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High-Accuracy Extrapolated ab Initio Thermochemistry of the Propargyl Radical and the Singlet C_3H_2 Carbenes[†]

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Total atomization energies and enthalpies of formation (0 and 298.15 K) are evaluated using the high-accuracy extrapolated ab initio thermochemistry (HEAT) scheme for the two stable singlet C_3H_2 carbenes [cyclopropenylidene (c-C_3H_2) and propadienylidene (vinylidencarbene, l-C_3H_2)], as well as for the 2-propynyl (propargyl, C_3H_3) radical. In the case of propargyl, the HEAT protocol predicts an enthalpy of formation of 354.9 ± 1.0 kJ mol^{-1} for 0 K; corresponding values of 498.1 ± 1.0 and 555.6 ± 1.0 kJ mol^{-1} are estimated for c-C_3H_2 and l-C_3H_2. Additional consideration of temperature corrections leads to estimates of 352.2 ± 1.0, 497.1 ± 1.0, and 556.7 ± 1.0 kJ mol^{-1} for the heats of formation at 298.15 K of the propargyl radical, c-C_3H_2, and l-C_3H_2, respectively. Potential strategies for simplifying the HEAT protocol are also investigated and shown to have negligible impact on accuracy.

I. Introduction

Due to their high reactivity, the isolation and spectroscopic characterization of unsaturated carbenes and radicals is a difficult task.[1] However, significant progress has been made over the years in the investigation of these species; information on their reactivity as well as their spectroscopic properties has become more and more abundant. Besides C_3H and C_2H_2 (vinylidene), another class of small unsaturated carbenes is the various isomers of C_3H_2, i.e., propynylidene (prop-2-ynylidene), t-C_3H_2, propadienylidene (vinylidencarbene), l-C_3H_2, and cyclopropenylidene, c-C_3H_2. These molecules are related to the quite stable propargyl (2-propynyl, C_3H_3) radical (see Figure 1), which we consider here, as well.

Propynylidene, t-C_3H_2, is the only C_3H_2 isomer with a triplet electronic ground state. Although it was the first of the three species obtained by laboratory synthesis,[2] its molecular structure has been a subject of controversy. A linear geometry was first deduced from experiments,[3] but some theoretical studies predicted a planar acetylenic structure[4] or a nonplanar C_2 structure.[5] The latter, which corresponds to a 1,3-diradical, has been the most favored by electron spin resonance (ESR) and infrared measurements (IR), and ab initio calculations.[6] Cyclopropenylidene, c-C_3H_2, was the next C_3H_2 isomer to be identified,[7] but its characterization and laboratory synthesis were not carried out until a few years later.[8,9] The third C_3H_2 isomer, i.e., vinylidencarbene (propadienylidene), l-C_3H_2, was first detected in the photolysis products of cyclopropenylidene, c-C_3H_2.[10] Actually, all three isomers can be interconverted by photolysis.[6,11] Cyclopropenylidene and vinylidencarbene have been identified in the gas phase[12,13] and in the interstellar medium.[14,15] However, to the best of our knowledge, only a few estimates for the enthalpy of formation of the C_3H_2 isomers are available. Experimentally inferred values have been reported for the enthalpy of formation of cyclopropenylidene (c-C_3H_2);[16,17] theoretical predictions for all three isomers are given in refs 17−22.

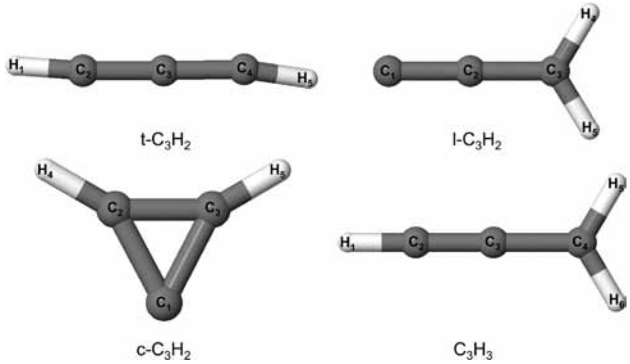

Figure 1. Propynylidene (prop-2-ynylidene, t-C_3H_2), propadienylidene (vinylidencarbene, l-C_3H_2), cyclopropenylidene (c-C_3H_2), and 2-propynyl (propargyl, C_3H_3).

Contrary to the situation concerning C_3H_2, the resonance-stabilized propargyl (2-propynyl) radical has been the target of many studies. This is due both to its innate stability and to its relevance for combustion research;[23] it is believed to be an important precursor (via dimerization) to benzene and all subsequent aromatics formed in the combustion of fuels.[24] Propargyl is also appreciated to be the most stable isomer on the C_3H_3 potential surface[25,26] and has a $^2B_1$ electronic ground state.

The goal of the present work is to provide accurate thermochemical information for the two closed-shell C_3H_2 species, i.e., cyclopropenylidene (c-C_3H_2) and propadienylidene (l-C_3H_2) as well as for the propargyl radical. For this task we will employ a theoretical model chemistry known as high-accuracy extrapolated ab initio thermochemistry (HEAT) that has been developed by our groups.[27−29] We note that the thermochemical HEAT protocol is closely related to other approaches such as focal-point analysis[30] and the Wn family of methods,[31,32] which are

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also exquisitely accurate methods. The HEAT scheme was defined and tested for a set of 31 atoms and small molecules of quite limited size (four or fewer atoms).[33] In this work, it is applied to somewhat larger five and six atom molecules. This extension in scope of application is possible due to algorithmic improvements, especially the parallelization of the quantum chemistry package CFOUR.[34]

II. Theoretical Methods

A HEAT Protocol. Within this work, the HEAT345-Q and HEAT345-(Q) protocols[28,29] are applied. Both are based on the following additivity expression for the total energy of a molecule

$$E = E_{\mathrm{HF}}^{\infty} + \Delta E_{\mathrm{CCSD(T)}}^{\infty} + \Delta E_{\mathrm{CCSDT}} + \Delta E_{\mathrm{HLC}} + \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{REL}} + \Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{DBOC}} \quad (1)$$

where E_{HF}^{∞} is the estimate of the Hartree−Fock (HF) limit based on extrapolation of HF-SCF energies using the aug-cc-pCVXZ hierarchy (X = T, Q, and 5) of the basis sets of Dunning and co-workers,[35−39] and the extrapolation formula suggested by Feller.[27−29,40] $\Delta E\infty$CCSD(T) denotes the coupled-cluster singles and doubles with perturbative treatment of the triples (CCSD(T))[41] correlation energy at the basis-set limit, which is estimated from correlation energies obtained with the aug-cc-pCVQZ and aug-cc-pCV5Z basis sets that are extrapolated using the approach of Helgaker et al.[42] $\Delta E_{\mathrm{CCSDT}}$ and ΔE_{HLC} account for electron-correlation effects beyond CCSD(T); $\Delta E_{\mathrm{CCSDT}}$ is estimated via the difference between CCSDT (coupled-cluster singles, doubles, and triples)[43] and CCSD(T) correlation energies, obtained by extrapolating[42] the difference of the CCSDT and CCSD(T) correlation energies with the cc-pVTZ and cc-pVQZ basis sets. Beyond CCSD(T), core-correlation effects are not included. ΔE_{HLC} refers to "higher-level correlation" effects and is given by the difference of CCSDTQ (coupled-cluster singles, doubles, triples, and quadruples)[45] in HEAT345-Q or CCSDT(Q)[44] (coupled-cluster singles, doubles and triples with perturbative treatment of quadruples) in HEAT345-(Q) and CCSDT correlation energies. These latter energies are obtained in valence-only calculations employing the cc-pVDZ basis set. ΔE_{ZPE} is the zero-point vibrational contribution to the energy obtained from vibrational second-order perturbation theory (VPT2)[46] at the CCSD(T)/cc-pVQZ level, correlating all electrons.[47] ΔE_{REL} estimates the scalar-relativistic contribution to the total energy by computing the perturbative corrections for the mass velocity and the one- and two-electron Darwin terms.[48,49] These calculations are performed at the CCSD(T)/aug-cc-pCVTZ level of theory. ΔE_{SO} refers to the difference between the true zero-point level of radicals in degenerate electronic states and the weighted average of spin−orbit levels that are represented by the nonrelativistic electronic Schrödinger equation.[50] Finally, ΔE_{DBOC} is the diagonal Born−Oppenheimer correction (DBOC), which can be considered as a first-order correction to the electronic energy associated with the nuclear (mass-dependent) kinetic energy operator. This correction is calculated at the CCSD/aug-cc-pCVQZ level of theory as described in ref 51.

B. Temperature Corrections. Most of the experimental and previous theoretical determinations of the enthalpy of formation of c-C_3H_2, and especially of propargyl, refer to a temperature of 298.15 K, a practice that will be continued in this publication. For the molecules given in this work, i.e., C_3H_n ($n = 2, 3$), the theoretical prediction of $\Delta_f H_{298}°$ (C_3H_n) is accomplished by correcting the values for 0 K, $\Delta_f H_0°$ (C_3H_n), according to[52]

$$\Delta_f H_{298}°(C_3H_n) = \Delta_f H_0°(C_3H_n) + [H_{298}°(C_3H_n) - H_0°(C_3H_n)] - 3[H_{298}°(C_{\mathrm{graphite}}) - H_0°(C_{\mathrm{graphite}})] - \frac{n}{2}[H_{298}°(H_2(g)) - H_0°(H_2(g))] \quad (2)$$

The corrections for the C_3H_n ($n = 2, 3$) molecules are based on the evaluation of the translational, rotational, and vibrational partition functions within the traditional ideal gas model. The high temperature approximation is made for translations ((3/2)RT) and rotations ((3/2)RT for nonlinear molecules) and CCSD(T)/cc-pVQZ harmonic frequencies are used to evaluate the corresponding vibrational partition function[53] in the harmonic approximation.

C. Computational Details. All calculations were performed at geometries obtained at the CCSD(T)/cc-pVQZ level with all electrons correlated.[54] Restricted and unrestricted Hartree−Fock wavefunction (RHF and UHF) are used for closed-shell and open-shell molecules, respectively. However, for the evaluation of ΔE_{ZPE}, restricted open-shell (ROHF) reference wavefunctions have been used in the case of open-shell species, as corresponding unrestricted Hartree−Fock (UHF) calculations can show large spin-contamination effects.[55] Due to technical problems in the calculation of the corresponding force fields for propargyl, its force constants have been determined in this case only at the CCSD(T)/cc-pVTZ level of theory. Values of 216.03 and 711.58 kJ mol^{-1} were used for the calculation of the enthalpies of formation at 0 K of hydrogen and carbon, respectively.[28,56] For the estimates at 298.15 K, $H_{298}°(C_{\mathrm{graphite}}) - H_0°(C_{\mathrm{graphite}}) = 1.051$ kJ mol^{-1} and $H_{298}°(H_2(g)) - H_0°(H_2(g)) = 8.467$ kJ mol^{-1} from ref 57 were applied.

All calculations have been performed using the quantum chemical program package CFOUR (Coupled-Cluster Techniques for Computational Chemistry)[58] except those at the CCSDT(Q) and CCSDTQ levels of theory, which have been carried out with the string-based many-body code MRCC[59] interfaced to CFOUR. Some of the results presented here required an enormous computational effort; for example, for both C_3H_2 isomers, the most demanding RHF-CCSD(T) calculations involved 703 basis functions together with 20 correlated electrons; in the case of propargyl, the UHF-CCSD(T)/aug-cc-pCV5Z single point energy calculation required 783 basis functions and 21 correlated electrons.[60] For such examples, the computational demand was relieved by using the recently developed parallel version of CFOUR.[34]

III. Results and Discussion

Table 1 summarizes the different contributions, as defined in the previous section, to the total energy of the species studied in this work. Table 2 presents the total atomization energies (TAE) calculated from the total energies reported in Table 1. The values for the enthalpy of formation of all species, $\Delta_f H_0°$ and $\Delta_f H_{298}°$, are reported in Tables 3 and 4. In the following section, we first discuss the results obtained for the two singlet carbenes, before moving on to the propargyl radical. Finally, the effects of some approximations to the original HEAT scheme are investigated.

A. Singlet C_3H_2 Carbenes. ***Cyclopropenylidene, c-C_3H_2, and Propadienylidene, l-C_3H_2.*** Because of limited (c-C_3H_2) or nonexistent (l-C_3H_2) experimental information on the enthalpy of formation of these C_3H_2 isomers and limited theoretical work for both species, these values are still not precisely known. This is especially true for cyclopropenylidene where the experimental information has been inconclusive. The current status of the

TABLE 1: Contributions to the Total Energies (in Atomic Units) for the Five Species Studied in This Work

	$\Delta E_{\mathrm{HF}}^{\infty}$	$\Delta E_{\mathrm{CCSD(T)}}^{\infty}$	$\Delta E_{\mathrm{CCSDT}}$	ΔE_{HLC}[a]		ΔE_{ZPE}	ΔE_{rel}	ΔE_{SO}	$\Delta E_{\mathrm{DBOC}}^{\mathrm{CCSD}}$	total	
H	−0.500022	0.000000	0.000000	0.000000		0.000000	−0.000007	0.000000	0.000272	−0.49976	
C	− 37.693774	−0.151042	−0.000466	−0.000021	(Q)	0.000000	−0.016285	−0.000144	0.001711	−37.860021	(Q)
				−0.000029	Q					−37.860029	Q
C_3H_3	−115.302911	−0.697328	−0.000660	−0.001274	(Q)	0.040242[b]	−0.048147	0.000000	0.005864	−116.004214	(Q)
				−0.001152	Q					−116.004092	Q
c-C_3H_2	−114.671559	−0.684522	0.000262	−0.001142	(Q)	0.032004	−0.048228	0.000000	0.005580	−115.367605	(Q)
				−0.001068	Q					−115.367531	Q
l-C_3H_2	−114.641165	−0.690626	−0.000220	−0.001628	(Q)	0.030558	−0.048330	0.000000	0.005665	−115.345746	(Q)
				−0.001500	Q					−115.345618	Q

[a] Higher-level electron correlation effects, ΔE_{HLC}, are given by the difference between the CCSDTQ or CCSDT(Q) and the CCSDT correlation energies. The use of CCSDT(Q) or CCSDTQ energies is denoted by (Q) and Q, respectively. [b] CCSD(T)/cc-pVTZ cubic and semidiagonal quartic force constants were used to estimate the anharmonic contribution to the ZPE.

TABLE 2: Contributions to the Total Atomization Energies (TAE, in kJ mol^{-1}) for the Three Molecules Considered in This Study

	$\Delta E_{\mathrm{HF}}^{\infty}$	$\Delta E_{\mathrm{CCSD(T)}}^{\infty}$	$\Delta E_{\mathrm{CCSDT}}$	ΔE_{HLC}[a]		ΔE_{ZPE}	ΔE_{rel}	ΔE_{SO}	$\Delta E_{\mathrm{DBOC}}^{\mathrm{CCSD}}$	total	
C_3H_3	1894.36	641.16	−1.94	3.18	(Q)	−105.66[b]	−1.92	−1.13	0.22	2428.27	(Q)
				2.80	Q					2427.89	Q
c-C_3H_2	1549.55	607.53	−4.36	2.83	(Q)	−84.03	−1.68	−1.13	0.26	2068.97	(Q)
				2.57	Q					2068.71	Q
l-C_3H_2	1469.75	623.56	−3.09	4.11	(Q)	−80.23	−1.42	−1.13	0.03	2011.58	(Q)
				3.71	Q					2011.18	Q

[a] Higher-level electron correlation effects, ΔE_{HLC}, are given by the difference between the CCSDTQ or CCSDT(Q) and the CCSDT correlation energies. The use of CCSDT(Q) or CCSDTQ energies is denoted by (Q) and Q, respectively. [b] CCSD(T)/cc-pVTZ cubic and semidiagonal quartic force constants were used to estimate the anharmonic contribution to the ZPE; the harmonic ZPE correction was calculated at the CCSD(T)/cc-pVQZ level.

TABLE 3: Enthalpies of Formation, $\Delta_f H°$ (in kJ mol^{-1}), of Cyclopropenylidene, c-C_3H_2, and Propadienylidene, l-C_3H_2

determination	type	$\Delta_f H°$	*T* (K)	ref
		c-C_3H_2		
Clauberg et al. (1991−92)	exp[a]	≥472.8 ± 12.6	298	16
		≤481.2 ± 8.4	298	
Chyall et al. (1995)	exp[a]	500.0 ± 9.2	298	17
Wong et al. (1993)	G2	498.7	298	18
Montgomery et al. (1994)	CBS/QCI/APNO	497.5	298	19
Vereecken et al. (1998)	DFT	497.9	298	67
Nguyen et al. (2001)	CCSD(T)//B3LYP[b]	493.7 ± 4.2	298	20
Taatjes et al. (2005)	QCISD(T)	494.1	0	21
Lau et al. (2006)	CCSD(T)/CBS	500.5	0	22
Aguilera-Iparraguirre et al. (2008)	explicitly correlated CCSD(T)[c]	498.9	0	68
this work	HEAT345-Q	498.1 ± 1.0	0	
		497.1 ± 1.0	298	
		l-C_3H_2		
Clauberg et al. (1992)	scaled ab initio[d]	540 ± 17	298	16
Nguyen et al. (2001)	CCSD(T)//B3LYP[b]	556	298	20
Lau et al. (2006)	CCSD(T)/CBS	559.5	0	22
Aguilera-Iparraguirre et al. (2008)	explicitly correlated CCSD(T)[c]	558.1	0	68
this work	HEAT345-Q	555.6 ± 1.0	0	
		556.7 ± 1.0	298	

[a] For description of the experimental techniques see text. [b] See text for details about the used theoretical method. [c] From atomization energy calculated in ref 68 and the $\Delta_f H°$ of carbon and hydrogen used in this work.[28−56] [d] See ref 16 for details.

scarce literature for both systems is summarized in Table 3 together with the results of the present study.

Starting with c-C_3H_2, Clauberg et al.[16] were the first to derive an experimental value for its enthalpy of formation. This was obtained by combining the ionization energy, derived by using photoelectron spectroscopy, with the enthalpy of formation of the corresponding cation. The reported upper and lower bounds for the heat of formation of cyclopropenylidene are 472.8 ± 12.6 kJ mol^{-1} ≤ $\Delta_f H_{298}°$ ≤ 481.2 ± 8.4 kJ mol^{-1}. The lower limit was obtained from the measured ionization potential and an upper limit for $\Delta_f H°$(c-$C_3H_2^+$)[61] of 1364 ± 8 kJ mol^{-1}, while the upper bound was determined via the enthalpy of formation and a lower bound proton affinity of cyclopropenyl radical cation (c-$C_3H_3^+$). The precision of these estimates was compromised to some degree because Clauberg et al.[16] used a combination of 298.15 and 0 K data in their analysis.[17] In addition to this, the values used for $\Delta_f H°$(c-$C_3H_2^+$)[61] and $\Delta_f H°$(c-$C_3H_3^+$)[62,63] were later revised[18,64−66] and in this way affected the predicted values as well.[17] A few years later, Chyall et al.[17] combined the proton affinity (PA_{298}) of cyclopropenylidene (951.0 ± 8.8 kJ mol^{-1}) with the known heats of formation of the protonated radical ($\Delta_f H_{298}°$ (c-$C_3H_3^+$)) and the proton ($\Delta_f H_{298}°$(H^+)) in order to obtain $\Delta_f H_{298}°$ (c-C_3H_2). Their

TABLE 4: Enthalpies of Formation $\Delta_f H°$ (in kJ mol^{-1}) of Propargyl

determination	type	$\Delta_f H°$	T (K)	ref
Tsang et al. (1996)	exptl[a]	339.0 ± 4.0	298	82
Robinson et al. (1995)	exptl[a]	345.2 ± 12.6	298	70
Roth et al. (1994)	exptl[a]	356.5	0	69
Nguyen et al. (2001)[b]	G3	350.6	298	20
	RHF-RCCSD(T)[b]	355.2	298	
	ROHF-CCSD(T)[c]	352.7	298	
	G3	351.9[d]	0	
Wheeler et al. (2007)	focal point	354.6	0	81
	focal point	351.9	298	
Aguilera-Iparraguirre et al. (2008)	explicitly correlated CCSD(T)	358.6	0	68
this work	HEAT345-Q	354.9 ± 1.0[e]	0	
		352.2 ± 1.0[e]	298	

[a] For description of the experimental techniques see text. [b] See refs 90 and 91 for description of this method. [c] See ref 92 for further description. [d] Via atomization energy. [e] $\Delta E_{\mathrm{anh}}^{\mathrm{ZPE}}$ was calculated at the CCSD(T)/cc-pVTZ level of theory, all electrons correlated.

estimated value for the enthalpy of formation of c-C_3H_2 at 298.15 K is 500.0 ± 9.2 kJ mol^{-1}.

With regard to the theoretical predictions, the experimental value of Chyall et al.[17] is consistent with the value of 498.7 kJ mol^{-1} obtained using G2 theory,[18] the value of 497.5 kJ mol^{-1} calculated using the CBS/QCI/APNO method,[19] and the value of 497.9 kJ mol^{-1} computed using density-functional theory (DFT).[67] However, more recent, UHF-CCSD(T)/6-311+G(3df,2p) calculations using B3LYP/6-311G(d,p) geometries for the isodesmic reaction: c-C_3H_2 + CH_4 → c-C_3H_4 + :CH_2 ($^1A_1$) led to a value of 491.2 kJ mol^{-1} for the heat of formation of c-C_3H_2 at 298.15 K.[20] In the same study, an alternative approach using the proton affinity of cyclopropenylidene calculated at the UHF-CCSD(T) level and the same basis set, PA(c-C_3H_2 = 943.07 kJ mol^{-1}), and the experimental data for $\Delta_f H_{298}°$ (H^+) and $\Delta_f H_{298}°$ (c-$C_3H_3^+$) gave a value of 490 kJ mol^{-1} for $\Delta_f H_{298}°$. The authors finally recommended a value of 493.7 ± 4.18 kJ mol^{-1}. Accurate values for the heat of formation of c-C_3H_2 at 0 K have been more recently calculated at the quadratic-configuration interaction (QCISD(T)) level together with basis-set extrapolation, which gave a value of 494.1 kJ mol^{-1}.[21] Later, Lau et al.[22] combined ionization energies computed at the CCSD(T) level with basis-set extrapolation techniques to give a value of 500.5 kJ mol^{-1} (0 K). With the HEAT345-Q protocol we obtain a result of 498.1 kJ mol^{-1}, just below the previous, presumably most accurate prediction. The atomization energy is calculated to be 2068.7 kJ mol^{-1} and found to be in good agreement with the explicitly correlated CCSD(T) value of 2067.9 kJ mol^{-1} reported by Aguilera et al.[68] Our value for 298.15 K is 497.1 kJ mol^{-1}, i.e., 1.0 kJ mol^{-1} smaller than the value at 0 K and in agreement with the available experimental data within the given uncertainties.[17] However, our value is slightly lower, i.e., about 0.9 kJ mol^{-1}, than the best previous computed estimate.

So far, no experimental information needed to determine $\Delta_f H_0°$ of the second singlet C_3H_2 carbene, propadienylidene (l-C_3H_2, $H_2C{=}C{=}C$), is available; the few theoretical values are given together with our results in Table 3. Our calculated value for 0 K, 555.6 kJ mol^{-1}, is only 0.1 kJ mol^{-1} lower than the value computed at 298.15 K. Clauberg et al.[16] proposed for $\Delta_f H_{298}°$ a value of 540 ± 17 kJ mol^{-1} based on scaled ab initio calculations. Nguyen et al.[20] suggested 556 kJ mol^{-1}, a value in closer agreement with our best result. Their value is based on UHF-CCSD(T)/6-311+G(3df,2p) calculations using B3LYP/6-311G(d,p) geometries. On the other hand, $\Delta_f H_0°$ calculated using the CCSD(T)/CBS approach with the additional consideration of calculated ionization energies[22] is 3.9 kJ mol^{-1} larger than our 0 K result. Concerning the atomization energy, a value of 2011 kJ mol^{-1} is found by employing the HEAT protocol, which is 3 kJ mol^{-1} larger than the result obtained with explicitly correlated CCSD(T) calculations.[68]

B. Propargyl (CH_2CCH). The HEAT enthalpy of formation for propargyl at 0 K (354.9 kJ mol^{-1}) is in excellent agreement with experiment; it is only 1.6 kJ mol^{-1} smaller than the experimental value of Roth et al.[69] at 0 K (compare Table 4). Our proposed $\Delta_f H_{298}°$ value is also within the error bar of the experimental result obtained by Robinson et al.[70] but disagrees in about 13 kJ mol^{-1} with the value recommended by Tsang[82] and based on experiments carried out between 1970 and 1978. The importance of propargyl in combustion research has led to extensive experimental and theoretical studies of its thermochemical properties and, in particular, its enthalpy of formation.[71−80] Wheeler et al.[81] compiled a list of previously determined values of $\Delta_f H°$ for propargyl up to 2007. In Table 4 we only include three experimental values, i.e., (a) the one from Tsang et al.[82] based on a review on single-pulse shock-tube studies and pyrolysis experiments at low pressure in which a $\Delta_f H_{298}°$ of 338.9 ± 4.2 kJ mol^{-1} was recommended, (b) the experimental study based on the combined use of negative-ion photoelectron spectroscopy and gas-phase acidity measurements which lead to a $\Delta_f H_{298}°$ value of 345.2 ± 12.6 kJ mol^{-1},[70] and (c) the value for 0 K, $\Delta_f H_{298}° = 356.5$ kJ mol^{-1}, based on a single-pulse shock-tube experiment.[69] The enthalpy of formation of propargyl has also been computed several times in the past at modest and more sophisticated levels of theory, see ref 81 for an overview. Table 4 reports values determined by the G3 scheme[83] and with CCSD(T) calculations,[20] those by Wheeler et al.[81] using the focal-point analysis and based on two isodesmic reactions (H_2CCCH_2 + CH_3 → $HCCCH_2$ + CH_4; $HCCCH_3$ + CH_3 → $HCCCH_2$ + CH_4), and finally those based on atomization energies computed with explicitly correlated coupled-cluster theory.[68] Our recommended value for the heat of formation of propargyl at 0 K is virtually identical to that obtained by Wheeler et al.,[81] while it seems that the explicitly correlated CCSD(T) calculations overestimate the $\Delta_f H_0°$ by about 4 kJ mol^{-1}. The discrepancy with respect to ref 68 might be partially due to the fact that they did not include high level correlation effects beyond CCSD(T) in their estimate and also that the (T) corrections were not extrapolated to the basis set limit in the R12 treatment. By contrast, both of these effects were considered in the focal-point approach of Wheeler et al.[81] In addition, our recommended $\Delta_f H_{298}°$, i.e., 352.2 kJ mol^{-1}, is in good agreement with most of the previous theoretical calculations; it is within 0.5 kJ mol^{-1} of both the ROHF-CCSD(T) value of Nguyen et al.[20] and the result from the focal-point approach[81] (see Table 4).

TABLE 5: Enthalpies of Formation, $\Delta_f H_0°$, (in kJ mol^{-1}) Using Different Approximations to the Original HEAT Protocol

	HEAT345-Q			
	standard	$(\Delta E^{HF}_{DBOC})^a$	$(\Delta E^{PVTZ}_{ZPE})^b$	HEAT345-(Q)
C_3H_3		354.9[b]	354.9[c]	354.6[b]
c-C_3H_2	498.1	497.9	498.1	497.8
l-C_3H_2	555.6	555.4	555.5	555.2

[a] DBOC was calculated using the aug-cc-pVTZ basis set. [b] Cubic and diagonal and semidiagonal quartic force constants were calculated at the CCSD(T)/cc-pVTZ level. [c] Value considered in Table 3.

From the total atomization energies in Table 2, the following perhaps interesting and useful result can be inferred. The energy of the acetylenic CH bond in the propargyl radical (D_0) is calculated to be 416.7 kJ mol^{-1}, as breaking this bond leads to propadienylidene and its energy is therefore equal to the difference in atomization energies of the two species. This is in agreement with, but more precise than, a value of 418.4 ± 20.9 kJ mol^{-1} that was obtained from negative ion cycle measurements by Robinson et al.[70] The fact that this is so far below the CH bond energy of methylacetylene (also a nominal acetylenic CH bond, 544.7 ± 12.5 kJ mol^{-1}) may be attributed, at least in part, to the importance of the allenic resonance structure whose importance in propargyl has been pointed out by Jochnowitz et al.[85] The arguments of Jochnowitz and coworkers are equivalent to previous discussions[16,70] to rationalize the differences.

C. Study of Possible Approximations. While very accurate, the HEAT345-Q protocol is one of the most costly thermochemical models developed to date, which limits its applicability to rather small molecules. In the present work, it is applied to molecules consisting of five or six atoms. Accordingly, the required computational effort is high and it is worthwhile to investigate approximations to the original HEAT345-Q scheme. This is particularly important if one wishes to apply the HEAT protocol to even larger systems.

In the HEAT345-(Q) approximation to HEAT345-Q (see ref 45), the higher-level correlation corrections are obtained in CCSDT(Q) calculations[44] in which the effects of quadruple excitations are treated in a perturbative manner. Calculations at the CCSDT(Q) level involve a single noniterative N^9 step with N as a measure of the size of the molecular system. In this way, such calculations are considerably cheaper than corresponding CCSDTQ calculations which require iterative N^{10} steps. There is also some numerical evidence that correlation energies based on CCSDT(Q) are closer to those from coupled-cluster calculations with additional inclusion of quintuple excitations (CCSDTQP)[28] than in the CCSDTQ model, as the perturbative treatment tends to overshoot the correlation corrections due to quadruple excitations and in this way "covers" (fortuitously) effects due to higher excitations. In the present work, HEAT345-(Q) predicts TAEs of C_3H_3 (propargyl), c-C_3H_2, and l-C_3H_2 that are 0.4, 0.3, and 0.4 kJ mol^{-1} larger than the original HEAT345-Q protocol, respectively. For the heat of formation, $\Delta_f H_0°$, this means that the corresponding values are about 0.2−0.4 kJ mol^{-1} smaller (see Table 5).[86]

A more approximate treatment is also possible for the rather expensive calculation of the "diagonal Born−Oppenheimer correction" (DBOC) at the CCSD level. It is well-known that the DBOC is a small correction to the TAEs.[27−29] For the three species studied here, these corrections amount to 0.2, 0.3, and 0.0 kJ mol^{-1}, for C_3H_3 (propargyl), c-C_3H_2, and l-C_3H_2, respectively. Limiting the calculations to the HF-SCF level[84] yields corrections that are (only) 0.1, 0.1, and 0.2 kJ mol^{-1} larger. This is in line with previous observations[29,87] that inclusion of electron correlation reduced the DBOC to the TAEs of systems containing hydrogen atoms. Nevertheless, the error in neglecting electron correlation effects is so small that the use of DBOCs computed at the HF-SCF level is a justified and pragmatic alternative. Another possibility would be the use of perturbative schemes for the calculation of electron-correlation contributions to the DBOC.[88,89]

Another costly step in the HEAT protocol is the calculation of the ZPE correction. The HEAT scheme includes harmonic and anharmonic contributions to ΔE_{ZPE} with the latter estimated using VPT2. The VPT2 treatment requires the full cubic as well as diagonal and semidiagonal quartic force constants. Within the HEAT protocol, the force fields are computed at the CCSD(T)/cc-pVQZ level. However, in the present work, force fields for the propargyl radical could be determined only at the CCSD(T)/cc-pVTZ level. To investigate the effect of using a smaller basis set for the determination of the ZPE, additional CCSD(T)/cc-pVTZ anharmonic force field calculations were also carried out for the two singlet carbenes. The use of a smaller basis set has a negligible effect on the heat of formation for c-C_3H_2 and l-C_3H_2; see Table 5. It thus appears that the use of a smaller basis in the force field calculations is an appropriate means for reducing the computational cost while at the same time having virtually no effect on accuracy.

IV. Summary

The HEAT protocol has been applied to determine the heat of formation of the propargyl radical and the two stable singlet C_3H_2 isomers, i.e., cyclopropenylidene (c-C_3H_2) and propadienylidene (l-C_3H_2). Our recommended values for the enthalpy of formation at 0 K are $\Delta_f H_0°$(propargyl, C_3H_2) = 354.9 kJ mol^{-1}, $\Delta_f H_0°$(c-C_3H_2) = 498.1 kJ mol^{-1}, and $\Delta_f H_0°$(l-C_3H_2) = 455.6 kJ mol^{-1}, with an uncertainty of 1.0 kJ mol^{-1} in all cases. Additional consideration of thermal corrections leads to the following final estimates at 298.15 K: 352.2, 497.1, and 556.7 kJ mol^{-1} for $\Delta_f H_{298}°$ of propargyl radical, c-C_3H_2, and l-C_3H_2, respectively. The temperature corrections were especially small for the three molecular species here studied; the largest of these ($|[\Delta_f H_{298}° - \Delta_f H_0°]|$) is 2.7 kJ mol^{-1} for propargyl. Given the rather small magnitude of the temperature corrections of $\Delta_f H°$, it seems to be justified to assess the uncertainty of the values for 298.15 K to 1.0 kJ mol^{-1}.

The investigation of approximations to the HEAT scheme suggests, as already discussed before, that (a) the most expensive CCSDTQ calculations can be substituted by more economical CCSDT(Q) calculations, (b) electron-correlation effects on the diagonal Born−Oppenheimer corrections can be safely ignored, and (c) it is possible to compute the required force fields for the estimation of the ZPE using smaller basis set than originally suggested.

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References and Notes

(1) *Carbenes*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1973; Vols. I and II.

(2) Skell, P. S.; Klebe, J. *J. Am. Chem. Soc.* **1960**, *82*, 247.

(3) (a) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196. (b) Bernheim, R. A.; Kempf, R. J.; Reichenbecher, E. F. *J. Magn. Reson.* **1970**, *3*, 5.

(4) (a) DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31. (b) Čársky, P.; Špirko, V.; Hess, B. A.; Schaad, L. J. *J. Phys. Chem.* **1990**, *94*, 5493. (c) Jonas, V.; Böhme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640.

(5) (a) Herges, R.; Mebel, A. *J. Am. Chem. Soc.* **1994**, *116*, 8229. (b) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.

(6) (a) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 5183. (b) Seburg, R. A.; MacMahon, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2009. (c) Seburg, R. A.; DePinto, J. T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 835. (d) Seburg, R. A.; Patterson, E. V.; Stanton, J. F.; McMahon, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 5847, and references therein.

(7) MacAllister, T.; Nicholson, A. J. C. *Chem. Soc., Faraday Trans.* **1981**, *77*, 821.

(8) Reisenauer, H. P.; Maier, G.; Riemann, A.; Hoffmann, R. W. *Angew. Chem.* **1984**, *96*, 596. Reisenauer, H. P.; Maier, G.; Riemann, A.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 641.

(9) Lee, T. J.; Bunge, A.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1985**, *107*, 137.

(10) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 5183.

(11) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Špirko, V.; Hess, B. A.; Schaad, L. J. *J. Chem. Phys.* **1989**, *91*, 4763.

(12) (a) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, A. C. *Astrophys. J.* **1985**, *299*, L63. (b) Bogey, M.; Demuynck, C.; Destombes, L. J. *Chem. Phys. Lett.* **1986**, *125*, 383. (c) Hirahara, Y.; Masuda, A.; Kawaguchi, K. *J. Chem. Phys.* **1991**, *95*, 3975.

(13) (a) Vrtilek, J. M.; Gottlieb, C. A.; Gottlieb, E. W.; Killian, T. C.; Thaddeus, P. *Astrophys. J.* **1990**, *364*, L53. (b) Gottlieb, C. A.; Killian, T. C.; Thaddeus, P.; Botschwina, P.; Flügge, J.; Ostwald, M. *J. Chem. Phys.* **1993**, *98*, 4478.

(14) Thaddeus, P.; Guélin, M.; Linke, R. A. *Astrophys. J.* **1981**, *246*, L41.

(15) Cernicharo, J.; Gottlieb, C. A.; Guélin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, *368*, L39.

(16) (a) Clauberg, H.; Chen, P. *J. Am. Chem. Soc.* **1991**, *113*, 1445. (b) Clauberg, H.; Minsek, D. W.; Chen, P. *J. Am. Chem. Soc.* **1992**, *114*, 99.

(17) Chyall, L. J.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149*, 257.

(18) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 1507.

(19) Montgomery Jr, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(20) Nguyen, T. L.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2001**, *105*, 3284.

(21) Taatjes, C. A.; Klippenstein, S. J.; Hansen, N.; Miller, J. A.; Cool, T. A.; Wang, J.; Law, M. E.; Westmoreland, P. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 806.

(22) (a) Lau, K.-Ch.; Ng, Ch.-Y. *Chin. J. Chem. Phys.* **2006**, *19*, 29. (b) Lau, K.-Ch.; Ng, Ch.-Y. *Acc. Chem. Res.* **2006**, *39*, 823.

(23) (a) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 7783. (b) Giri, B. R.; Hippler, H.; Olzmann, M.; Unterreiner, A. N. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4641.

(24) (a) Miller, J. A.; Pilling, M. J.; Troe, J. *J. Proc. Combust. Inst.* **2005**, *30*, 43. (b) Frenklanch, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2028. (c) Richter, H.; Howard, J. B. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2038. (d) Miller, J. A.; Melius, C. F. *Combust. Flame* **1992**, *91*, 21.

(25) (a) Walch, S. P. *J. Chem. Phys.* **1995**, *103*, 8544. (b) Guadagnini, R.; Schatz, G. C.; Walch, S. P. *J. Phys. Chem. A* **1998**, *102*, 5857. (c) Nguyen, T. L.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2001**, *105*, 3284.

(26) The molecular point group of propargyl is C_{2v} which is known (together with the D_2 and D_{2h} groups) for presenting ambiguities. In the present case (propargyl) the plane containing the hydrogen and carbon atoms is the *yz* plane of the propargyl electronic ground state. Consequently the electronic ground state transforms according to the irreducible representation B_1, and the two hydrogen stretching modes have a_1 and b_2 symmetry.

(27) Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599.

(28) Bomble, Y. J.; Vázquez, J.; Kállay, M.; Michauk, C.; Szalay, P. G.; Császár, A. G.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2006**, *125*, 064108.

(29) Harding, M. E.; Vázquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2008**, *128*, 024806.

(30) Császár, A. G.; Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **1998**, *108*, 9751.

(31) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.

(32) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(33) Recently, a modified HEAT scheme has been applied to the thermochemistry of vinyl chloride, see: (a) Harding, M. E.; Gauss, J.; Pflüger, K.; Werner, H.-J. *J. Phys. Chem. A* **2007**, *111*, 13623. (b) Harding, M. E.; Gauss, J.; Pflüger, K.; Werner, H.-J. *J. Phys. Chem. A* **2008**, *112*, 5024.

(34) Harding, M. E.; Metzroth, T.; Gauss, J.; Auer, A. A. *J. Chem. Theory Comput.* **2008**, *4*, 64.

(35) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(36) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(37) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(38) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(39) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(40) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(41) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(42) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

(43) (a) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 1041. (b) Scuseria, G. E.; Schaefer, H. F., III *Chem. Phys., Lett.* **1988**, *132*, 382. (c) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *93*, 6104.

(44) Bomble, Y. J.; Stanton, J. F.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 054101.

(45) (a) Kucharski, S. A.; Bartlett, R. J. *Theor. Chim. Acta* **1991**, *80*, 387. Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys* **1992**, *97*, 4282. (b) Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1991**, *94*, 1229.

(46) Mills, I. M. In *Modern Spectroscopy: Modern Research*; Rao, K. N., Matthews, C. W., Eds.; Academic: New York, 1972; pp 115−140.

(47) ΔE_{ZPE} was calculated by using a new expression recently developed in our group and which is equivalent to that presented in ref 81. Its derivation is based on the total sum over vibrational states and considers simultaneously the contribution from G_o and the one from the anharmonicity constants (x_{ii}, x_{ij}). The final equation is free of resonance denominators. Additional contributions resulting by the inclusion of the pseudopotential term of the nuclear Hamiltonian, $\hat{U}$ (Watson term), in the VPT2 treatment were also taken into account.

(48) Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.

(49) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226.

(50) Although this correction does not apply to the three molecular species studied here, it plays a role in the carbon atom.[27] The first-order spin−orbit correction of the carbon atom decreases the molecular atomization energies and consequently increases the molecular enthalpies of formation relative to the value obtained if this correction is not included. See Tables 1 and 2.

(51) Gauss, J.; Tajti, A.; Kállay, M.; Stanton, J. F.; Szalay, P. G. *J. Chem. Phys.* **2006**, *125*, 144111.

(52) Perhaps one of the first thermochemistry protocols using temperature corrections was the Gaussian-*n* (Gn) thermochemical series of Pople and co-workers. See for example: Curtiss, A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(53) Laurendeau, N. M. *Statistical Thermodynamics: fundamentals and applications*; Cambridge University Press: New York, 2005.

(54) Optimized structural parameters calculated at the CCSD(T)/cc-pVQZ level of theory. For propargyl results using both UHF and ROHF (in parentheses) reference wavefunctions are presented. Propadienylidene (vinylidencarbene, l-C_3H_2): $r(C_1C_2) = 1.2876$ Å, $r(C_2C_3) = 1.3276$ Å, $r(C_3H_4) = 1.0825$ Å, $\angle(C_2C_3H_4) = 121.30°$. Cyclopropenylidene (c-$C_3H_2$): $r(C_1C_2) = 1.4177$ Å, $r(C_2C_3) = 1.3226$ Å, $r(C_3H_4) = 1.0740$ Å, $\angle(C_2C_3H_4) = 149.98°$, $\angle(C_2C_1C_3) = 55.61°$. 2-Propynyl (propargyl): $r(H_1C_2) = 1.0608$ (1.0610) Å, $r(C_2C_3) = 1.2209(1.2229)$ Å, $r(C_3C_4) = 1.3746(1.3740)$ Å, $r(C_4H_5 = 1.0773(1.0775)$ Å, $\angle(C_3C_4H_5) = (120.51°)$. See Figure 1 for numeration of atoms.

(55) Szalay, P. G.; Vázquez, J.; Simmons, C.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 7624.

(56) As previously discussed in the literature (see for example ref [28]), the value of $\Delta_f H°$ for carbon atom carries a significant error bar, consequently a systematic error exists in all the $\Delta_f H°$ calculated using the TAE scheme. The magnitude of this error is proportional to the number of carbon atoms.

(57) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, 4th ed.; Monographic No. 9 *J. Phys. Chem. Ref. Data* 1998.

(58) *CFOUR, Coupled Cluster techniques for Computational Chemistry*, a quantum-chemical program package by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Christiansen,

O.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D.; Metzroth, T.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Ruud, K.; Schiffmann, F.; Stopkowicz, S. M.; Varner, E.; Vázquez, J.; Wang, F.; Watts J. D. and the integral packages MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V.; van Wüllen, C. For the current version, see http://www.cfour.de.

(59) Kállay, M. *MRCC, a string-based many-body program*; For current version, see http://www.mrcc.hu.

(60) CCSD(T)/aug-cc-pCV5Z (RHF) calculation of c-C_3H_2 required 6 h on 84 nodes of the TACC Dell Linux Cluster ("Lonestar") based on Intel Xeon 5100 series 2.66 GHz dual core processors, 8 GB RAM using a parallel Lustre file system. The CCSD(T)/aug-cc-pCV5Z (UHF) calculation of propargyl needed 19 h on 26 cores of the local Supermicro Linux Cluster in Mainz based on Intel Xeon 5100 series 3.0 GHz dual core processors with 16 GB memory and 8 striped SATA hard drives for direct attached storage.

(61) Prodnuk, S. D.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 693.

(62) Matthews, C. S.; Warneck, P. *J. Chem. Phys.* **1969**, *51*, 854.

(63) (a) Parr, A. C.; Elder, F. A. *J. Chem. Phys.* **1968**, *49*, 2659. (b) Parr, A. C.; Jason, A. J.; Stockbauer, R. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 23. (c) Parr, A. C.; Jason, A. J.; Stockbauer, R. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 243.

(64) Smith, D.; Adams, N. G.; Ferguson, E. E. *Int. J. Mass Spectrom. Ion Processes* **1984**, *61*, 15.

(65) Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, 307.

(66) Dannacher, J.; Heilbronner, E.; Stadelamnn, J.; Vogt, J. *Helv. Chim. Acta* **1979**, *62*, 2186.

(67) Vereecken, L.; Pierloot, K.; Peeters, J. *J. Chem. Phys.* **1998**, *108*, 1068.

(68) Aguilera-Iparraguirre, J.; Boese, A. D.; Klopper, W.; Ruscic, B. *Chem. Phys.* **2008**, *346*, 56.

(69) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1781.

(70) Robinson, M. S.; Polak, M. L.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766.

(71) Walsh, R. *Trans. Faraday Soc.* **1971**, *67*, 2085.

(72) Tsang, W. *Int. J. Chem. Kinet.* **1970**, *2*, 23.

(73) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 687.

(74) King, K. D. *Int. J. Chem. Kinet.* **1978**, *10*, 545.

(75) King, K. D.; Nguyen, T. T. *Phys. Chem.* **1979**, *83*, 1940.

(76) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(77) Harkless, J. A. W.; Lester, W. A. *J. Chem. Phys.* **2000**, *113*, 2680.

(78) Saeys, M.; Reyniers, M. F.; Marin, G. B.; Speybroeck, V. V.; Waroquier, M. *J. Phys. Chem. A* **2003**, *107*, 9147.

(79) Melius, C. F. *BAC-MP$_4$ Heats of Formation and Free Energies*; Sandia National Laboratories: Levermore, CA, 1996.

(80) Miller, J. A.; Klippenstein, S. *J. Chem. Phys.* **2003**, *113*, 2680.

(81) Wheeler, S. E.; Robertson, K. A.; Allen, W. D.; Schaefer, H. F.; Bomble, Y. J.; Stanton, J. F. *J. Phys. Chem. A* **2007**, *111*, 3819.

(82) Tsang, W. In *Energetics of Organic Free Radicals*; Martinho Simões, J. A., Greenberg, A., Liebman, J. F., Eds.; Academic and Professional: London, 1996; p 22.

(83) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(84) Handy, N. C.; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 4481.

(85) Jochnowitz, E. B.; Zhang, X.; Nimlos, M. R.; Varner, M. E.; Stanton, J. F.; Ellison, G. B. *J. Phys. Chem. A* **2005**, *109*, 3812.

(86) In particular, the contribution from the full quadruples excitation on the TAE of propargyl, c-C3H_2 and l-C_3H_2 is 2.80, 2.57, and 3.71 kJ mol^{-1}, respectively; the perturbative quadruples correction overestimates these values in 0.28, 0.26, and 0.40 kJ mol^{-1} for the same molecules.

(87) Valeev, E. F.; Sherrill, C. D. *J. Chem. Phys.* **2003**, *118*, 3921.

(88) Tajti, A.; Szalay, P. G.; Gauss, J. *J. Chem. Phys.* **2007**, *127*, 014102.

(89) For example, evaluation of the DBOC at the MP2/aug-cc-pVTZ level of theory leads to values of 355.2, 498.3, and 555.7 kJ mol^{-1} for $\Delta_f H_0°$ of C_3H_3, c-C_3H_2, and l-C_3H_2, respectively.

(90) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(91) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **2000**, *712*, 712.

(92) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.

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