Heats of Formation of Triplet Ethylene, Ethylidene, and Acetylene†

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Heats of formation of the lowest triplet state of ethylene and the ground triplet state of ethylidene have been predicted by high level electronic structure calculations. Total atomization energies obtained from coupled-cluster CCSD(T) energies extrapolated to the complete basis set limit using correlation consistent basis sets (CBS), plus additional corrections predict the following heats of formation in kcal/mol: $\Delta H_f^0(C_2H_4,{}^3A_1) = 80.1$ at 0 K and 78.5 at 298 K, and $\Delta H_f^0(CH_3CH,{}^3A'') = 86.8$ at 0 K and 85.1 at 298 K, with an error of less than ±1.0 kcal/mol. The vertical and adiabatic singlet−triplet separation energies of ethylene were calculated as $\Delta E_{S-T,vert} = 104.1$ and $\Delta E_{S-T,adia} = 65.8$ kcal/mol. These results are in excellent agreement with recent quantum Monte Carlo (DMC) values of 103.5 ± 0.3 and 66.4 ± 0.3 kcal/mol. Both sets of computational values differ from the experimental estimate of 58 ± 3 kcal/mol for the adiabatic splitting. The computed singlet−triplet gap at 0 K for acetylene is $\Delta E_{S-T,adia}(C_2H_2) = 90.5$ kcal/mol, which is in notable disagreement with the experimental value of 82.6 kcal/mol. The heat of formation of the triplet is $\Delta H_f^0(C_2H_2,{}^3B_2) = 145.3$ kcal/mol. There is a systematic underestimation of the singlet−triplet gaps in recent photodecomposition experiments by ∼7 to 8 kcal/mol. For vinylidene, we predict $\Delta H_f^0(H_2CC,{}^1A_1) = 98.8$ kcal/mol at 298 K (exptl. 100.3 ± 4.0), $\Delta H_f^0(H_2CC,{}^3B_2) = 146.2$ at 298 K, and an energy gap $\Delta E_{S-T-adia}(H_2CC) = 47.7$ kcal/mol.

Introduction

The prediction of the energies of the excited states of small hydrocarbons C_nH_m remains a challenging task for both experimental and theoretical chemists alike, even though this issue has been investigated extensively. After decades of research, the heat of formation (ΔH_f) and the singlet−triplet gap (ΔE_{S-T}) of methylene have now been well established,[1−3] and there is excellent agreement between experiment and theory (cf. ref 4 for a list of benchmark studies on CH_2).

The agreement between theory and experiment is currently not as good for ΔE_{S-T} of acetylene. The singlet−triplet gap in acetylene has extensively been investigated by molecular orbital theory[5−8] and experiment.[9] Suits and co-workers[9] reported an experimental value of $T_0 = \Delta E_{S-T,adia}(C_2H_2) = 82.6$ kcal/mol (28 900 cm^{-1}) for triplet acetylene $C_2H_2(\tilde{a}\ {}^3B_2)$ evaluated by photodissociation of the vinyl radical in a molecular beam. This experimental estimate did not agree with a previous theoretical result of 86.6 kcal/mol (30 270 cm^{-1}) determined by Yamaguchi et al.[6] from coupled-cluster CCSD(T)[10−14] calculations with the TZ2Pf basis set. Subsequent calculations using also the coupled-cluster CCSD(T) method but instead with correlation consistent basis sets[15] by Le et al.[7] and Sherrill et al.[8] led to larger energy gaps of 87.2 kcal/mol (30 500 cm^{-1}) with the aug-cc-pVTZ basis set and 88.3 kcal/mol (30 900 cm^{-1}) with the energies from the cc-pVnZ basis sets extrapolated to the complete basis set (CBS) limit.[16] Thus, the high level theoretical results predict a singlet−triplet energy gap up to ∼6 kcal/mol larger than experiment.

The situation is not significantly improved for the ΔE_{S-T} of ethylene. The lowest-lying triplet state was identified as the *T*-state in the electronic spectrum of ethylene and described by Mulliken and co-workers.[17,18] The electronic spectrum of ethylene is dominated by the $N-V$ ($\pi^* \leftarrow \pi$) singlet excitation, at ∼7.6 eV.[18] Earlier experimental studies using optical spectroscopy[19] established that the excitation to the triplet *T*-state is at a much smaller energy, 4.6 eV (106.1 kcal/mol). Subsequent low-energy electron impact spectrometric studies (EIS)[20−29] provided similar vertical excitation energies at 4.32−4.70 eV (99.6−108.4 kcal/mol). Ion impact experiments[30,31] agree with the lower end of this range giving a value of 4.3 eV (99.2 kcal/mol). More recently, Suits and co-workers[32−34] studied the photodissociation reaction of ethylene sulfide (C_2H_4S) to generate excited states of C_2H_4 and were able to identify triplet ethylene as a product. A small amount of triplet ethylene was produced near its equilibrium geometry, and from the maximum extent of the translational energy distribution, these authors[32] determined the adiabatic singlet−triplet gap of ethylene $\Delta E_{S-T}(C_2H_2)$ to be 58 ± 3 kcal/mol, which yields an upper limit for the heat of formation of triplet ethylene, $\Delta H_f = 70 \pm 3$ kcal/mol.

There are extensive electronic structure calculations on the excited states of C_2H_4 going back to the earliest days of quantum chemistry.[35−37] Ab initio molecular orbital calculations[38−43] predict that the lowest vertical triplet state should be assigned

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to the $^3B_{1u}$ transition, although the absolute values obtained for the vertical excitation energy vary from 3.5 to 4.6 eV. Higher level calculations (CASSCF/CASPTS2)[42] yield a gap of 4.39 eV, whereas MRD-CI calculations[43] gave a slightly larger value of 4.59 eV (30 700 cm^{-1} or 105.8 kcal/mol). Gemein and Peyerimhoff[43] performed a theoretical study of the radiationless transition between the singlet ground and first excited triplet states of ethylene, based on a value of T_e = 63.7 kcal/mol (without zero-point corrections) obtained at the MRD-CI/DZP level. Kim et al.[44] explored several portions of the triplet C_2H_4 potential energy surface using coupled-cluster methods in their study of the C + CH_4 reaction. From the energies[44] calculated at the CCSD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) level, a value of $\Delta E_{S-T}(C_2H_4)$ = 64.5 kcal/mol can be derived, including a ZPE correction of 3.2 kcal/mol. Lester and coworkers[45] carried out diffusion Monte Carlo (DMC) calculations on the ground state singlet and first excited triplet state of ethylene at the MP2/6-311++G** geometries, with trial functions constructed from Hartree−Fock, complete active space self-consistent field, and multiconfigurational self-consistent field wavefunctions. Total atomization energies (TAEs) were calculated for the singlet and triplet states at these optimized geometries. Zero point energies were obtained by scaling the MP2/6-311++G(d,p) values by 0.97. The vertical and adiabatic singlet−triplet gaps were predicted to be 103.5 ± 0.3 and 66.4 ± 0.3 kcal/mol, respectively. The DMC vertical transition energy is consistent with the MRD-CI value of 105.8 kcal/mol,[43] as well as the experimental EIS result of 4.36 eV (100.5 kcal/mol).[25,26] No experimental error bars are reported. The DMC adiabatic energy difference between the ground state and the first exited triplet state is close to the previous CCSD(T) result[44] of 64.5 kcal/mol, and both are substantially larger than the experimental estimate of 58 ± 3 kcal/mol.[32]

As it is now possible to perform higher level calculations with basis sets that can be extrapolated to the complete basis set limit for such species, we have calculated the singlet−triplet gap of ethylene using current state-of-the-art electronic structure calculations. The triplet state of ethylidene, the H_3CCH carbene isomer, and the 1,2-H shift pathway connecting both isomers[46] were also studied. In addition, we calculated the adiabatic singlet−triplet gaps of the C_2H_2 isomers acetylene and vinylidene. Extensive investigations on thermochemical parameters[47−49] including singlet−triplet splittings[4] have demonstrated that the TAEs of small molecules and radicals can be predicted within ±1.0 kcal/mol, when coupled-cluster CCSD(T) electronic energies obtained with the correlation-consistent basis sets and extrapolated to the complete basis set limit (CBS), can be used, and other smaller corrections can be included.

Computational Methods

Electronic structure calculations were done by using the Gaussian 03[50] and MOLPRO[51] suites of programs. Geometry parameters of each structure were fully optimized using molecular orbital theory at the second-order perturbation theory[52] MP2 and coupled-cluster theory CCSD(T) levels[10−14] with the correlation-consistent aug-cc-pVTZ basis set.[15] For open shell electron configurations, the fully unrestricted formalism was used for calculations done with Gaussian 03. Single-point electronic energies were also calculated using the restricted coupled-cluster R/UCCSD(T) formalism in conjunction with the correlation-consistent aug-cc-pV*n*Z (*n* = D, T, Q, 5) basis sets at the (U)CCSD(T)/aug-cc-pVTZ optimized geometries. For simplicity, the basis sets are denoted hereafter as aV*n*Z. In the R/UCCSD(T) approach, a restricted open shell Hartree−Fock (ROHF) calculation is initially performed and the spin constraint is relaxed in the coupled cluster calculation.[53−55] The CCSD-(T) energies were extrapolated to the complete basis set (CBS) limit energies using the following expressions:

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

where x = 2−4 for the aV*n*Z basis, D, T, and Q, respectively, and[56]

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

where x = 4 and 5 for aVQZ and aV5Z, respectively.

After the valence electronic energy, the largest contribution to the TAE is the zero-point energy (ZPE). Evaluation of the ZPEs is described below. To evaluate the TAEs, smaller corrections were also included. Core−valence corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[57] 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 mass−velocity Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[58] The spin−orbit correction is 0.085 kcal/mol for C from the excitation energies of Moore.[59] By combining our computed ΣD_0 values with the known heats of formation at 0 K for the elements (ΔH_f^0(H) = 51.63 ± 0.001 kcal/mol and ΔH_f^0(C) = 169.98 ± 0.1 kcal/mol), we have derived ΔH_f^0 values at 0 K 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.[60] All other thermochemical parameters were derived form the corresponding heats of formation.

Results and Discussion

Table 1 lists the different components of the TAEs of the five C_2H_4 and four C_2H_2 structures that we studied. The C_2H_4 structures include ethylene **1** (^1A_g), triplet twisted ethylene **2** ($^3A_1$), the transition state for rotation of triplet ethylene **2rot** ($^3B_2$), triplet ethylidene **3** ($^3A''$), and the transition state **4** (^3A) for the 1,2-H shift connecting triplet isomers **2** and **3**. The calculated total energies and zero point energies are given as Supporting Information. Both singlet and triplet C_2H_2 isomers were studied, including acetylene **5** ($^1\Sigma^+_g$), triplet *cis*-acetylene **6** ($^3B_2$), vinylidene **7** ($^1A_1$) and triplet vinylidene **8** ($^3B_2$). Table 2 lists the calculated heats of formation of all structures considered at both 0 and 298 K. Table 3 summarizes the vertical and adiabatic singlet−triplet gaps of ethylene obtained using different methods, whereas Table 4 gives the corresponding results for C_2H_2 isomers. The spin-contamination in the triplet electronic state of C_2H_4 is not particularly severe, as shown by the expectation values $\langle S^2\rangle$ of 2.010−2.057 for the UHF wavefunctions. Similarly, the T_1 diagnostic[61] for the CCSD wavefunctions are reasonably small, ranging from 0.011 to 0.015 for the C_2H_4 structures and from 0.014 to 0.020 for the C_2H_2 isomers (Table 1).

Triplet Ethylene and Ethylidene. The ZPE of ethylene was previously estimated[62] as the average of one-half the sum of the calculated harmonic frequencies and one-half the sum of the experimental fundamentals which include anharmonic corrections. For ethylene **1**, the value from the experimental fundamentals is $0.5\Sigma\nu_i$ = 30.90 kcal/mol, and the value obtained from CCSD(T)/aVTZ harmonic frequencies is $0.5\Sigma\omega_i$ = 31.84

TABLE 1: Calculated Atomization Energies of the C_2H_2 and C_2H_4 Structures (kcal/mol)

molecule	CBS (DTQ)[a]	CBS (Q5)[b]	ΔE_{ZPE}	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	ΣD_0(0 K) (DTQ)	ΣD_0(0 K) (Q5)	T_1 diagnostic
CH_2CH_2 **1**(^1A_g)	561.73	561.99	31.38[f]	2.06	−0.34	−0.17	531.90	532.16	0.0114
CH_2CH_2 **2**($^3A_1$)	492.96	493.16	28.16[g]	1.94	−0.37	−0.17	466.20	466.40	0.0115
CH_2CH_2 **2rot** ($^3B_2$)	476.01		28.06[h]	2.12	−0.37	−0.17	449.54		0.0090
CH_3CH **3** ($^3A''$)	487.92		29.53[h]	1.83	−0.37	−0.17	459.69		0.0147
$CH(H)CH_2$ **4** (^3A)	441.28		26.17[h]	1.93	−0.36	−0.17	416.51		0.0154
CHCH **5** ($^1\Sigma_g^+$)	402.85	403.17	16.38[f]	2.11	−0.29	−0.17	388.13	388.45	0.0137
CHCH **6** ($^3B_2$)	312.90	313.02	16.12[i]	1.50	−0.29	−0.17	297.82	297.94	0.0166
CCH_2 **7** ($^1A_1$)	357.78	358.02	14.53[i]	1.51	−0.21	−0.17	344.37	344.37	0.0177
CCH_2 **8** ($^3B_2$)	311.16	311.26	15.46[i]	1.62	−0.32	−0.17	296.83	296.93	0.0204

[a] From CCSD(T)/CBS energies extrapolated using eq 1 with n = D, T, and Q and the CCSD(T)/aVTZ optimized geometries, unless otherwise noted. [b] From CCSD(T)/CBS energies extrapolated using eq 2 with n = Q and 5 and the CCSD(T)/aVTZ optimized geometries. [c] Core/valence corrections were obtained at the CCSD(T)/cc-pwCVTZ level. [d] The scalar relativistic correction (MVD) is from CISD/aVTZ calculations. [e] Spin orbit atomic values taken from reference 59. [f] Average between the experimental (ref 62) and the CCSD(T) values. [g] CCSD(T)/aVTZ value scaled by 0.9848 obtained from ethylene at the CCSD(T)/aVTZ level. [h] MP2/aVTZ value scaled by 0.9752 obtained from ethylene at the MP2/aVTZ level. [i] CCSD(T)/aVTZ value scaled by 0.9888 obtained from acetylene at the CCSD(T)/aVTZ level.

TABLE 2: Calculated Heats of Formation for the C_2H_2 and C_2H_4 Structures (kcal/mol)

	ΔH_f(0 K)		ΔH_f(298 K)	
structure	(DTQ)[a]	(Q5)[b]	(DTQ)[a]	(Q5)[b]
CH_2CH_2 **1** (^1A_g)	14.6	14.3	12.6	12.3
CH_2CH_2 **2** ($^3A_1$)	80.3	80.1	78.7	78.5
CH_2CH_2 **2rot** ($^3B_2$)	96.9		95.1	
CH_3CH **3** ($^3A''$)	86.8		85.1	
$CH(H)CH_2$ **4**	130.0		128.2	
HCCH **5** ($^1\Sigma_g^+$)	55.1	54.8	55.0	54.7
HCCH **6** ($^3B_2$)	145.4	145.3	145.3	145.2
H_2CC **7** ($^1A_1$)	98.8	98.6	99.0	98.8
H_2CC **8** ($^3B_2$)	146.4	146.3	146.3	146.2

[a] From CCSD(T)/CBS energies extrapolated using eq 1 with n = D, T, and Q and the CCSD(T)/aVTZ optimized geometries, unless otherwise noted. [b] From CCSD(T)/CBS energies extrapolated using eq 2 with n = Q and 5 and the CCSD(T)/aVTZ optimized geometries.

TABLE 3: Summary of the Calculated Vertical and Adiabatic Singlet−Triplet Gap of Ethylene (kcal/mol)[a]

method	ΔE_{S-T} (vertical)[b] **2vert−1**	$\Delta E_{S-T,e}$ (adiabatic)[c] **2−1**	ΔE_{S-T} (adiabatic)[d] **2−1**
present work			
CCSD(T)/aVDZ	103.8	65.6	62.4
CCSD(T)/aVTZ	103.7	67.7	64.5
CCSD(T)/aVQZ	103.9	68.4	65.2
CCSD(T)/aV5Z	104.0	68.6	65.4
CCSD(T)/CBS(1)	104.0	68.8	65.6
CCSD(T)/CBS(2)	104.1	68.8	65.6
TAE[e]			65.8
DMC[f]	103.5 ± 0.3		66.4 ± 0.3
Experimental	100.5[g]		58 ± 3[h]

[a] (U)CCSD(T)/aVTZ optimized geometries. [b] Energy difference between **2vert** $^3B_{1u}$ and **1** ^1A_g states at the singlet **1** geometry. [c] Energy difference between **2** $^3A_1$ and **1** ^1A_g without zero-point corrections. [d] Energy difference between **2** $^3A_1$ and **1** ^1A_g including zero-point corrections from Table 1. [e] Negative difference between **2** $^3A_1$ and **1** ^1A_g based on the calculated (Q5) atomization energies given in Table 1. [f] Diffusion Monte Carlo calculations taken from ref 45. [g] EIS experiment from ref 26 (4.36 eV). [h] Experimental estimate from ref 32.

kcal/mol, giving a best estimate of ZPE(**1**) = 31.38 kcal/mol.[62] Evaluation of the ZPEs for triplet structures is less straightforward, as no experimental information is available. Comparison of the calculated and experimental results for ethylene yields a scaling factor, obtained as the ratio of the best ZPE estimate to the calculated $0.5\Sigma\omega_i$ at a given level of theory. We used the scaling factor of 0.9752 derived with the calculated (U)MP2/aVTZ frequencies for structures **2rot**, **3**, and **4**. For the (U)CCSD(T)/aVTZ frequencies of **2** we used a scaling factor of 0.9848 leading to ZPE(**2**) = 28.16 kcal/mol. We note that the difference between the ZPEs of **1** and **2** obtained at the MP2 is 3.0 kcal/mol, which is close to the CCSD(T) difference of 3.2 kcal/mol.

For ethylene **1**, the calculated TAEs of 531.9 and 532.2 kcal/mol with CCSD(T)/CBS energies extrapolated using eqs 1 and 2, respectively, are essentially the same as the experimental value.[63]

In its singlet ground state, ethylene belongs to the D_{2h} point group and its orbital configuration is **1** ^1A_g: ...$(b_{3g})^2$ $(b_{3u})^2$ $(b_{2g})^0$. The vertical triplet state resulting from a HOMO → LUMO excitation corresponds to a configuration **2vert** $^3B_{1u}$: ...$(b_{3g})^2$ $(b_{3u})^1$ $(b_{2g})^1$. As shown in Table 3, the vertical gap computed using the CCSD(T) method is essentially independent of extension of the one-electron basis set. Thus our calculations predict a vertical excitation energy of $\Delta E_{S-T,vert}(^3B_{1u}-^1A_g)$ = 104.1 kcal/mol for **1**. This is in excellent agreement with the diffusion Monte Carlo (DMC) result of 103.5 ± 0.3 kcal/mol[45] but differs somewhat from the experimental value of 100.5 kcal/mol (4.36 eV)[26] and the earlier CASPT2 result of 101.2 kcal/mol (4.39 eV).[42] The smaller CASPT2 value could in part be due to the use of a much smaller TZP basis set

The structural changes due to geometry relaxation from the vertical triplet position **2vert** are schematically illustrated in Figure 1 using the CCSD(T)/CBS energies. Maintaining the planar D_{2h} conformation, the triplet state is stabilized by undergoing a C−C stretch motion, reaching a value of 1.540 Å (essentially a carbon−carbon single bond) at the energy minimum position **2pl** of the $^3B_{1u}$ state. This stretch strongly stabilizes the triplet by 17.9 kcal/mol, the energy difference between **2vert** and **2pl**. The planar structure **2pl** is characterized by three imaginary frequencies, a_u at 687i cm^{-1}, b_{3u} at 384i cm^{-1}, and b_{2g} at 245i cm^{-1}, at the UMP2/aVTZ level. The imaginary vibrational modes correspond to distortions of H-atoms in different directions. Geometry relaxation following the smallest imaginary b_{2g} mode leads to the structure **2trans**, which actually has a *trans*-bent C_{2h} conformation (a ^3B_u electronic state). Such a motion is energetically negligible; the energy difference between **2pl** and **2trans** is 0.01 kcal/mol. **2trans** remains characterized by two imaginary frequencies, a_u at 649i cm^{-1} and b_u at 254i cm^{-1}. Geometry relaxation of **2trans** along the smaller imaginary mode b_u gives rise to the structure **2rot**, which is 0.38 kcal/mol lower in energy than **2trans**. **2rot** has a $^3B_2$ electronic state in C_{2v} symmetry with a *cis*-bent configuration and only one imaginary frequency, a_2 at 681i

TABLE 4: Summary of the Adiabatic Singlet−Triplet Gaps of Acetylene and Vinylidene and the Energy Difference of Singlet Isomers (kcal/mol)[a]

method	$\Delta E_{S-T,e}$ (adiabatic)[b] **6**−**5**	$\Delta E_{S-T,adia}$ (adiabatic)[c] **6**−**5**	$\Delta E_{S-T,e}$ (adiabatic)[d] **8**−**7**	$\Delta E_{S-T,adia}$ (adiabatic)[e] **8**−**7**	ΔE^f **5**−**7**
present work					
CCSD(T)/aVDZ	82.0	81.7	43.9	44.8	37.4
CCSD(T)/aVTZ	88.2	88.0	45.8	46.7	42.2
CCSD(T)/aVQZ	89.4	89.1	46.3	47.2	42.9
CCSD(T)/aV5Z	89.8	89.5	46.5	47.5	43.1
CCSD(T)/CBS(1)	90.0	89.7	46.6	47.5	43.2
CCSD(T)/CBS(2)	90.1	89.9	46.8	47.7	43.3
TAE[g]		90.5		47.7	43.8
experimental[h]		82.6			45.8

[a] (U)CCSD(T)/aVTZ optimized geometries. [b] Energy difference between **6** $^3B_2$ and **5** $^1\Sigma_g$ without zero-point corrections. [c] Energy difference between **6** $^3B_2$ and **5** $^1\Sigma_g^+$ including zero-point corrections from Table 1. [d] Energy difference between **8** $^3B_2$ and **7** $^1A_1$ without zero-point corrections. [e] Energy difference between **8** $^3B_2$ and **7** $^1A_1$ including zero-point corrections from Table 1. [f] Energy difference between **7** $^1A_1$ and **5** $^1\Sigma_g$ including zero-point corrections from Table 1. [g] Energy difference based on the calculated (Q5) atomization energies given in Table 1. [h] Reference 9.

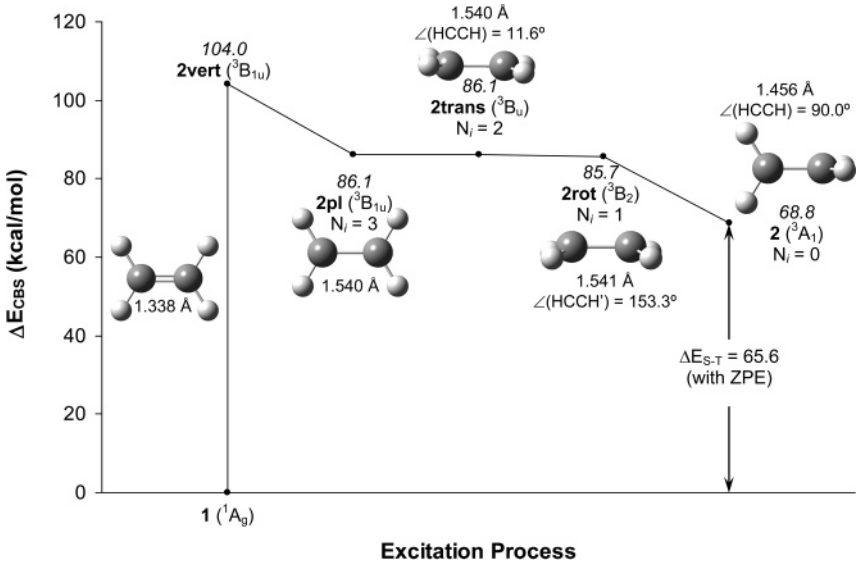

Figure 1. Illustration of the structural modification of triplet ethylene upon geometry relaxation. Geometry parameters were obtained from UCCSD(T)/aug-cc-pVTZ optimizations. In *italic* are relative energies obtained from UCCSD(T)/CBS total energies, with respect to ethylene **1** without zero-point corrections. N_i is the number of imaginary frequencies. ΔE_{S-T} is the adiabatic singlet−triplet energy gap of acetylene obtained from CBS energies and zero-point corrections. For **2trans**, the ∠(HCCH) corresponds to a *cis* dihedral angle; for **2rot**, the ∠(HCCH′) corresponds to a *trans* dihedral angle.

cm^{-1}. The rotation−distortion mode a_2 makes **2rot** the transition state structure for internal rotation around the C−C bond connecting the energy minimum triplet ethylene **2** to itself. These changes in geometry are consistent with the models for ethylene originally proposed by Mulliken and co-workers.[18]

The equilibrium structure of **2** has D_{2d} point group symmetry, with the two CH_2 planes perpendicular to each other, and has a $^3A_1$ electronic state.[64] Taking the TAEs given in Table 1, the rotational barrier of triplet ethylene, evaluated as the energy difference between **2rot** and **2**, is 16.7 kcal/mol. This is substantially larger than the rotation barrier around a single C−C bond in ethane of ∼3 kcal/mol.[65] The energy differences between **2pl**, **2trans**, and **2rot** are small (∼0.4 kcal/mol) and the differences in their ZPEs are larger (from 1 to 1.3 kcal/mol) showing that the surface is quite flat in this region. In fact, the planar form **2pl** becomes lower in energy after including zero-point corrections, as it has less real modes. To get values more precise than 0.3−0.5 kcal/mol would require a detailed fit of a potential energy surface, which would include anharmonic corrections. Thus, it is reasonable to consider that internal rotation of triplet ethylene simply corresponds to a rotation about the C−C bond from the perpendicular minimum **2** to the planar structure **2pl**.

The adiabatic singlet−triplet energy gap of ethylene $\Delta E_{S-T,adia}(C_2H_4)$ is the energy difference between **2** and **1** at the respective equilibrium positions and is calculated to be 68.8 kcal/mol without ΔZPE and 65.8 kcal/mol with ΔZPE (Table 3). The results given in Table 3 show that this gap increases slightly with respect to the increasing the size of the basis set. Again, our result for $\Delta E_{S-T,adia}(C_2H_4)$ is very close to that of 66.4 ± 0.3 kcal/mol obtained from the quantum Monte Carlo calculations,[45] and both differ significantly from the experimental estimate of 58 ± 3 kcal/mol.[43,32,33] From TAE(**2**), the heat of formation of triplet ethylene is predicted to be $\Delta H_f^0(\mathbf{2},^3A_1) = 80.1 \pm 0.5$ and 78.5 ± 0.5 kcal/mol at 0 and 298 K, respectively. Suits and co-workers[32] calculated the latter parameter at 70 ± 3 kcal/mol from their experimental value of the gap and the heat of formation of C_2H_4.

The heat of formation of triplet methylene was determined to be 92.9 kcal/mol at 0 K.[4] Thus the C−C bond energy of **2** to form two triplet CH_2 molecules is 105.7 kcal/mol. This corresponds to the simplest model of a $C(sp^2)-C(sp^2)$ σ bond energy where the two sp2 C atoms have their π-electron perpendicular to each other.

Similar to methylene (CH_2), ethylidene **3** has a triplet ground state ($^3A''$ in C_s symmetry, Figure 2). Singlet CH_3CH does not

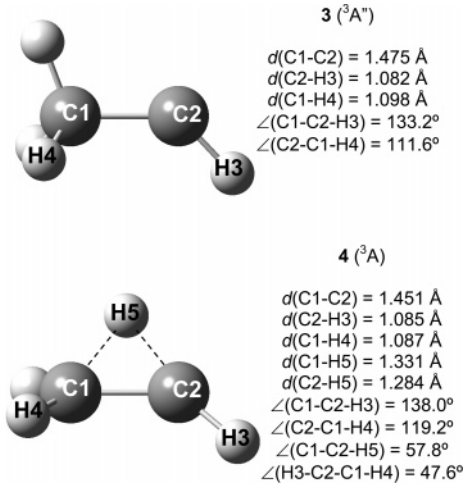

Figure 2. Selected UCCSD(T)/aug-cc-pVTZ geometrical parameters of ethylidene **3** ($^3A''$) and transition state structure **4** (^3A) for 1,2-H-shift. Bond lengths are given in angstrom, and bond angles, in degree.

exist as an equilibrium structure but rather is a transition state for hydrogen scrambling in C_2H_4.[46,66] Our CBS results listed in Table 1 show that **3** is 6.5 kcal/mol less stable than triplet ethylene **2**, and 72.2 kcal/mol above **1**, the global minimum of the C_2H_4 energy surfaces. Previous studies using coupled-cluster theory with a smaller basis set[44] obtained a value of 5.8 kcal/mol for the energy gap between **3** and **2**, and placed **3** about 65.0 kcal/mol below the $C(^3P) + CH_4$ limit. The heats of formation of ethylidene, $\Delta H_f^0(CH_3CH)$ are 86.8 and 85.1 kcal/mol at 0 and 298 K, respectively. Thus **3** is 68.4 kcal/mol below the $C(^3P) + CH_4$ limit.

On the triplet potential energy surface, the equilibrium structures **2** and **3** are linked through the transition state **4** for the 1,2-shift of hydrogen. The optimized geometry of **4** is also displayed in Figure 2. Our CBS results are in agreement with previous the previous result[44] that the energy barrier for the 1,2 hydrogen shift is substantial, 43.2 kcal/mol with respect to ethylidene **3**. The heat of formation of the vinyl radical at 0 K has been calculated[62] to be 72.6 kcal/mol in excellent agreement with the experimental value,[67] which is the same. The C−H bond energy of **2** can then be calculated to be 43.9 and 37.4 kcal/mol in **3**. Thus the transition state **4** is slightly below the C−H bond energy of **2** but above that for **3**, so it is unlikely that **3** can be isomerized to **2** without undergoing C−H bond scission.[44]

Triplet Acetylene and Vinylidene. The calculated TAEs for the C_2H_2 isomers are reported in Table 1 with heats of formation in Table 2. *cis*-**6** corresponds to the lowest-energy form of triplet acetylene. For acetylene **5**, the value from the experimental fundamentals is $0.5\Sigma\nu_i = 16.19$ kcal/mol, and the value obtained from CCSD(T)/aVTZ harmonic frequencies is $0.5\Sigma\omega_i = 16.56$ kcal/mol, giving a best estimate of ZPE(**5**) = 16.38 kcal/mol, close to the value of 16.50 kcal/mol obtained by Feller and Dixon.[62] For the (U)CCSD(T)/aVTZ frequencies of structures **6** to **8** we used a scaling factor of 0.9888.

We obtain a value of $\Delta E_{S-T,adia}(C_2H_2) = 90.5$ kcal/mol as the energy difference between **6** ($^3B_2$) and **5** (Table 4), 7.7 kcal/mol or 2693 cm^1 larger than the experimental estimate by Suits and co-workers.[8] Our result is consistent with that of previous calculations.[7,8] The results in Table 4 clearly show that calculations with more extended one-electron functions tend to increase the singlet−triplet gap. In addition, our results confirm that the experimental singlet−triplet splitting is too low for C_2H_2.

For vinylidene, we predict $\Delta H_f^0(H_2CC) = 98.6$ and 98.8 kcal/mol at 0 and 298 K, respectively. Thus, in the singlet ground state, vinylidene is 43.7 kcal/mol less stable than its acetylene isomer. From gas phase acidity measurements, Ervin et al.[68] derived heats of formation of 102.1 ± 4.0 and 102.2 ± 4.0 kcal/mol at 0 and 298 K, respectively. From their photodecomposition experiments, Suits et al.[9] determined a value of 100.3 ± 4 kcal/mol at 298 K. Our calculated value is within the error bars of both sets of experiments. In the first excited triplet state, both triplet acetylene and triplet vinylidene have similar heats of formation, with triplet acetylene being ~1 kcal/mol more stable. The singlet−triplet gap for vinylidene, is $\Delta E_{S-T,adia}(H_2CC) = 47.7$ kcal/mol (Table 4).

Using $\Delta H_{f,0K}(CH_2,{}^3B_1) = 93.4$ kcal/mol,[4] $\Delta H_{f,0K}$(**7**) = 98.7 kcal/mol (the average of the DTQ and Q5 values in Table 2), and $\Delta H_{f,0K}(C) = 169.98$ kcal/mol, we obtain the C−C bond dissociation energy (BDE) of **7** as

$$H_2CC \rightarrow H_2C + C \qquad BDE = 164.7 \text{ kcal/mol}$$

We can also estimate the C−C BDE of **3** by using $\Delta H_{f,0K}$(**3**) = 86.7 kcal/mol (Table 2), $\Delta H_{f,0K}(CH) = 141.6$ kcal/mol, and $\Delta H_{f,0K}(CH_3) = 36.0$ kcal/mol (see ref 3) as

$$CH_3CH \rightarrow CH_3 + CH \qquad BDE = 90.9 \text{ kcal/mol}$$

Thus **7** has a C=C bond strength slightly below that of C_2H_4 of 172.4 kcal/mol (taking the average for the heat of formation of C_2H_4 in Table 2) and can best be described as having a double bond with a bond length of 1.307 Å. The C−C bond energy in **3** is slightly higher than that in CH_3-CH_3 of 87.9 kcal/mol (see ref 3) and is consistent with the bond being described as a single bond with a bond length of 1.475 Å.

Conclusions

The vertical and adiabatic singlet−triplet separation gaps of ethylene were evaluated to be 104.1 and 65.8 kcal/mol, respectively. The adiabatic gaps of acetylene and vinylidene were determined as 90.5 and 47.7 kcal/mol, respectively. The error bar of our calculated results is expected to be less than ±1.0 kcal/mol. Thus our calculated adiabatic singlet−triplet splittings are larger than experiment by 7.8 and 7.7 kcal/mol, respectively. This difference is substantially larger than the experimental error bar of ±3 kcal/mol. In addition, other high accuracy computational approaches yield comparable differences from the experimental values. On the basis of the computational results, we suggest that there is a systematic overestimation of the stability of the triplet state of C_2H_4 and C_2H_2 in the photodecomposition experiments of Suits and co-workers by 7−8 kcal/mol.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set extrapolated to the complete basis set limit and zero point energy corrections. Calculated and experimental vibrational modes (in cm^{-1}) and unscaled ZPEs (in kcal/mol). This material is available free of charge via the Internet at http://pubs.acs.org.

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