fock level. Such a procedure should provide a more balanced treatment of both electronic states if there are not extensive correlation corrections. The closed-shell singlet two-configuration wave function thus includes the SCF configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$ and the corresponding doubly excited configuration $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$. Full configuration interaction (FCI) calculations[54] showed that truncated CI methods based on single-reference SCF wave functions often led to errors greater than 1.0 kcal/mol in the $^1A_1$-$^3B_1$ energy gap of

TABLE 1: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (deg) for CH_2 and Related Systems

molecule	basis set	r_{CH}	∠HCH
CH_2 ($^1A_1$)	aVDZ	1.1270	101.16
	aVTZ	1.1107	101.87
	expt[a]	1.11	102
CH_2 ($^3B_1$)	aVDZ	1.0943	133.10
	aVTZ	1.0792	133.62
	expt[b]	1.0748	133.8
CH_2^-	aVDZ	1.1409	102.00
CH_2^+	aVDZ	1.1098	139.48
CH_3^+	aVDZ	1.1233	120.00

[a] Herzberg G.; Johns, J. W. C. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 107. [b] Jensen, P.; Bunker, P. R.; Karpfen, A.; Kofranek, M.; Lischka, H. *J. Chem. Phys.* **1990**, *93*, 6266.

methylene. When a triple-ζ plus polarization functions (TZP) basis set was used, multireference configuration interaction MRCISD(Q) calculations[55] based on complete active space CASSCF references provided a $^1A_1$-$^3B_1$ energy gap of 10.0 kcal/mol, which is 1.0 kcal/mol larger than the experimental value of 9.0 ± 0.09 kcal/mol.[3d] Application of different types of corrections led to improvement in the calculated singlet−triplet splittings, including relativistic effects,[54b] adiabatic corrections,[56] or empirical corrections based on the singlet−triplet gap of the hydrogen molecule.[57]

It has recently been demonstrated that the methylene singlet−triplet gap can be calculated reliably from single-reference wave functions by using coupled-cluster theory,[4,58−60] although an earlier theoretical study[61] suggested that within the restricted open-shell formalism, a two-configuration coupled-cluster wave function was needed to treat singlet methylene on the same footing as for the triplet counterpart. The coupled cluster method is capable of accounting for the bulk of quadruple excitation effects through the disconnected coupled-pair (T^2_2 terms), which are absent in a single and double excitation CI treatment. In addition, when the triple substitutions are accounted for, for example, the CCSD(T) approach including perturbative triple excitations, the derived results are expected to approach the FCI counterparts. In other words, errors encountered in previous calculations were likely to originate from the incompleteness of the one-electron basis functions employed, rather than from the inherent single-reference character of the starting wave function used in the CC method. Results for the :CH_2 energy gap using CCSD(T) with various basis sets have been reported.[4a,60] At the CBS limit, the heats of formation (0 K) for methylene in the triplet and singlet states were calculated to be 93.4 and 102.6 kcal/mol, respectively, by the CCSD(T) method (see Tables 1−4 for further details).[4a] The most recent recommended values for these quantities are 93.18 ± 0.20 and 102.21 ± 0.20 kcal/mol.[3d] These data lead to a theoretical singlet−triplet separation of 9.2 kcal/mol, which is in good agreement with the experimental value of 9.0 ± 0.09 kcal/mol (see Table 4).[3]

Using atomization energies computed at the CCSD(T)/CBS level, we confirm previous results[4a] and obtain a value of 102.6 kcal/mol for the heat of formation (at 0 K) of singlet methylene (102.7 kcal/mol at 298 K) and 93.4 kcal/mol for $\Delta H_f(^3CH_2)$ at 0 K and 93.5 kcal/mol for $\Delta H_f(^3CH_2)$ at 298 K. We supplement this result with other thermochemical properties for CH_2 (Table

TABLE 2: Calculated Atomization Energies for Singlet and Triplet CH_2[a]

molecule	CBS(1)[b]	CBS(2)[c]	ΔE_{ZPE}	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0 (0 K) [CBS(1)][g]	ΣD_0 (0 K) [CBS(2)][h]
CH_2 ($^1A_1$)	180.69	180.80	10.24[i]	0.34	−0.08	−0.085	170.62	170.73
CH_2 ($^3B_1$)	189.97	189.98	10.65[j]	0.72	−0.15	−0.085	179.81	179.82
CH_2^-	203.81	203.97	9.45[k]	0.56	−0.14	−0.085	194.70	194.86
CH_2^+	−49.35	−49.36	10.16[k]	0.24	−0.10	−0.085	−59.47	−59.60
CH_3^+	81.32	81.39	19.37[k]	0.50	−0.12	−0.085	62.25	62.40

[a] Results are given in kcal/mol. [b] Extrapolated by using eq 1 with aV*n*Z, where *n* = D, T, and Q. [c] Extrapolated by using eq 2 with aVQZ and aV5Z; cf. Table S-3 (Supporting Information). [d] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the CCSD(T)/aVTZ optimized geometries. [e] The scalar relativistic correction is based on a CISD/aVTZ calculation. [f] Reference 49 [g] ΣD_0 (0 K) [CBS(1)] was computed with the CBS obtained by eq 1. [h] ΣD_0 (0 K) [CBS(2)] was computed with the CBS obtained by eq 2. [i] The zero point energy was obtained from the average of CCSD(T)/aVTZ and experimental values as reported in Table S-1 (Supporting Information). [j] The zero point energy was obtained at the CCSD(T)/aVTZ level with a scale factor of 0.983 obtained form CH_2 ($^1A_1$). [k] The zero point energy was obtained at the CCSD(T)/aVDZ level with a scale factor of 0.983 obtained form CH_2 ($^1A_1$).

TABLE 3: CCSD(T) and Experimental Heats of Formation at 0 and 298 K (kcal/mol)

molecule	ΔH_f (0 K) this work[a]	ΔH_f (0 K) other work[b]	ΔH_f (0 K) experimental	ΔH_f (298 K) this work[c]	ΔH_f (298 K) experimental
CH_2 ($^1A_1$)	102.6	101.9	102.21 ± 0.20[d]	102.7	102.31 ± 0.20[d]
CH_2 ($^3B_1$)	93.4	92.9	93.18 ± 0.20[e]	93.5	93.31 ± 0.20[e]
CH_2^-	78.5		78.14 ± 0.20[f]	78.6	78.27 ± 0.20[f]
CH_2^+	332.8		332.92 ± 0.19[e]	332.9	333.04 ± 0.19[e]
CH_3^+	262.5		262.73 ± 0.06[e]	261.6	261.83 ± 0.06[e]

[a] The reported heat of formation was obtained by the average of columns 8 and 9 from Table 2. [b] Doltsinis, N. L.; Knowles, P. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2025. [c] The theoretical values were obtained by the same procedure of ref 52. [d] Hayden, C. C.: Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T. *J. Chem. Phys.* **1982**, *76*, 3607 and ref 3d. [e] Reference 3d. [f] References 3a and 3d.

TABLE 4: Thermochemical Parameters of Methylene Calculated Using Different Quantum Chemical Methods[a]

method	ΔE_{ST} (kcal/mol)	IE_a (eV)	EA (eV)	PA (kcal/mol)	HA (kcal/mol)
CCSD(T)/CBS	9.2	10.38	0.65	197.6	109.5
G3	9.5	10.39	0.58	197.5	109.3
exptl.	9.0 ± 0.09[b]	10.3962 ± 0.0036[c]	0.6520 ± 0.006[b]	197.2[d]	109.0[e]

[a] All values are at 0 K excepting PA which is at 298 K. [b] Reference 3a. [c] Reference 3d. [d] Reference 3d plus $\Delta H_f(H^+)$ = 365.69 kcal/mol at 298 K. [e] Hydrogen affinity of triplet methylene. ΔH_f (0 K) of CH_3 is 35.5 ± 0.3 kcal/mol (theoretical, this work), and 35.86 ± 0.07 kcal/mol (experimental, ref 3d). ΔH_f (0 K) of H is 51.63 kcal/mol.

TABLE 5: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (°) for HCOH, $H_2C{=}O$, CH_3-C−OH, $CH_3CH{=}O$ and Related Systems

molecule	basis set	r_{HC}	r_{CO}	r_{OH}	∠HCO	∠COH	∠HCOH
cis-HC:OH singlet	aVDZ	1.1209	1.3187	0.9721	106.1	114.1	0.0
trans-HC:OH singlet	aVDZ	1.1138	1.3195	0.9677	102.1	107.7	180.0
HC:OH triplet	aVDZ	1.0899	1.3440	0.9670	123.6	110.4	103.1
$HC:OH^+$	aVDZ	1.0993	1.2255	0.9895	124.4	117.3	180.0

molecule	basis set	r_{HC}	r_{CO}	r_{OH}	∠HCO	∠HCH	∠COH	∠HCOH
H_2CO singlet	aVDZ	1.1031	1.2115		121.7	116.6		180.0
	expt[a]	1.1005	1.2033		121.9	116.2		180.0
H_2CO triplet	aVDZ	1.0957	1.3155		113.6			134.9
H_2CO^+	aVDZ	1.1143	1.2001		119.4	121.2		180.0
H_2COH^+	aVDZ	1.0878, 1.0900	1.2529	0.9818	115.6, 121.5		114.9	180.0

molecule	basis set	r_{HC}	r_{CC}	r_{CO}	r_{OH}	∠HCC	∠CCO	∠COH
$CH_3C:OH$ singlet	6-311++G**	1.0995, 1.0991	1.5092	1.3255	0.9657	114.6, 107.4	107.1	106.9
$CH_3C:OH$ triplet	6-311++G**	1.0952, 1.1028, 1.1026	1.4970	1.3563	0.9654	109.6, 111.6, 110.5	123.5	109.1
$CH_3C:OH^+$	6-311++G**	1.0972, 1.0997	1.4623	1.2426	0.9825	110.6, 107.4	129.0	114.8

molecule	basis set	∠HCCO	∠HCCH	∠CCOH
$CH_3C:OH$ singlet	6-311++G**	0.0	123.2, −123.2	180.0
$CH_3C:OH$ triplet	6-311++G**	176.3	120.2, 119.4	109.3
$CH_3C:OH^+$	6-311++G**	0.0	122.5, −122.5	180.0

molecule[b]	basis set	r_{HC}	r_{CC}	r_{CO}	r_{CHx}	r_{OH}	∠HCC	∠CCO
CH_3CHO singlet	6-311++G**	1.0939, 1.0986	1.5134	1.2143	1.1129		110.5, 109.3	124.4
	expt[c]	1.091, 1.085	1.504	1.213	1.106		110.6, 110.3	124.0
CH_3CHO triplet	6-311++G**	1.0942, 1.1003, 1.0952	1.5173	1.3314	1.0978		108.8, 111.6, 110.4	114.5
CH_3CHO^+	6-311++G**	1.0904, 1.0984	1.5140	1.2081	1.1134		111.2, 105.8	123.1
CH_3CHOH^+	6-311++G**	1.0913, 1.1016	1.4636	1.2673	1.0965	0.9766	112.2, 107.6	119.9

molecule[b]	basis set	$∠CCH_x$	∠HOC	∠HCCO	∠HCCH	$∠H_xCCO$	$∠H_xCOC$	∠HOCC
CH_3CHO singlet	6-311++G**	115.3		0.0	121.4, −121.4	180.0		
	expt[b]	114.9		0.0			180.0	
CH_3CHO triplet	6-311++G**	118.3		175.0	120.3, −119.1	134.3		
CH_3CHO^+	6-311++G**	121.5		0.0	122.2, −122.2	180.0		
CH_3CHOH^+	6-311++G**	121.5	113.7	0.0	123.2, −123.2	180.0		180.0

[a] Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177. [b] H_x is the hydrogen from −CHO. [c] Kilb, R. W.; Lin, C. C.; Wilson, E. B., Jr. *J. Chem. Phys.* **1957**, *26*, 1695. Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A,; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 61.

4) including its ionization energy, electron affinity, proton affinity and hydrogen affinity as determined for the triplet ground state of CH_2. The calculated electron affinity of the triplet methylene ($^3B_1$), derived from energies of the corresponding CH_2^- anion ($^2B_1$), converges to a value of EA($^3CH_2$) = 0.65 eV, in excellent agreement with the experimental photodetachment value of 0.6520 ± 0.006 eV.[3a] The adiabatic ionization energy, giving rise to the CH_2^+($^2A_1$) cation, is IE_a($^3CH_2$) = 10.38 eV, in very good agreement with the experimental value of 10.3962 ± 0.0036 eV.[3d] Similarly the calculated proton affinity PA($^3CH_2$) = 197.6 kcal/mol and hydrogen affinity (C−H bond energy in CH_3) HA($^3CH_2$) = 109.5 kcal/mol are both very close to the experimental values of 197.2 and 109.0 kcal/mol, respectively.[3d] The agreement with experiment for all of the values is very good. On the basis of these values and our best estimates for the errors in the calculations, we assign a maximum error limit of ±1 kcal/mol for the thermodynamic values reported below.

Hydroxymethylene. The results for hydroxymethylene (HC:OH) are given in Tables 5−8. For comparison, values determined by the G3 method[62] are also given. The parameters include the energy difference ΔE_1 between HC:OH and its more stable isomer, formaldehyde (H_2CO), in the lowest-lying singlet, triplet and ionized states, the singlet−triplet energy separation ΔE_{ST}, the adiabatic ionization energy IE_a, and the proton affinity PA. The latter three properties were evaluated for both isomers. Unless otherwise noted, the relative energies quoted hereafter refer to the CCSD(T)/CBS results.

The experimental value for the standard heat of formation of formaldehyde is ΔH_f(H_2CO) = −26.0 kcal/mol,[21] in excellent agreement with our value, −26.0 kcal/mol. The predicted heat of formation for *trans*-HC:OH at 298 K is 26.1 kcal/mol. The cis conformer is 4.4 kcal/mol (see Table 7) higher in energy. The energy of *trans*-^{1}HC:OH relative to H_2CO (isomerization energy ΔE_1) converges to a value of 52.1 kcal/mol. The G3 counterpart is marginally larger (52.2 kcal/mol, Table 8). Previous full fourth-order perturbation MP4SDTQ/6-31G(d,p) calculations[23] on the (CH_2O) potential energy surface provided a larger gap of 55 kcal/mol (see also ref 63). A more recent paper[24] reported values of 57.6 and 46.4 kcal/mol obtained from CASSCF(10,10) and MRCI(8,8)//CASSCF(8,8) calculations, respectively, using a cc-pVTZ basis set. Our best estimate of ΔE_1 = 52.1 kcal/mol is slightly smaller than the original 1982 experimental value of 54.2 ± 2 kcal/mol,[20] but markedly smaller than the recently revised value of 60 ± 2 kcal/mol.[22] In view of the expected accuracy of the method that we are using, both experimental energy gaps are too large.

The carbene becomes strongly stabilized relative to formaldehyde following electronic excitation and ionization. Indeed, the ΔE_1 is substantially reduced amounting to only 5.0 and 6.1 kcal/mol in the triplet and cation states, respectively (the corresponding G3 values are 4.5 and 6.2 kcal/mol). The potential

TABLE 6: Calculated Atomization Energies[a]

molecule	CBS(1)[b]	ΔE_{ZPE}	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	ΣD_0 (0 K)
cis-HC:OH singlet	316.77	15.91[f]	0.70	−0.42	−0.308	300.83
trans-HC:OH singlet	321.57	16.37[f]	0.75	−0.43	−0.308	305.21
HC:OH triplet	294.86	15.11[f]	1.03	−0.52	−0.308	279.95
$HC:OH^+$	115.82	16.04[f]	0.86	−0.55	−0.308	99.78
H_2CO singlet	373.34	16.37[g]	1.12	−0.43	−0.308	357.35
H_2CO triplet	298.75	14.24[h]	1.10	−0.38	−0.308	284.91
H_2CO^+	120.28	14.71[h]	0.96	−0.29	−0.308	105.93
H_2COH^+	237.22	24.86[h]	1.04	−0.47	−0.308	212.63
$CH_3C:OH$ singlet	624.62	34.03[i]	1.88	−0.63	−0.393	591.44
$CH_3C:OH$ triplet	593.21	33.25[i]	2.08	−0.74	−0.393	560.92
$CH_3C:OH^+$	435.66	33.78[i]	2.01	−0.66	−0.393	402.85
CH_3CHO singlet	675.11	34.23[g]	2.21	−0.65	−0.393	642.05
CH_3CHO triplet	595.27	32.95[i]	2.12	−0.60	−0.393	563.45
CH_3CHO^+	437.31	33.10[i]	2.03	−0.51	−0.393	405.34
CH_3CHOH^+	552.70	42.44[i]	2.19	−0.68	−0.393	511.38

[a] Results are given in kcal/mol. [b] Extrapolated by using eq 1 with aV*n*Z, where n = D, *T* and Q. Total energies are given Table S-4 (Supporting Information). [c] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the CCSD(T)/aVTZ optimized geometries for systems with 1 carbon atom, and CCSD(T)/6-311++G(d, p), for systems with 2 carbon atoms. [d] The scalar relativistic correction is based on a CISD/aVTZ calculation. [e] Values obtained from ref 49. [f] A scale factor of 0.985, obtained from methanol, was applied. [g] The zero point energy was obtained from the average of theoretical and experimental values as reported in Table S-2 (Supporting Information). [h] A scale factor of 0.976, obtained from H_2CO, was applied. [i] A scale factor of 0.981, obtained from CH_3CHO, was applied.

TABLE 7: CCSD(T) Heats of Formation at 0 and 298 K (kcal/mol)

molecule	ΔH_f (0 K) this work	ΔH_f (298 K) this work
cis-HC:OH singlet	31.4	30.5
trans-HC:OH singlet	27.0	26.1
HC:OH triplet	52.3	51.6
$HC:OH^+$	232.4	231.6
H_2CO singlet[a]	−25.1	−26.0
H_2CO triplet	47.3	46.5
H_2CO^+	226.3	225.4
H_2COH^+	171.2	169.3
$CH_3C:OH$ singlet[b]	14.0	11.2
$CH_3C:OH$ triplet	44.5	42.3
$CH_3C:OH^+$	202.6	200.2
CH_3CHO singlet[c]	−36.6	−39.1
CH_3CHO triplet	42.0	39.6
CH_3CHO^+	200.1	197.7
CH_3CHOH^+	145.7	142.2

[a] The experimental values are −25.06 at 0 K, −25.95 at 298 K; see ref 21. [b] The experimental value is 16 ± 4 at 298 K; see ref 22. [c] The experimental values are −38.29 at 0 K, −40.80 at 298 K; see ref 21.

energy surface of the ionized system has been explored in detail, and the $HC:OH^+$ cation has been generated in mass spectrometry experiments and features a nonergodic behavior in dissociative processes.[64]

We can use the following reactions to estimate how the OH group stabilizes the carbene moiety.

$$\text{HC:OH}\ (^1\text{A}') + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{:CH}_2\ (^3\text{B}_1) \qquad (3)$$

$$\text{HC:OH}\ (^1\text{A}') + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{:CH}_2\ (^1\text{A}_1) \qquad (4)$$

$$\text{HCO:H}\ (^3\text{A}'') + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{:CH}_2\ (^3\text{B}_1) \qquad (5)$$

The energy of reaction 3 is ΔH_{rxn}(298 K) = 39.9 kcal/mol, while it is ΔH_{rxn}(298 K) = 49.1 kcal/mol for reaction 4. The energy of reaction 5 is only 14.4 kcal/mol. We used the following experimental heats of formation at 298 K: $\Delta H_f(CH_4) = -17.9$ kcal/mol and $\Delta H_f(CH_3OH) = -45.44$ kcal/mol.[21] The positive heat of the reactions 3 and 4 indicates a substantial stabilization of the singlet carbene HC:OH by the OH group. In contrast, the stabilization of the triplet carbene (reaction 5) by substitution of the H for OH is much smaller.

The singlet−triplet splitting in formaldehyde is well-established from experiment.[65] The CCSD(T), CBS-estimate, result is 72.4 (CBS) kcal/mol, in good agreement with the value of 72.0 kcal/mol (3.12 eV) from electronic spectroscopy[65] and a previous theoretical MRDCI result of 74.2 kcal/mol (3.22 eV).[66] The singlet−triplet energy separation in HC:OH is 25.3 ± 0.5 kcal/mol at the CBS limit; as far as we are aware, there is no experimental report on this quantity yet. The good agreement for both formaldehyde and methylene suggests that we are reliably predicting the gap in the isomeric carbene. The hydroxyl stabilizes the singlet over the triplet most likely through π-electron delocalization, by about 34 kcal/mol as compared to CH_2. It has been previously discussed that π-donor substituents stabilize the singlet carbene more than the triplet counterpart.[17]

The IEs and PAs have also been calculated. The CCSD(T)/CBS values for PA(CH_2O) of 170.4 kcal/mol and $IE_a(CH_2O)$ of 10.90 eV are in good agreement with the experimental values of 170.4 kcal/mol and 10.88 ± 0.001 eV, respectively.[21] For the carbene, HC:OH, the PA is 222.5 ± 0.5 kcal/mol and the IE_a(HCOH) is 8.91 ± 0.03 eV at the CBS limit. Protonation of both isomers ends up in the same protonated form H_2COH^+, which corresponds to O-protonation of formaldehyde and to C-protonation of hydroxycarbene. As in the 1982 MS experiment,[20] evaluation of these PAs allows the energy difference between the two neutral isomeric forms to be determined. In the NIST Chemistry webbook,[21] a value for PA(HCOH) = 230.9 kcal/mol has been tabulated, which is 10 kcal/mol higher than our result. This arises from the revised energy difference ΔE_1 = 60.5 kcal/mol from the 1998 rescaling of the PAs. Clearly this value for the PA is incorrect as we have shown this energy difference to be incorrect. The carbene IE is about 2 eV smaller than that in formaldehyde as expected as it is far easier to remove the nonbonding electrons. The HOMO of HC:OH is an in-plane (a′) orbital with a larger component on C as expected from a simple molecular orbital model of a carbene based on the electronic structure of CH_2.

1-Hydroxyethylidene. Tables 5−7 and 9 summarize the calculated and available experimental values for the thermochemical parameters of the methyl homologue. Here we focus on the energy difference ΔE_2 between the carbene and its lower-energy isomer acetaldehyde, and the ΔE_{ST} splitting in each isomer. The heat of formation for acetaldehyde, CH_3CHO, at

TABLE 8: Calculated Thermochemical Parameters of Hydroxymethylene (HC:OH) Calculated at Different Levels of Theory[a]

	ΔE_1 (kcal/mol)			ΔE_{ST} (kcal/mol)		IE_a (eV)		PA (kcal/mol)	
method	singlet	triplet	ionized	HC:OH	CH_2O	HC:OH	CH_2O	HC:OH	CH_2O
CCSD(T)/CBS[b]	52.1	5.0	6.1	25.3	72.4	8.91	10.90	222.5	170.4
G3	52.2	4.5	6.2	25.3	73.0	8.92	10.92	222.6	170.3
exptl	54.2 ± 2[c]				72.0[e]		10.88 ± 0.01[f]	230.9[f]	170.4[f]
	60 ± 2[d]								

[a] All values are at 0 K excepting PA which is at 298 K. [b] Results based on ΔH_f values (Table 7). [c] Experimental value taken from ref 20. [d] Reference 22. [e] Reference 65. [f] Reference 21.

TABLE 9: Calculated Thermochemical Parameters of 1-Hydroxyethylidene (CH_3C:OH) Calculated at Different Levels of Theory[a]

	ΔE_2(kcal/mol)			ΔE_{ST}(kcal/mol)		IE_a (eV)		PA (kcal/mol)	
method	singlet	triplet	ionized	CH_3C:OH	CH_3CHO	CH_3C:OH	CH_3CHO	CH_3C:OH	CH_3CHO
CCSD(T)/CBS[b]	50.6	2.5	2.5	30.5	78.6	8.18	10.26	234.7	184.4
G3	50.9	2.8	3.0	30.4	78.5	8.20	10.27	235.4	184.4
exptl	57 ± 4[c]			∼28[c]	77.8[d]		10.229 ± 0.0007[e]		183.7[e]

[a] All values are at 0 K excepting PA which is at 298 K. [b] Results based on ΔH_f values (Table 7). [c] Reference 22. [d] Reference 69. [e] Reference 21.

298 K is predicted to be −39.1 kcal/mol. The most recently reported experimental value is −40.8 ± 0.35 kcal/mol,[67] clearly different from our value. An even larger calculation using the same approach[37a] gives a total dissociation energy of 642.6 kcal/mol which converts to $\Delta H_f(CH_3CHO) = -39.6$ kcal/mol. Our value and the higher level one are both in excellent agreement with the older value[68] of −39.7 ± 0.1 kcal/mol. This is also the value recommended in ref 69. As a further check on our values we can evaluate the energy of the isodesmic reaction 6 as well as reaction 7. The enthalpy of reaction for (6) and (7)

$$C_2H_6 + H_2CO \rightarrow CH_3CHO + CH_4 \quad (6)$$

$$CH_4 + H_2CO \rightarrow CH_3CHO + H_2 \quad (7)$$

are $\Delta H_{rxn}(298\ K) = -10.6$ kcal/mol for reaction 6, and $\Delta H_{rxn}(298\ K) = 4.7$ kcal/mol for reaction 7. Using the experimental heats of formation at 298 K for C_2H_6, CH_4 and H_2CO ($\Delta H_f(C_2H_6) = -20.0$ kcal/mol, $\Delta H_f(CH_4) = -17.9$ kcal/mol, $\Delta H_f(H_2CO) = -26.0$ kcal/mol),[21] we calculate $\Delta H_f(CH_3CHO)$ to be −38.7 kcal/mol from reaction 6 and −39.2 kcal/mol from reaction 7. Our results show that the earlier value for the heat of formation of CH_3CHO from gas-phase hydrogenation is more reliable than the more recent experimental determination from the enthalpies of reduction with lithium triethylborohydride in triglyme. The heat of formation for CH_3C:OH, at 298 K is predicted to be 11.2 ± 1 kcal/mol.

The singlet−triplet energy splittings are calculated to be 30.5 and 78.6 kcal/mol in CH_3C:OH and CH_3CHO, respectively. The splitting for acetaldehyde is in very good agreement with the spectroscopically derived value of 77.8 kcal/mol (3.378 eV or 27240 cm^{-1}).[70] The splitting for the isomeric carbene of $\Delta E_{ST}(CH_3COH) = 30.5 \pm 1$ kcal/mol can be compared with the recent experimental result of ∼28 kcal/mol tabulated from the BDE(C−H)'s of ethanol.[22]

For acetaldehyde, the calculated adiabatic ionization energy $IE_a(CH_3CHO)$ is 10.26 eV and the proton affinity $PA(CH_3CHO)$ is 184.4 kcal/mol in excellent agreement with the experimental values of 10.229 ± 0.0007 eV and 183.7 kcal/mol.[21] The relevant parameters for the carbene are $IE_a(CH_3COH) = 8.18 \pm 0.02$ eV and proton affinity $PA(CH_3COH) = 234.7 \pm 1$ kcal/mol. Again, the energy difference ΔE_2 between the two isomeric forms is substantially reduced, amounting to only 2.5 kcal/mol, in both the ionized and triplet states.

The results in Table 9 show a CCSD(T)/CBS value for ΔE_2 of 50.6 kcal/mol. The G3 value of 50.9 kcal/mol is close to our CBS value. A value of similar magnitude, 50−51 kcal/mol, has been obtained from density functional theory using the B3LYP functional, irrespective of the basis set used. The value of $\Delta E_2 = 50.6 \pm 1$ kcal/mol is 6.4 kcal/mol smaller than the recent experimental estimate of 57 and does not lies within the uncertainty of ± 4 kcal/mol.[22]

Comparing the HCOH/CH_2O pair to the methyl CH_3COH/CH_3CHO pair shows that the isomerization energy is slightly reduced by 1.5 kcal/mol (from 52.1 to 50.6 kcal/mol), lowering the energy of the carbene with respect to its more stable isomer. This can, in part, be attributed to the hyperconjugative effect of the methyl group whose interaction with the carbenoid 2p-lobe is stabilizing.

It is interesting to investigate the effect of methyl substitution on the properties of the analogous systems: (1) *heat of formation*, ΔH_f (kcal/mol), HC:OH/CH_3C:OH, −14.9; H_2CO/CH_3CHO, −13.1; (2) *ionization energy*, ΔIE_a (eV), HC:OH/CH_3C:OH, −0.73; H_2CO/CH_3CHO, −0.64; and (3) *singlet−triplet splitting* ΔE_{ST} (kcal/mol), HC:OH/CH_3COH, 5.2; H_2CO/CH_3CHO, 6.2. These show that, within 1−2 kcal/mol, the methyl group exerts a similar effect in both carbenes and aldehydes.

Conclusions

Various thermochemical parameters of both hydroxymethylene and 1-hydroxyethylidene have been predicted by using coupled-cluster CCSD(T) theory extrapolated to the CBS limit. Where comparison of calculated results with experimental data can be made, in particular for those of methylene, formaldehyde, and acetaldehyde, there is a good agreement attaining an average deviation of <1.0 kcal/mol in most of the cases. We recommend our values for the heats of formation of the carbenes and the thermodynamic quantities associated with them including the energy difference between them and the more stable aldehyde isomers as being the best available for these species.

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Supporting Information Available: Tables of calculated and experimental vibrational frequencies and total CCSD(T) energies (E_h) as a function of basis set and extrapolated to the complete basis set limit. This material is available free of charge via the Internet at http://pubs.acs.org.

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