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Thermochemistry of Key Soot Formation Intermediates: C_3H_3 Isomers[†]

Steven E. Wheeler, Kenneth A. Robertson, Wesley D. Allen,* and Henry F. Schaefer III

Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Yannick J. Bomble and John F. Stanton

Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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Accurate standard enthalpies of formation for allene, propyne, and four C_3H_3 isomers involved in soot formation mechanisms have been determined through systematic focal point extrapolations of ab initio energies. Auxiliary corrections have been applied for anharmonic zero-point vibrational energy, core electron correlation, the diagonal Born−Oppenheimer correction (DBOC), and scalar relativistic effects. Electron correlation has been accounted for via second-order Z-averaged perturbation theory (ZAPT2) and primarily through coupled-cluster theory, including single, double, and triple excitations, as well as a perturbative treatment of connected quadruple excitations [ROCCSD, ROCCSD(T), ROCCSDT, and UCCSDT(Q)]. The correlation-consistent hierarchy of basis sets, cc-pVXZ (X = D, T, Q, 5, 6), was employed. The CCSDT(Q) corrections do not exceed 0.12 kcal mol^{-1} for the relative energies of the systems considered here, indicating a high degree of electron correlation convergence in the present results. Our recommended values for the enthalpies of formation are as follows: $\Delta_f H_0^\circ$ (propargyl) = 84.76, $\Delta_f H_0^\circ$ (1-propynyl) = 126.60, $\Delta_f H_0^\circ$ (cycloprop-1-enyl) = 126.28, $\Delta_f H_0^\circ$ (cycloprop-2-enyl) = 117.36, $\Delta_f H_0^\circ$ (allene) = 47.41, and $\Delta_f H_0^\circ$ (propyne) = 46.33 kcal mol^{-1}, with estimated errors no larger than 0.3 kcal mol^{-1}. The corresponding C_3H_3 isomerization energies are about 1 kcal mol^{-1} larger than previous coupled-cluster results and several kcal mol^{-1} below those previously obtained using density functional theory.

1. Introduction

Unraveling the complex mechanism of soot formation stands at the forefront of modern combustion research. A primary focus is the formation and growth of polycyclic aromatic hydrocarbons (PAHs), which are the primary precursors to soot particles. The rate-limiting step in PAH formation is thought to be the formation of the first aromatic compounds (benzene or naphthalene) from smaller precursors.[1−3] Although both C3 and C4 species have been hypothesized to play important roles in ring formation (via the so-called odd- and even-carbon-atom pathways),[3] it is now generally accepted that the dominant reaction leading to the formation of benzene during combustion of aliphatic fuels is the self reaction of the resonance-stabilized propargyl radical (2-propynyl, **1**).[1]

Several other isomeric forms of C_3H_3 are also energetically accessible during combustion, including the 1-propynyl (**2**), cycloprop-1-enyl (**3**), and cycloprop-2-enyl (**4**) radicals, though propargyl is universally accepted to be the lowest energy isomer. Canonical Lewis structures for species **1**−**4** are shown in Figure 1. The propargyl radical is often not the initial isomer formed under typical combustion conditions: for example, the addition of CH to acetylene initially yields (**4**), rather than (**1**) directly,[4,5] while the reaction of C(^3P) with vinyl radical passes through (**3**) before settling into the propargyl radical potential energy well.[6] Pathways connecting C_3H_3 isomers **1**−**4** have been explored[6−8] using density functional theory (DFT), and details of the associated isomerization energy surface play a vital role in the lifetime and kinetics of the propargyl radical during combustion. Additional C_3H_3 isomers also exist (2-propen-1-yl-3-ylidene and 1-propen-1-yl-3-ylidene), although these alternative isomers are kinetically unstable with respect to isomerization to structures **1**−**4**.[6,7]

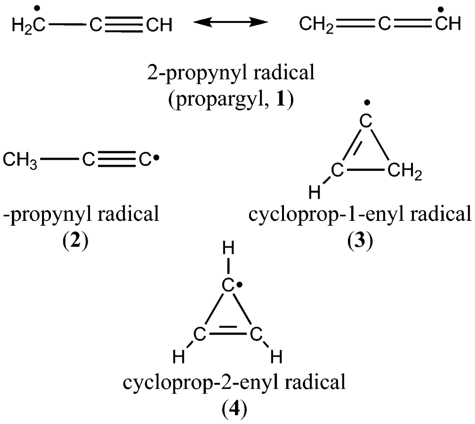

Figure 1. Canonical Lewis structures for four C_3H_3 isomers.

Despite the central role of C_3H_3 radicals in the formation of aromatic rings during combustion, there are few high-level, purely ab initio predictions of the relative energies of C_3H_3 species available in the literature. Previous studies to characterize **1**−**4** have almost universally relied on DFT for the optimization of geometries. However, DFT, and in particular the popular B3LYP functional (hybrid three-parameter Becke exchange and Lee−Yang−Parr correlation functional),[9,10] is known to perform

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* Corresponding author. E-mail: wdallen@ccqc.uga.edu. Phone: (706) 542-7729.

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poorly for some unsaturated hydrocarbon radicals. For the closely related *i*-C_4H_3 radical, previous work from our group[11] found that B3LYP with a series of basis sets yields optimum geometries that are qualitatively different from the structure predicted by ROCCSD(T) (restricted open-shell coupled-cluster theory including single, double, and perturbative triple excitations)[12] computations with a flexible TZ(2d1f,2p1d) basis set.

In a series of papers based on 6-311+G(3df,2p) RCCSD(T)[12] computations at 6-311G(d,p) B3LYP optimized geometries, Mebel and co-workers[6,8] predicted energies of 40.1, 40.1, and 31.3 kcal mol^{-1} for the 1-propynyl (**2**), cycloprop-1-enyl (**3**), and cycloprop-2-enyl (**4**) radicals relative to propargyl, respectively. Their relative energy for the 1-propynyl radical was in good agreement with the experimental value of 40 ± 3 kcal mol^{-1} determined by Robinson et al.[13] Energies computed using 6-311G(d,p) B3LYP give separations consistently several kilocalories per mole higher than the RCCSD(T) values: 1-propynyl at 46.0, cycloprop-1-enyl at 44.2, and cycloprop-2-enyl at 34.5 kcal mol^{-1}.[6,8] Previously, Vereecken et al.[7] had reported similar computations using both 6-31G(d,p) B3LYP and complete-active-space second-order perturbation theory (CASPT2) with an atomic natural orbital (ANO) basis set. The CASPT2 relative energies, computed at the B3LYP optimized geometries, were 41.3, 43.7, and 35.7 kcal mol^{-1} for **2**, **3**, and **4**, respectively.

Given the prominent role played by the propargyl radical in the formation of benzene in most models of PAH formation,[1,3] any effort to fully characterize soot formation pathways must include accurate enthalpies of formation of these low-lying C_3H_3 radicals. A representative list of previously determined $\Delta_f H°$ values for the propargyl radical appears in Table 1. A review by Tsang[14] in 1996 of single-pulse shock-tube[15,16] and very low pressure pyrolysis[17,18] studies led to a recommendation of $\Delta_f H^\circ_{298}$ (propargyl) = 81.0 ± 1 kcal mol^{-1}. A previous review of the literature by McMillen and Golden[19] concluded that $\Delta_f H^\circ_{298}$ (propargyl) = 81.5 ± 2 kcal mol^{-1}. In their more recent experimental study, Robinson et al.[13] derived the enthalpy of formation of the propargyl radical by conjoining negative-ion photoelectron spectroscopy with gas-phase acidity measurements. The resulting value of 82.5 ± 3 kcal mol^{-1} at 298 K is in reasonable agreement with the earlier experiments. In 1994, Roth et al.[20] determined an enthalpy of formation of 85.2 kcal mol^{-1} at 0 K on the basis of a single-pulse shock-tube study. While this value is within the error bars of ref 13, it is noticeably higher than and outside of the error estimates of the older experimental results, even accounting for 0 K → 298 K thermal corrections (ca. −0.6 kcal mol^{-1}).[6]

Harkless and Lester[21] computed the enthalpy of formation for propargyl radical via an atomization route using diffusion Monte Carlo (DMC) methods, obtaining 81.5 ± 1.3 and 82.5 ± 0.6 kcal mol^{-1} at 298 K using two different effective core potentials. They also found that the B3LYP and B3PW91 DFT functionals, paired with the 6-311G(d,f) basis set and atomization reactions, predict enthalpies of formation (298 K) of 84.0 and 79.9 kcal mol^{-1}, respectively. Likewise, in 2003, Saeys et al.[22] assessed the accuracy of the CBS-QB3 method and the B3LYP functional in determining enthalpies of formation via atomization reactions for a large set of systems, including the propargyl radical. Both methods were seen to overshoot previous theoretical and experimental values, yielding enthalpies of formation (298 K) of 85.3, 86.8, and 85.9 kcal mol^{-1} at the CBS-QB3, 6-31G(d) B3LYP, and 6-311G(d,p) B3LYP levels of theory, respectively. Earlier, Melius reported[23] an estimate of $\Delta_f H^\circ_{298}$(propargyl) = 83.6 ± 5.8 kcal mol^{-1} based on the bond-additivity-corrected fourth-order Møller−Plesset (BAC-MP4) method. The most thorough theoretical investigation of the enthalpy of formation of C_3H_3 isomers is due to Nguyen et al.,[6] who employed B3LYP optimizations with the G3 method and coupled-cluster theory to predict the enthalpies of formation for all four low-lying C_3H_3 isomers from a series of isodesmic reactions. The result was a very consistent set of enthalpies, with average values for propargyl (298 K) of 83.8, 84.9, and 84.3 kcal mol^{-1} using G3 theory, RCCSD(T), and ROCCSD(T),[12] respectively. Finally, Miller and Klippenstein[24] computed the enthalpy of formation of the propargyl radical at 0 and 298 K by adopting the reference reaction $2C_3H_3 + 9H_2 \rightarrow 6CH_4$ and employing two composite methods, termed HL1 and HL2, for single-point energies at 6-311++G(d,p) B3LYP geometries. HL1 was based on the quadratic configuration interaction (QCI) method 6-311G(d,p) QCISD(T) with 6-311++G(3df,2pd) MP2 basis set incompleteness corrections. HL2 involved cc-pV(D,T)Z QCISD(T) and cc-pV(D,T,Q)Z MP2 computations with extrapolation estimates of complete basis set (CBS) limits. The HL1 and HL2 results for the propargyl radical differed by only 0.2 kcal mol^{-1}, the HL2 values being $\Delta_f H^\circ_0$ = 84.7 kcal mol^{-1} and $\Delta_f H^\circ_{298}$ = 84.3 kcal mol^{-1}.

TABLE 1: Enthalpies of Formation ($\Delta_f H°$, kcal mol^{-1}) for Propargyl Radical

year	$\Delta_f H°$	*T* (K)	method	ref
1970	80.7	298	single-pulse shock-tube study	15
1978	82.7	298	single-pulse shock-tube study	16
1971	86	298	iodine catalyzed isomerization	116
1973	82	298	positive ion thermochemical cycle	117
1978	81.5 ± 1.0	298	very low-pressure pyrolysis	17, 18
1982	81.5 ± 2.0	298	review of previous experiments	19
1996	81.0 ± 1.0	298	review of previous experiments	14
1994	85.2	0	single-pulse shock-tube study	20
1995	82.5 ± 3.0	298	negative ion thermochemical cycle	13
1996	83.6 ± 5.8	298	BAC-MP4	23
2000	81.5 ± 1.3[a]	298	DMC/SBK-ECP	21
2000	82.5 ± 0.6[a]	298	DMC/soft ECP	21
2000	84.0	298	6-311G** B3LYP via atomization energy	21
2000	79.9	298	6-311G** B3PW91 via atomization energy	21
2003	85.3	298	CBS-QB3	22
2003	86.8	298	6-31G(d) B3LYP	22
2003	85.9	298	6-311G(d,p) B3LYP	22
2003	84.9	0	HL1[b]	24
2003	84.5	298	HL1	24
2003	84.7	0	HL2[b]	24
2003	84.3	298	HL2	24
2001	83.8[c]	298	G3 theory	6
2001	84.9[c]	298	RCCSD(T)	6
2001	84.3[c]	298	ROCCSD(T)	6
2001	84.1	0	G3 theory via atomization energy	6
2007	**84.8**	0	focal point extrapolation	*d*
2007	**84.1**	298	focal point extrapolation	*d*

[a] DMC results are computed using two different effective core potentials. [b] HL1 based on 6-311G(d,p) QCISD(T) with a 6-311++G (3df,2pd) MP2 basis set incompleteness correction; HL2 based on cc-pV(D,T)Z QCISD(T) with CBS extrapolations by means of cc-pV(D,T,Q)Z MP2. [c] Average enthalpy obtained using six isodesmic reactions. [d] Present work, mean enthalpy determined from two independent formation reactions.

Closely tied to the enthalpy of formation of the propargyl and 1-propynyl radicals are the C−H bond dissociation energies (BDE) of propyne,[8,13,25−28] as well as the stabilization energy[5,7,13,29] of propargyl below CH($^2\Pi$) + C_2H_2 (see Table 2). For

$$HCCCH_3 \rightarrow HCCCH_2 + H \qquad (1)$$

TABLE 2: Enthalpies of Reaction (0 K, kcal mol^{-1}) for C−H Bond Cleavage in Propyne and Formation of Propargyl Radical

reaction enthalpy	method	ref
	$HCCCH_3 \rightarrow HCCCH_2 + H$	
92.5 ± 2	MCPF with an ANO basis set	25
95.0[a]	cc-pVDZ UCCSD	26
100.4[a]	cc-pVDZ UCCSD(SAC)	26
99.8[a]	CBSI(W1)	26
99.8[a]	CBSII	26
90.5	CBSII + ZPVE	26
85.6	UB3LYP	27
87.6	RB3LYP	27
86.7	RMP2 at UB3LYP geometries	27
86.7	RMP2	27
89.3	G3(MP2)-RAD	27
90.2	CBS-RAD	27
90.5	W1′	27
88.7	CBS-Q	28
88.7	6-311+G(3df,2p) CCSD(T) at B3LYP geometries	8
90.3 ± 3	negative ion thermochemical cycle	13
90.1	focal point extrapolation	*b*
	$HCCCH_3 \rightarrow CCCH_3 + H$	
135.9 ± 2	MCPF with an ANO basis set	25
133.6	CBS-Q	28
130.5	6-311+G(3df,2p) CCSD(T) at B3LYP geometries	8
130.2 ± 3	negative ion thermochemical cycle	13
131.9	focal point extrapolation	*b*
	$CH\ (^2\Pi) + C_2H_2 \rightarrow HCCCH_2$	
−102.8	ICCI with a small basis	29
−113	BAC-MP4	30
−107.2	ICCI with a truncated cc-pVTZ basis	5
−118.3	6-31G(d,p) B3LYP	7
−109.0	CASPT2 with an ANO-type basis	7
−113 ± 3	negative ion thermochemical cycle	13
−111.7	focal point extrapolation	*b*

[a] Without ZPVE corrections. [b] Present work.

Bauschlicher and Langhoff[25] report $D_0 = 92.5 \pm 2$ kcal mol^{-1} based on modified coupled-pair functional (MCPF) computations, compared to the experimental value[13] of 90.3 ± 3 kcal mol^{-1}. The more recent 6-311+G(3df,2p) CCSD(T) work of Mebel and co-workers[8] [computed at 6-311+G(3df,2p) B3LYP optimized geometries] gives a somewhat smaller value of 88.7 kcal mol^{-1}. There are disparities of a similar magnitude in reported values for the BDE of the acetylenic C−H bond in propyne (see Table 2),

$$HCCCH_3 \rightarrow CCCH_3 + H \qquad (2)$$

although there are far fewer theoretical predictions of this quantity in the literature. Likewise, for the enthalpy of the reaction

$$CH(^2\Pi) + C_2H_2 \rightarrow HCCCH_2 \qquad (3)$$

Walch[29] determined −102.8 kcal mol^{-1} using internally contracted configuration interaction (ICCI) with a small basis set in 1995. In contrast, the BAC-MP4 method yields[30] −113 kcal mol^{-1}. In 1998, Guadagnini et al.[5] performed ICCI computations with a truncated cc-pVTZ basis set, yielding a reaction enthalpy of −107.2 kcal mol^{-1}, while Vereecken et al.[7] found −118.3 and −109.0 kcal mol^{-1} using 6-31G** B3LYP and CASPT2, respectively. The ion-molecule thermochemical measurements of Robinson et al.[13] produced −113 ± 3 kcal mol^{-1}. It is unsettling that the theoretical predictions for this important reaction span more than 15 kcal mol^{-1}, with none falling within the experimental error bars.

In the present work, we obtain definitive results for C_3H_3 isomerization energies, enthalpies of formation, and associated reactions utilizing flexible triple-ζ quality basis sets and coupled-cluster methods to compute accurate geometries, paired with focal point extrapolations to predict relative energies and enthalpies of formation at the CBS CCSDT limit. Auxiliary corrections are appended to account for connected quadruple excitations, the correlation of core electrons, scalar relativistic effects, anharmonic zero-point vibrational energies, and the diagonal Born−Oppenheimer correction (DBOC) in order to obtain relative energies of subchemical accuracy (errors near 0.1 kcal mol^{-1}). Given the predominance of the propargyl radical in the formation of soot during combustion, such accuracy in basic thermodynamic parameters is long overdue. The present results are by far the most accurate reported for these key soot formation intermediates and stand at the forefront[31,32] of current computational capabilities of ab initio thermochemistry for species with more than two heavy atoms.

II. Theoretical Methods

Precise standard enthalpies of formation and relative energies have been computed via the focal point extrapolation scheme of Allen and co-workers.[33−38] Geometries were optimized using coupled-cluster singles and doubles theory (CCSD)[39−42] appended with perturbative inclusion of connected triple excitations [CCSD(T)],[43−46] freezing the carbon 1s orbitals. Semicanonical orbitals[47] were utilized in all open-shell CCSD(T) computations carried out in *ACES II*,[48] while pseudo-semicanonical orbitals[49] were used in *MOLPRO*.[50,51] Reference electronic wave functions were determined using spin-restricted open-shell Hartree−Fock theory (ROHF), to avoid the possibility of spurious energetic predictions resulting from spin contamination. The geometry optimizations utilized a TZ(2d1f,2p1d) basis,[11,52] composed of the Dunning C(10s6p/5s3p) and unscaled H(5s/3s) triple-ζ segmented sp contractions[53] augmented with correlation-optimized[54] polarization functions [$\alpha_d(C) = 0.318, 1.097$; $\alpha_f(C) = 0.761$; $\alpha_p(H) = 0.388, 1.407$; $\alpha_d(H) = 1.057$]. All polarization manifolds contained only pure spherical harmonics. The geometry optimizations were carried out by analytic gradients using the *ACES II* program package.[48]

In the focal point scheme, the correlation-consistent basis sets of Dunning[54] are utilized to achieve systematic dual one- and *n*-particle expansions. Electron correlation is treated through second-order perturbation theory and primarily by coupled-cluster theory including single and double excitations (CCSD)[39−42] and either perturbative [CCSD(T)][43−46] or full treatments (CCSDT)[55−58] of triple excitations. The first component of the energy for the focal point procedure was obtained using spin restricted Hartree−Fock theory. Likewise, higher-order correlation effects were included via spin restricted coupled-cluster analogues,[12,42,47,59,60] denoted by ROCCSD, ROCCSD(T), and ROCCSDT, respectively. A final correction was appended to the extrapolated valence energies to account for connected quadruple excitations. This term was computed with the cc-pVDZ basis set using the recently developed[61] CCSDT(Q) method, whose (Q) term is derived from a non-Hermitian perturbation theory analogous to that used to justify the ever-popular (T) correction for connected triple excitations.[62] From an extensive test set,[61] CCSDT(Q) energies have been shown to compare favorably with the full singles, doubles, triples, and quadruples coupled-cluster method (CCSDTQ). The CCSDT(Q) computations were carried out using the Mainz−Austin−Budapest (MAB) version[48] of *ACES II* and were based on an unrestricted Hartree−Fock reference wave function in

TABLE 3: Standard Enthalpies of Formation ($\Delta_f H_0^\circ$, kcal mol^{-1}) for Reference Species

species	$\Delta_f H_0^\circ$	uncertainty	ref[a]
H(^{2}S)	51.63	0.00	78
CH($^2\Pi$)	141.78	0.09	78
CH_3	35.84	0.03	78
CH_4	−15.92	0.08	79
C_2H_2 (acetylene)	54.69	0.07	78
C_2H_4 (ethylene)	14.56	0.12	79
C_2H_6 (ethane)	−16.34	0.10	79

[a] Enthalpies of formation from ref 78 are from the active thermochemical tables (ATcT) of Ruscic et al.[74−77]

the case of the open-shell systems (because of program limitations). Since high-order coupled-cluster wave functions are only very weakly dependent on reference orbitals, the use of an unrestricted formalism is expected to have a negligible effect, even in the presence of spin contamination. All energies for the focal point analyses were computed at the frozen-core TZ(2d1f,2p1d) ROCCSD(T) optimized geometries described above. Examination of the T_1 and T_2 amplitudes within the converged CCSD wave functions for all structures considered did not reveal any significant multireference character, providing justification for our consistent use of high-order single-reference methods.

For spin-restricted open-shell Møller-Plesset perturbation theory there is some ambiguity in the choice of partitioning of the electronic Hamiltonian, resulting in a number of unique formulations in the literature.[49,63−67] An analysis of results from Z-averaged perturbation theory (ZAPT)[66] has suggested that the convergence properties of ZAPT*n* energies are similar to the popular restricted Møller-Plesset (RMP)[49,64] theory but without the added computational expense associated with the use of different orbitals for different spins. Furthermore, our unpublished comparisons of predicted equilibrium bond lengths and harmonic vibrational frequencies has indicated that at second and fourth order, ZAPT performs at least as well as RMP theory. In light of the computational advantages offered by ZAPT theory and the availability of the efficient, parallel implementation in the MPQC package,[68] ZAPT2 energies were utilized for the leading contribution to the correlation energy in all focal point analyses [with the exception of the energy of 1-propynyl (**2**) relative to propargyl (**1**); see section III] involving open-shell species.

Valence energies were first computed within the focal point procedure using the correlation-consistent polarized valence [cc-pVXZ (X = D, T, Q, 5, 6)] hierarchy of basis sets[54,69] to achieve a systematic approach to the CBS limit. Similarly, core correlation contributions were evaluated through a second set of focal point extrapolations, available as Supporting Information (Tables S1−S6), utilizing the cc-pCVXZ (X = D, T, Q, 5) family of basis sets.[70]

All correlated energy computations involved freezing the carbon 1s orbitals, except where noted otherwise for the explicit evaluation of the core correlation contribution. The functional form[71] for the basis set extrapolation of the Hartree−Fock energies was

$$E_{HF} = a + b e^{-cX} \tag{4}$$

while the correlation energies were extrapolated via[72]

$$E_{corr} = a + bX^{-3} \tag{5}$$

The focal point scheme was utilized to evaluate relative energies of three low-lying C_3H_3 isomers, relative to the propargyl radical, and the energy of allene, relative to propyne. Enthalpies of formation (0 K) of allene and propyne were predicted using the focal point procedure paired with the isodesmic[73] reactions

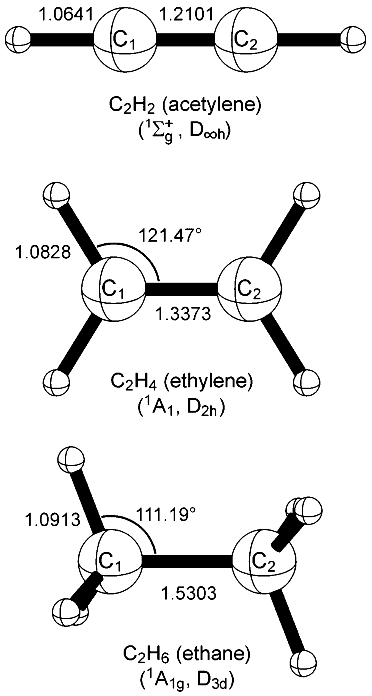

Figure 2. Optimized geometries of acetylene, ethylene, and ethane, computed at the frozen-core TZ(2d1f,2p1d) CCSD(T) level of theory.

$$H_2C{=}CH_2 + H_2C{=}CH_2 \rightarrow H_2CCCH_2 + CH_4 \tag{6}$$

and

$$HC{\equiv}CH + H_3C{-}CH_3 \rightarrow HCCCH_3 + CH_4 \tag{7}$$

The enthalpy of formation for the propargyl radical was determined through the isodesmic reactions

$$H_2CCCH_2 + CH_3 \rightarrow HCCCH_2 + CH_4 \tag{8}$$

and

$$HCCCH_3 + CH_3 \rightarrow HCCCH_2 + CH_4 \tag{9}$$

Isodesmic reactions,[73] in which the number of bonds of each formal type is retained, balance errors on each side of the reaction, offering accelerated convergence to the Born−Oppenheimer limit compared to the determination of enthalpies via atomization reactions.

Established enthalpies of formation were adopted for CH($^2\Pi$), CH_3, CH_4, acetylene, ethane, and ethlyene, as given in Table 3. The data for these reference compounds were taken either from the active thermochemical tables (ATcT) of Ruscic and co-workers[74−78] or the compendium by Gurvich et al.[79] The error bars on the reference enthalpies do not exceed 0.12 kcal mol^{-1}. An experimental r_e bond length was employed in our computations on CH_4 (1.085 Å),[80] while an equilibrium bond length of 1.0763 Å, obtained at the all-electron cc-pCVQZ ROCCSD(T) level of theory, was utilized for CH_3. Geometric structures for acetylene, ethylene, and ethane are included in Figure 2, optimized at the frozen-core TZ(2d1f,2p1d) CCSD(T) level of theory.

Extrapolated energies were further refined via the DBOC,[81−85] which constitutes the first-order perturbative correction to the clamped-nucleus electronic energy. Special relativity was accounted for by the application of standard perturbation formulas for the mass-velocity and one-electron Darwin scalar relativistic effects.[86−90] The DBOC was evaluated at the all electron cc-pVDZ UCISD (unrestricted configuration interaction with single and double excitations) level of theory based on analytic second derivatives[91,92] computed using *MRCC*[93,94] paired with *ACES II*. Relativistic effects were evaluated at the cc-pCVTZ ROCCSD(T) level of theory using *ACES II*.[48]

Harmonic vibrational frequencies were computed at the frozen-core ANO4321 ROCCSD(T) level of theory by finite differences of analytic gradients[47,95] using *ACES II*, with frequencies and IR intensities provided as Supporting Information. The ANO-type basis sets[96] have been shown[97] to yield more satisfactory vibrational frequencies than other triple- and quadruple-ζ sets, particularly in the case of linear bends in unsaturated hydrocarbons. The resulting unscaled harmonic zero-point vibrational energies (ZPVEs) were further corrected using anharmonicities computed from a normal-coordinate quartic force field determined at the frozen-core ANO4321 RMP2 (second-order restricted Møller-Plesset theory)[49,64] level of theory. This method should provide ZPVE differences within the target accuracy of 0.1 kcal mol^{-1}. Within second-order vibrational perturbation theory (VPT2),[98,99] the ZPVE is given by

$$\mathrm{ZPVE} = G_0 + \frac{1}{2}\sum_i d_i\omega_i + \frac{1}{4}\sum_i d_i d_j \chi_{ij} = \frac{1}{2}\sum_i \omega_i - \frac{1}{32}\sum_{ijk}\frac{\phi_{iik}\phi_{kjj}}{\omega_k} - \frac{1}{48}\sum_{ijk}\frac{{\phi_{ijk}}^2}{\omega_i+\omega_j+\omega_k} + \frac{1}{32}\sum_{ij}\phi_{iijj} + Z_{\mathrm{kinetic}} \quad (10)$$

where the ω_i are harmonic frequencies, the χ_{ij} are anharmonicity constants, the d_i are normal-mode degeneracies, the ϕ_{ijk} and ϕ_{iijj} are cubic and quartic force constants in the reduced normal coordinate space, and Z_{kinetic} is a kinetic energy contribution arising from vibrational angular momentum. The second form[100] of eq 10 is derived by the addition of the G_0 term to eliminate all of the resonance denominators in the χ_{ij} constants. The G_0 quantity has traditionally been neglected (often unknowingly) in electronic structure computations, but some recent high-accuracy studies have included this contribution.[37,78,101] In this work G_0 was omitted from the anharmonic ZPVE computations, because the isodesmic reactions 6−9 are already mode-balanced, and the general form of Z_{kinetic} for spherical tops was unavailable. Accordingly, a resonance cutoff of 100 cm^{-1} was invoked to ensure the validity of the χ_{ij} constants

The HF, CCSD, and CCSD(T) energies for the focal point extrapolations were computed using *MOLPRO*[50] while the ZAPT2 energies were evaluated using *MPQC 2.1*.[68] The MAB version of *ACES II*[48] was utilized for the RMP2, CCSDT, CCSDT(Q), and CISD DBOC computations.

III. Geometric Structures

Optimized structures for allene, propyne, and the four C_3H_3 isomers of concern are given in Figures 3 and 4, as obtained at the frozen-core TZ(2d1f,2p1d) ROCCSD(T) level of theory. The propargyl radical (**1**) exhibits C_{2v} symmetry, with a ground $^2B_1$ electronic state (with the z axis along the C−C−C framework and the molecule in the yz plane). Compared to these ROCCSD(T) optimized structures (Figure 4), previously reported[6−8] B3LYP geometries for propargyl underestimate the length of the C_1−C_2 bond by between 0.02 and 0.04 Å, depending on the basis set employed. The contraction of the C_1−C_2 distance in the B3LYP geometry corresponds to an enhanced contribution from the cumulenic resonance form of propargyl relative to the acetylenic form (see Figure 1), reflective of known shortcomings of some DFT functionals for describing acetylenic and cumulenic systems.[102] Moreover, this bond-length contraction in the B3LYP optimized structure will artificially increase any ab initio energy computed at this geometry, potentially altering predicted relative energies and enthalpies of formation. The B3LYP functional better reproduces the TZ(2d1f,2p1d) ROCCSD(T) optimized C_2−C_3 bond length, fortuitously giving agreement to within 0.001 Å when paired with the 6-31G(d,p) basis set. Relative to the parent allene structure (Figure 3), the propargyl radical has a C_1−C_2 bond length shorter by 0.07 Å and a C_2−C_3 distance longer by 0.09 Å. Alternatively, viewing the propargyl radical as arising from the abstraction of a methyl hydrogen from propyne (Figure 3), the C_1−C_2 bond length exhibits a decrease of 0.09 Å accompanied by a much smaller increase in the C_2−C_3 bond length of 0.02 Å.

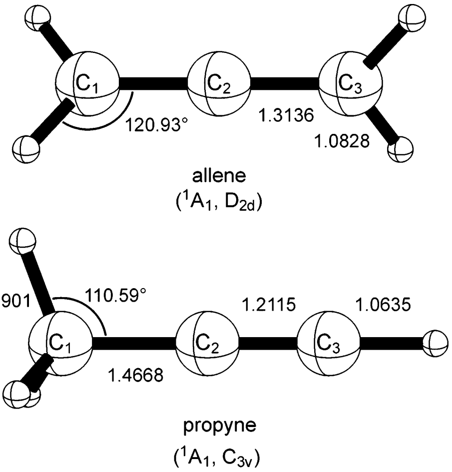

Figure 3. Optimized geometries of allene and propyne, computed at the frozen-core TZ(2d1f,2p1d) ROCCSD(T) level of theory.

For the C_{3v}-symmetric 1-propynyl radical (**2**), there are two low-lying doublet electronic states, arising when the unpaired electron occupies either a π orbital or a predominantly nonbonding carbon σ orbital of a_1 symmetry. The single occupation of one of the degenerate C−C π orbitals yields a ^2E electronic state, so Jahn−Teller distortion will occur, giving bent $^2A'$ and $^2A''$ structures. On the other hand, single occupation of the σ orbital leads to a $^2A_1$ state not subject to Jahn−Teller distortion. Vereeken et al.[7] reported a bent $^2A'$ ground state for the 1-propynyl radical at the 6-31G(d,p) B3LYP level of theory. However, Mebel et al.[8] write that single-point 6-311+G(3df, 2p) CCSD(T) energies computed at 6-311G(d,p) B3LYP geometries place the $^2A'$ C_s structure 1.8 kcal mol^{-1} *higher* in energy than the $^2A_1$ C_{3v} structure. In 1992, Bauschlicher and Langhoff[25] reported that the ^2E state was some 9.7 kcal mol^{-1} lower than the $^2A_1$ state using Hartree−Fock theory with a double-ζ basis set, although they did not report any structures distorted from the C_{3v} symmetry.

The C_{3v}-symmetric 1-propynyl radical poses a difficulty for typical electronic structure theory packages, in which molecular orbitals are constructed to transform as irreducible representations of the largest Abelian subgroup (C_s symmetry in the case of structure **2**) of the full molecular point group. The problem is that the singly occupied a_1 nonbonding σ orbital and in-plane π orbital transform as the same irreducible representation of the C_s point group (a'), and some mixing of the two can occur

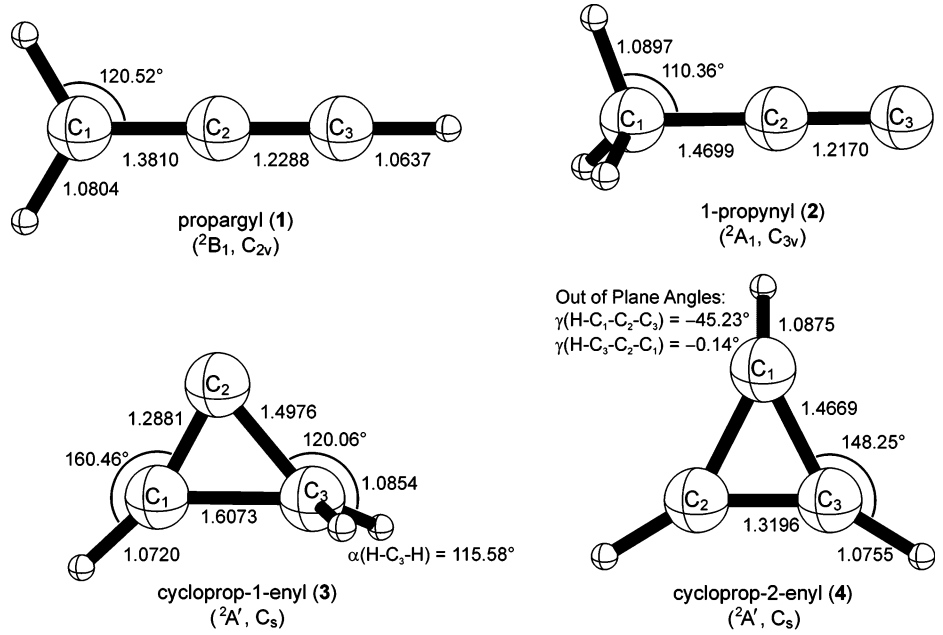

Figure 4. Optimized geometries of C_3H_3 isomers, computed at the frozen-core TZ(2d1f,2p1d) ROCCSD(T) level of theory. In **4**, the hydrogens on C_1 and (C_2,C_3) are bent out of the ring plane in opposite directions.

TABLE 4: Incremental Valence Focal Point Table (kcal mol^{-1}) for Isomerization of Propyne to Allene[a]

basis set	ΔE_e[RHF]	$+\delta$[MP2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	ΔE_e[CCSDT]
			Propyne → Allene			
cc-pVDZ	1.081	+3.180	−3.499	−0.271	−0.170	0.320
cc-pVTZ	1.573	+3.139	−3.262	−0.286	−0.169	0.995
cc-pVQZ	1.571	+3.208	−3.168	−0.309	[−0.169]	[1.133]
cc-pV5Z	1.543	+3.274	−3.148	−0.320	[−0.169]	[1.180]
cc-pV6Z	1.536	+3.322	[−3.158]	[−0.324]	[−0.169]	[1.206]
CBS limit	[1.534]	[+3.387]	[−3.172]	[−0.330]	[−0.169]	[1.250]
	δ[CCSDT(Q)/cc-pVDZ] = +0.10 kcal mol^{-1}; Final ΔE_{fp}(V) = 1.25 + 0.10 = **1.35** kcal mol^{-1}					
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points ($X =$)	4, 5, 6	5, 6	4, 5	4, 5		

[a] The symbol δ denotes the increment in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), while unbracketed numbers were explicitly computed.

during the self-consistent-field procedure, resulting in a nondegeneracy of the in-plane and out-of-plane π orbitals and an artifactual lowering of the Hartree−Fock energy. However, in *ACES II*, one can constrain the ROHF orbitals to transform as irreducible representations of the full point group (C_{3v}), giving orbitals that exhibit the proper degeneracies and full symmetry of the molecular framework.

To obtain a balanced description of the lowest lying states of the 1-propynyl radical, we optimized geometries for both the ^{2}E and $^2A_1$ states using the equation-of-motion CCSD (EOM-CCSD)[103] method with the cc-pVDZ basis set,[54] adopting the $^2A_1$ state as the reference to construct the similarity-transformed Hamiltonian and employing Hartree−Fock orbitals with full C_{3v} symmetry. The $^2A_1$ equilibrium structure of **2** appeared 7.2 kcal mol^{-1} below the optimum ^{2}E geometry in the C_{3v} space. This finding is consistent with detailed spectroscopic analyses and ab initio computations placing the $^2\Sigma^+ \rightarrow {}^2\Pi$ excitation energy of C_2H very near 10.3 kcal mol^{-1}.[104−106] We also found that the Jahn−Teller distortion of the ^{2}E state of the 1-propynyl radical will not lower the energy enough to bring the resulting ($^2A'$,$^2A''$) pair of states below the C_{3v} minimum of the $^2A_1$ σ radical. Therefore, the TZ(2d1f,2p1d) ROCCSD(T) $^2A_1$ geometry was used in all subsequent computations on **2**. Comparing the structure of **2** with that of the parent propyne (cf. Figures 3 and 4), we find there is negligible change in geometry upon removal of the acetylenic hydrogen, indicating that the singly occupied a_1 orbital of **2** is particularly nonbonding with respect to the carbon framework.

The optimized CCSD(T) structures for cyclic isomers **3** and **4** are quite similar to previously reported B3LYP geometries,[6−8] with all deviations in bond lengths less than 0.01 Å. The cycloprop-1-enyl radical (**3**) exhibits a remarkably long C_1−C_3 bond length of 1.61 Å, presumably due to the large strain in this unconventional cyclic radical. The C_1−C_3−C_2 bond angle of 48.9° is quite notable. The cycloprop-2-enyl radical (**4**) distorts from D_{3h} symmetry due to the Jahn−Teller effect,[107,108] yielding a $^2A'$ electronic state and the C_s global minimum geometry displayed in Figure 4, wherein the C_1−H bond vector is directed 45.2° out of the ring plane. At the frozen-core TZ(2d1f,2p1d) ROCCSD(T) level of theory, the relaxation from D_{3h} to C_s symmetry lowers the energy by 14.5 kcal mol^{-1}. Previous theoretical results indicate a 3−4 kcal mol^{-1} barrier to pseudorotation, passing through an allylic transition state.[108]

IV. Isomerization Energies

A. Allene versus Propyne. The valence focal point table for the energy of allene relative to propyne is provided in Table 4. The computed energy exhibits excellent convergence with respect to basis set completeness for the Hartree−Fock and

TABLE 5: Determination of Isomerization Energies (kcal mol^{-1}) for C_3H_4 and C_3H_3[a]

reaction	ΔE_{fp}(V)	Δ_{fp}(core)	ΔZPVE	ΔAnharm	ΔDBOC	ΔRel	ΔE_0(final)
propyne → allene	1.35	+0.10	−0.33	−0.08	+0.02	−0.01	**1.06**
propargyl → **2**	39.93	+0.26	+1.67	*b*	−0.03	+0.01	**41.84**
propargyl → **3**	39.45	+0.51	+1.45	+0.16	+0.01	−0.05	**41.52**
propargyl → **4**	31.18	+0.22	+1.06	+0.20	−0.10	+0.04	**32.60**

[a] ΔE_{fp}(V) = focal point energy difference from Tables 4, 6, and 7 including UCCSDT(Q) corrections; Δ_{fp}(core) = focal point core correlation correction from supplementary Tables S1−S3; ΔZPVE = harmonic ZPVE correction [ANO4321 ROCCSD(T)]; ΔAnharm = anharmonic contribution to ZPVE from ANO4321 RMP2 quartic force field; ΔDBOC = diagonal Born−Oppenheimer correction (cc-pVDZ UCISD); ΔRel = scalar relativistic corrections [cc-pCVTZ ROCCSD(T)]; ΔE_0(final) = sum of previous six columns. [b] Because of the technical difficulties arising from the intricate electronic structure of the 1-propynyl radical described in the text, we were unable to compute a reliable anharmonic ZPVE for this species.

TABLE 6: Incremental Valence Focal Point Tables (kcal mol^{-1}) for Isomerization of Propargyl Radical (1) to 1-Propynyl Radical (2)[a]

basis set	ΔE_e[ROHF]	+δ[RMP2]	+δ[CCSD]	+δ[CCSD(T)]	+δ[CCSDT]	ΔE_e[CCSDT]
			Propargyl → 1-Propynyl (**2**)			
cc-pVDZ	34.134	+4.385	−2.301	+0.284	−0.104	36.398
cc-pVTZ	35.240	+5.755	−2.178	+0.419	+0.005	39.241
cc-pVQZ	35.206	+6.171	−2.261	+0.482	[+0.005]	[39.603]
cc-pV5Z	35.249	[+6.319]	[−2.291]	[+0.504]	[+0.005]	[39.786]
cc-pV6Z	35.252	[+6.385]	[−2.304]	[+0.514]	[+0.005]	[39.851]
CBS limit	[35.252]	[+6.475]	[−2.322]	[+0.528]	[+0.005]	[39.937]
			δ[CCSDT(Q)/cc-pVDZ] = −0.01 kcal mol^{-1}; Final ΔE_{fp}(V) = 39.94 − 0.01 = **39.93** kcal mol^{-1}			
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points (X =)	4, 5, 6	3, 4	3, 4	3, 4		

[a] The symbol δ denotes the increment in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), while unbracketed numbers were explicitly computed.

coupled-cluster methods: the cc-pV6Z HF relative energy is within 0.002 kcal mol^{-1} of the extrapolated limit (1.534 kcal mol^{-1}), while the cc-pV5Z CCSD(T) relative energy is within 0.07 kcal mol^{-1} of the extrapolated CCSD(T) limit. For the leading (MP2) contribution to the correlation energy, the cc-pV6Z value is only 0.065 kcal mol^{-1} smaller than the extrapolated CBS value.

The CBS limit MP2 contribution raises the energy of allene relative to propyne by nearly 3.4 kcal mol^{-1} to 4.9 kcal mol^{-1}. This effect is cancelled out by the coupled-cluster contributions to yield a final valence relative energy of 1.35 kcal mol^{-1}, after the inclusion of +0.10 kcal mol^{-1} to account for connected quadruple excitations. The failure of MP2 to accurately predict the relative energy of allene and propyne has been documented previously[102] and is a testament to the importance of the more complete treatment of dynamic correlation provided by coupled-cluster methods. Popular DFT functionals exhibit a more dramatic failure, predicting allene to lie lower in energy than propyne.[102] Because the two molecules are nearly isoenergetic, the correction to the CCSD relative energy due to the complete inclusion of connected triple excitations (−0.50 kcal mol^{-1}) is nearly 40% of the final extrapolated valence energy difference. However, the CCSDT(Q) computations shift the result further by only +0.10 kcal mol^{-1}, suggesting that the final focal point relative energy is converged to within our target accuracy.

Upon accounting for harmonic and anharmonic ZPVE, as well as DBOC, core correlation, and scalar relativistic effects, the final propyne-to-allene isomerization energy becomes +1.06 kcal mol^{-1}(see Table 5). Note that the core correlation and DBOC (positive) shifts are nearly cancelled by the anharmonic ZPVE and relativistic (negative) shifts. As a check on the accuracy of our anharmonic force fields, theoretical and experimental[109] fundamental vibrational frequencies for allene and propyne are compared in Table S7 (Supporting Information). Our theoretical ν_i values exhibit mean errors of only 4 and 9 cm^{-1} for allene and propyne, respectively, in truly remarkable agreement with experiment. This comparison certainly bolsters confidence in the anharmonic ZPVEs computed here.

In 2002, Kobychev et al.[110] computed the energy of allene relative to propyne at a number of levels of theory, including the Gaussian-1 (G1) and -2 (G2) methods, which gave values of +0.79 and +0.77 kcal mol^{-1}, respectively. The aforementioned composite computations HL1 and HL2 of Klippenstein and Miller[24] produced +0.7 and +1.0 kcal mol^{-1}, respectively. In 2005, Yu and Muckerman[26] extrapolated CCSD(T) energies to arrive at +1.09 kcal mol^{-1} for the allene−propyne energy separation. The most involved theoretical prediction of the energy of allene relative to propyne in the literature is that of Feller and Dixon,[111] who extrapolated CCSD(T) atomization energies for these species and appended core correlation and scalar relativistic effects, as well as a “high order” correction designed to account for shortcomings in the CCSD(T) method relative to full configuration interaction (FCI). With the “high order” correction, their final, extrapolated valence result was ΔE_e(allene−propyne) = +1.25 kcal mol^{-1}, very close to our +1.35 kcal mol^{-1} with CCSDT(Q) included. Feller and Dixon then applied core correlation and ZPVE corrections of −0.20 and −0.22 kcal mol^{-1}, whereas our values for these shifts are +0.10 and −0.41 kcal mol^{-1}, respectively. Thus, their final result is about 0.2 kcal mol^{-1} lower than our isomerization energy because of the discrepancies in the auxiliary corrections. The ΔZPVE disparity can be accounted for by the different schemes used to evaluate the ZPVEs: Feller and Dixon sum the averages of the aug-cc-pVDZ CCSD(T) harmonic and experimental fundamental frequencies, whereas our more rigorous ZPVE comes from ANO4321 CCSD(T) harmonic frequencies and anharmonicity constants derived from an ANO4321 MP2 quartic force field.

B. C_3H_3 Isomers. Valence focal point tables for the energies of structures **2**, **3**, and **4** relative to propargyl radical (**1**) are provided in Tables 6 and 7. Because of the unavailability of programs capable of computing ZAPT2 energies that can also straightforwardly restrict the Hartree−Fock orbitals to transform

TABLE 7: Incremental Valence Focal Point Tables (kcal mol^{-1}) for the Isomerization of Propargyl Radical (1) to Cycloprop-1-enyl (3) and Cycloprop-2-enyl (4) Radicals[a]

basis set	ΔE_e[ROHF]	$+\delta$[ZAPT2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	ΔE_e[CCSDT]
			Propargyl → Cycloprop-1-enyl (**3**)			
cc-pVDZ	42.552	−5.010	+1.360	−0.912	+0.116	38.106
cc-pVTZ	43.968	−4.996	+1.580	−1.062	+0.310	39.800
cc-pVQZ	43.985	−4.869	+1.523	−1.068	[+0.310]	[39.881]
cc-pV5Z	44.018	−5.002	+1.506	−1.082	[+0.310]	[39.750]
cc-pV6Z	44.012	−5.004	[+1.441]	[−1.088]	[+0.310]	[39.671]
CBS limit	[44.009]	[−5.007]	[+1.352]	[−1.097]	[+0.310]	[39.568]
	δ[CCSDT(Q)/cc-pVDZ] = −0.12 kcal mol^{-1}; Final ΔE_{fp}(V) = 39.57 − 0.12 = **39.45** kcal mol^{-1}					
			Propargyl → Cycloprop-2-enyl (**4**)			
cc-pVDZ	27.704	+1.819	+1.150	+0.221	+0.140	31.035
cc-pVTZ	28.812	+1.630	+0.988	+0.182	+0.275	31.887
cc-pVQZ	28.747	+1.577	+0.826	+0.199	[+0.275]	[31.624]
cc-pV5Z	28.722	+1.423	+0.774	+0.193	[+0.275]	[31.386]
cc-pV6Z	28.702	+1.396	[+0.709]	[+0.190]	[+0.275]	[31.272]
CBS limit	[28.696]	[+1.360]	[+0.619]	[+0.186]	[+0.275]	[31.136]
	δ[CCSDT(Q)/cc-pVDZ] = +0.04 kcal mol^{-1}; Final ΔE_{fp}(V) = 31.14 + 0.04 = **31.18** kcal mol^{-1}					
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points ($X =$)	4, 5, 6	5, 6	4, 5	4, 5		

[a] The symbol δ denotes the increment in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), while unbracketed numbers were explicitly computed.

as irreducible representations of the C_{3v} point group (see section III), the leading correlation contribution in the focal point extrapolation for the energy of 1-propynyl radical comes from RMP2 energies. However, RMP2 and ZAPT2 have been shown to give similar results, and this difference will have no bearing on the final computed isomerization energy.

The one-particle basis set requirements for converging the relative energies of **2**, **3**, and **4** are not particularly severe, as in all three cases the cc-pVTZ basis provides a ΔE_e[CCSDT] result within 0.8 kcal mol^{-1} of the corresponding CBS limit. This observation is somewhat surprising given the large strain energy present in **3** and **4**. The correlation convergence is most protracted for the relative energy of cycloprop-1-enyl (**3**); for example, in Table 7 the successive ZAPT2, CCSD, CCSDT, and CCSDT(Q) increments computed with the cc-pVDZ basis set are −5.01, +1.36, −0.80, and −0.12 kcal mol^{-1}, in order. In contrast, the total post-CCSD(T) effect on the relative energy of 1-propynyl (**2**) is less than 0.01 kcal mol^{-1}. In the valence focal point limits, isomers **2**, **3**, and **4** lie 39.93, 39.45, and 31.18 kcal mol^{-1}, respectively, above the propargyl radical (**1**). Applying the auxiliary corrections in Table 5, we obtain ΔE_0(final) = 41.84, 41.52, and 32.60 kcal mol^{-1}, for isomers **2**, **3**, and **4**, in order. Thus, cycloprop-2-enyl is the lowest-lying isomer by far, while cycloprop-1-enyl and 2-propynyl are essentially isoenergetic.

Our present ΔE_0(final) isomerization energies are 2−4 kcal mol^{-1} below previously reported B3LYP values,[6−8] perhaps because of the failure of this density functional to accurately describe the cumulenic−acetylenic resonance in the propargyl radical. Furthermore, our isomerization energies are 1.8, 1.4, and 1.3 kcal mol^{-1} above the 6-311+G(3df,2p) RCCSD(T) values of Nguyen and co-workers.[6] Dissecting these latter disparities, we find that the 6-311+G(3df,2p) RCCSD(T) computations underestimate our ΔE_{fp}(V) limits by 0.9, 0.6, and 0.7 kcal mol^{-1} for **2**, **3**, and **4**, respectively. In addition to incompleteness of the 6-311+G(3df,2p) basis set, the use of B3LYP geometries in ref 6 is a likely source of error, because this density functional gives a poor C_1−C_2 bond distance for the propargyl radical (see section III). This geometric effect would erroneously raise the computed energy of **1** and lead to underestimation of the relative energies for the other C_3H_3 isomers. The ΔZPVE corrections in ref 6 for **2**, **3**, and **4** are given by B3LYP harmonic frequencies and differ by 0.7, 0.0, and 0.4 kcal mol^{-1}, respectively, from our total ZPVE corrections in Table 5, which incorporate vibrational anharmonicity for all species except **2**. The largest remaining source of error in the results of Nguyen et al.[6] is the neglect of core correlation, which raises the relative energies of **2**, **3**, and **4** by +0.26, +0.51, and +0.22 kcal mol^{-1}, respectively.

V. Enthalpies of Formation of Allene and Propyne

Valence focal point tables for the energies of reactions 6 and 7 are provided in Table 8. There is excellent one-particle basis set convergence for these isodesmic reactions, as the extrapolated CBS values for all correlation increments are within 0.04 kcal mol^{-1} of the largest explicit computations. For both reactions, the net correlation contribution to the reaction energy past the MP2 level does not exceed 1.0 kcal mol^{-1}. Nonetheless, the correlation convergence for allene formation is somewhat less rapid than for propyne, as might be expected since reaction 6 entails carbon rehybridization but reaction 7 does not. Indeed, at the CBS limit, the correction to the CCSD reaction energy arising from the complete inclusion of triple excitations is −0.30 kcal mol^{-1}, which constitutes nearly 8% of the final reaction energy and is significantly larger than the analogous increment for the propyne formation reaction (−0.03 kcal mol^{-1}). Again, however, the CCSDT(Q) perturbative treatment of connected quadruple excitations changes the reaction energies of 6 and 7 by only −0.04 and −0.02 kcal mol^{-1}, respectively, indicating strong convergence toward the FCI limit in both cases.

Correcting the valence focal point reaction energies in Table 8 with the core correlation, ZPVE, DBOC, and scalar relativistic shifts in Table 9, we arrive at enthalpies of formation (0 K) of 47.42 and 46.32 kcal mol^{-1} for allene and propyne, respectively. These values result from the reference enthalpies in Table 3 and the final reaction energies ΔE_0 in Table 9. The energy difference between propyne and allene derived from these independently computed enthalpies of formation is 1.10 kcal mol^{-1}, which is within 0.04 kcal mol^{-1} of the directly computed isomerization energy of 1.06 kcal mol^{-1} (Table 5). To mitigate

TABLE 8: Incremental Valence Focal Point Tables (kcal mol^{-1}) for Formation of Allene and Propyne via Isodesmic Reactions 6 and 7[a]

basis set	ΔE_e[RHF]	$+\delta$[MP2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	ΔE_e[CCSDT]
			$H_2C{=}CH_2 + H_2C{=}CH_2 \rightarrow$ Allene + CH_4			
cc-pVDZ	5.577	−2.001	+1.350	−0.253	+0.031	4.704
cc-pVTZ	5.501	−2.809	+1.327	−0.297	+0.020	3.752
cc-pVQZ	5.666	−2.996	+1.305	−0.323	[+0.020]	[3.672]
cc-pV5Z	5.767	−2.945	+1.285	−0.321	[+0.020]	[3.806]
cc-pV6Z	5.781	−2.919	[+1.273]	[−0.321]	[+0.020]	[3.834]
CBS limit	[5.783]	[−2.884]	[+1.257]	[−0.320]	[+0.020]	[3.856]
		δ[CCSDT(Q)/cc-pVDZ] = −0.04 kcal mol^{-1}; Final ΔE_{fp}(V) = 3.86 − 0.04 = **3.82** kcal mol^{-1}				
			$HC{\equiv}CH + H_3C{-}CH_3 \rightarrow$ Propyne + CH_4			
cc-pVDZ	−7.694	+0.169	+0.820	−0.088	+0.048	−6.744
cc-pVTZ	−7.828	−0.138	+0.837	−0.048	+0.036	−7.142
cc-pVQZ	−7.872	−0.231	+0.827	−0.071	[+0.036]	[−7.310]
cc-pV5Z	−7.886	−0.150	+0.807	−0.070	[+0.036]	[−7.262]
cc-pV6Z	−7.887	−0.134	[+0.818]	[−0.070]	[+0.036]	[−7.237]
CBS limit	[−7.888]	[−0.112]	[+0.833]	[−0.070]	[+0.036]	[−7.200]
		δ[CCSDT(Q)/cc-pVDZ] = −0.02 kcal mol^{-1}; Final ΔE_{fp}(V) = −7.20 − 0.02 = **−7.22** kcal mol^{-1}				
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points (X =)	4, 5, 6	5, 6	4, 5	4, 5		

[a] The symbol δ denotes the increment in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), while unbracketed numbers were explicitly computed.

TABLE 9: Determination of Enthalpies of Formation (kcal mol^{-1}) for Allene, Propyne, and Propargyl (1)[a]

reaction	ΔE_{fp}(V)	Δ_{fp}(core)	ΔZPVE	ΔAnharm	ΔDBOC	ΔRel	ΔE_0(final)	target	$\Delta_f H_0^\circ$
1	99.13	+0.12	−9.17	−0.16	+0.08	−0.02	89.98		
6	3.82	−0.20	−1.27	+0.06	−0.03	+0.01	2.38	allene	47.41[b]
7	−7.22	−0.13	−0.67	+0.08	−0.01	+0.00	−7.95	propyne	46.33[b]
8	−14.58	−0.18	+0.59	−0.26	+0.02	+0.01	−14.40	propargyl	84.77[c]
9	−13.24	−0.07	+0.26	−0.33	+0.04	+0.00	−13.34	propargyl	84.75[c]
							mean $\Delta_f H_0^\circ$(propargyl) = **84.76**		

[a] ΔE_{fp}(V) = focal point energy difference from Tables 8, 9, and S11 (Supporting Information) including UCCSDT(Q) corrections; Δ_{fp}(core) = focal point core correlation correction from supplementary Tables S1−S3; ΔZPVE = harmonic ZPVE correction [ANO4321 ROCCSD(T)]; ΔAnharm = anharmonic contribution to ZPVE from ANO4321 RMP2 quartic force field; ΔDBOC = diagonal Born−Oppenheimer correction (cc-pVDZ UCISD); ΔRel = scalar relativistic corrections [cc-pCVTZ ROCCSD(T)]; ΔE_0(final) = sum of previous six columns. [b] Direct computation of enthalpies of formation for allene and propyne via reactions 6 and 7 yields 47.42 and 46.32 kcal mol^{-1}, respectively. As described in the text, the final recommended enthalpies listed above include slight adjustments to account for the directly computed propyne → allene isomerization energy. [c] On the basis of the enthalpies of formation for allene and propyne given in this table.

this small discrepancy, we have adjusted our enthalpies of formation symmetrically to yield a final allene/propyne separation of 1.08 kcal mol^{-1}, that is, the average from the two routes. Thus, in Table 9, we recommend the final 0 K enthalpies $\Delta_f H_0^\circ$(allene) = 47.41 kcal mol^{-1} and $\Delta_f H_0^\circ$(propyne) = 46.33 kcal mol^{-1}. Uncertainties of 0.2−0.3 kcal mol^{-1} in these values are required to cover any uncertainties in the reference enthalpies or deficiencies in our theoretical computations.

The empirical enthalpies of formation tabulated by Pedley[112] are $\Delta_f H_0^\circ$(allene) = 47.4 ± 0.3 kcal mol^{-1} and $\Delta_f H_0^\circ$(propyne) = 46.0 ± 0.2 kcal mol^{-1}, the first being co-incident with our result and the second having error bars that overlap with ours. Our recommended $\Delta_f H_0^\circ$(allene) is 0.2 kcal mol^{-1} outside the lower bound given by the prior theoretical work of Feller and Dixon (48.1 ± 0.5 kcal mol^{-1}).[111] Finally, the HL2 computations by Miller and Klippenstein[24] place the enthalpies of formation of both allene and propyne 0.6 kcal mol^{-1} below our recommendations.

VI. Enthalpies of Formation of C_3H_3 Isomers

The enthalpy of formation for the propargyl radical has been determined using reactions 8 and 9, with the valence focal point tables shown in Table 10. For both of these isodesmic reactions, the one-particle basis set convergence down the columns for the successive increments is well within 0.1 kcal mol^{-1}. The approach to the FCI limit across the rows is somewhat slower than for the allene and propyne formation reactions (Table 8). For reactions 8 and 9, the full effect of triple excitations amounts to −0.76 and −1.26 kcal mol^{-1}, respectively, at the CBS limit. However, the CCSDT(Q) computations change the reaction energy of reaction 8 by −0.10 kcal mol^{-1} and that of reaction 9 by a mere −0.01 kcal mol^{-1}, lending confidence in the correlation convergence for both routes to the propargyl radical. The final valence focal point reaction energies [ΔE_{fp}(V)] are −14.58 and −13.24 kcal mol^{-1} for reactions 8 and 9, in order. The auxiliary corrections to these quantities are listed in Table 9. Note that the anharmonic ZPVE shifts are the largest corrections, about −0.3 kcal mol^{-1} in both cases. By taking from Table 9 the ΔE_0(final) results and our recommended $\Delta_f H_0^\circ$ values for allene and propyne, and assuming the reference enthalpies in Table 3, we arrive at 84.77 and 84.75 kcal mol^{-1} for the heat of formation of the propargyl radical from reactions 8 and 9, respectively. The mean of these two values, $\Delta_f H_0^\circ$(propargyl) = 84.76 kcal mol^{-1}, constitutes our final prediction. Utilizing our ANO4321 ROCCSD(T) structures and harmonic vibrational frequencies to compute thermal corrections, we obtain 84.1 kcal mol^{-1} for the 298 K enthalpy of formation of the propargyl radical.

The relatively wide range of previous experimental enthalpies of formation for the propargyl radical is shown in Table 1. Compared to our recommended enthalpy, the Tsang[14] and McMillan and Golden[19] values at 298 K (81.0 ± 1.0 and 81.5

TABLE 10: Incremental Valence Focal Point Tables (kcal mol^{-1}) for Formation of Propargyl Radical (1) via Reactions 8 and 9[a]

basis set	ΔE_e[ROHF]	$+\delta$[ZAPT2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	ΔE_e[CCSDT]
$H_2CCCH_2 + CH_3 \rightarrow HCCCH_2 + CH_4$						
cc-pVDZ	−6.762	−7.995	+2.279	−0.529	+0.033	−12.974
cc-pVTZ	−7.104	−8.523	+2.236	−0.670	−0.061	[−14.123]
cc-pVQZ	−7.020	−8.761	+2.178	−0.695	[−0.061]	[−14.359]
cc-pV5Z	−6.964	−8.838	+2.167	−0.697	[−0.061]	[−14.393]
cc-pV6Z	−6.956	−8.892	[+2.182]	[−0.697]	[−0.061]	[−14.424]
CBS limit	[−6.954]	[−8.966]	[+2.202]	[−0.698]	[−0.061]	[−14.477]
δ[CCSDT(Q)/cc-pVDZ] = −0.10 kcal mol^{-1}; Final ΔE_{fp}(V) = −14.48 − 0.10 = **−14.58** kcal mol^{-1}						
$HCCCH_3 + CH_3 \rightarrow HCCCH_2 + CH_4$						
cc-pVDZ	−5.681	−4.814	−1.220	−0.800	−0.137	−12.654
cc-pVTZ	−5.531	−5.384	−1.026	−0.956	−0.230	−13.128
cc-pVQZ	−5.449	−5.553	−0.989	−1.005	[−0.230]	[−13.226]
cc-pV5Z	−5.422	−5.564	−0.981	−1.016	[−0.230]	[−13.213]
cc-pV6Z	−5.420	−5.570	[−0.976]	[−1.021]	[−0.230]	[−13.213]
CBS limit	[−5.420]	[−5.579]	[−0.969]	[−1.028]	[−0.230]	[−13.226]
δ[CCSDT(Q)/cc-pVDZ] = −0.01 kcal mol^{-1}; Final ΔE_{fp}(V) = −13.23 − 0.01 = **−13.24** kcal mol^{-1}						
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points (X =)	4, 5, 6	5, 6	4, 5	4, 5		

[a] The symbol δ denotes the increment in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), while unbracketed numbers were explicitly computed.

± 2.0, respectively) appear to be too low. The two most recent experimental results, from Roth et al.[20] and Robinson et al.[13] (85.2 kcal mol^{-1} at 0 K and 82.5 ± 3.0 kcal mol^{-1} at 298 K, respectively) are in better agreement with our present recommendations. In the former case, the disparity is 0.4 kcal mol^{-1}, while in the latter case the 3.0 kcal mol^{-1} error bars easily envelope our result.

The previous theoretical enthalpies of formation for propargyl span a similar range (see Table 1). Nguyen et al.[6] report 298 K values of 84.9 and 84.3 kcal mol^{-1} based on two different formulations of open-shell coupled-cluster theory applied to isodesmic reaction energies, in reasonable agreement with our 298 K value of 84.1 kcal mol^{-1}. Application of the G3 method to an atomization reaction gave an enthalpy of formation (0 K) of 84.1 kcal mol^{-1}, 0.7 kcal mol^{-1} below our 0 K proposal of 84.8 kcal mol^{-1}. The HL1 and HL2 results of Miller and Klippenstein[24] are remarkably close to ours. However, the DMC results of Harkless and Lester[21] (81.5 ± 1.3 and 82.5 ± 0.6 kcal mol^{-1}) appear to be too small by 1.6−2.6 kcal mol^{-1}. These deficiencies could arise from inaccuracies in DFT optimized structures, unbalanced errors in the fixed-node approximation, an insufficient number of “walkers” within the Metropolis algorithm, or the use of effective core potentials to account for the innermost electrons.

Finally, combining our $\Delta_f H_0^\circ$(propargyl) = 84.76 kcal mol^{-1} with the isomerization energies for the three low-lying C_3H_3 isomers (Table 5), we obtain recommended enthalpies of formation (0 K) of 126.60, 126.28, and 117.36 kcal mol^{-1} for the 1-propynyl (**2**), cycloprop-1-enyl (**3**), and cycloprop-2-enyl (**4**) radicals, respectively.

VII. Related Thermochemistry

With our new enthalpies of formation for propyne, allene, and C_3H_3 isomers, coupled with the reference data in Table 3, we can determine the energies for reactions 1−3. For the methyl and acetylenic C−H bonds in propyne, we find D_0(HCCCH$_2$−H) = 90.1 kcal mol^{-1} and D_0(H−CCCH$_3$) = 131.9 kcal mol^{-1}, respectively. The focal point layout in Table S11 (Supporting Information) and the auxiliary corrections in Table 9 show that a direct computation of the reaction energy of reaction 1 yields the same D_0(HCCCH$_2$−H) within 0.1 kcal mol^{-1}. Our HCCCH$_2$−H dissociation energy is in excellent agreement with the experimental determination of Robinson et al. (90.3 ± 3 kcal mol^{-1}).[13] While our H−CCCH$_3$ dissociation energy is 1.7 kcal mol^{-1} higher than that reported by Robinson et al. (130.2 ± 3 kcal mol^{-1}),[13] it is still within the experimental error bars. The agreement of our propyne bond energies with the previous theoretical results compiled in Table 2 is generally what one would expect; namely, B3LYP and MP2 values are in error by up to 5 kcal mol^{-1}, whereas the various model chemistry approaches are accurate to within 2 kcal mol^{-1}. For both bond energies, the error bars reported with the MCPF values in ref 25 appear to be too optimistic.

The combustion relevance of reaction 3 has led to several theoretical determinations of its reaction energy, but as shown in Table 2 the various computational results span an unsatisfactory range of 15 kcal mol^{-1}. Our propargyl enthalpy of formation yields $\Delta E_0(3)$ = −111.7 kcal mol^{-1}, in excellent agreement with the experimental determination of Robinson et al. (−113 ± 3 kcal mol^{-1}).[13] Both the CASPT2 results of ref 7 and the BAC-MP4 estimate of ref 30 exhibit discrepancies of less than 3 kcal mol^{-1}. The 6-31G(d,p) B3LYP value[7] of −118.3 kcal mol^{-1} is in error by almost 7 kcal mol^{-1}, a testament to the pitfalls of common DFT functionals.

VIII. Summary

State-of-the-art focal point analyses have been executed to determine very accurate enthalpies of formation for allene and propyne, as well as the propargyl (**1**), 1-propynyl (**2**), cycloprop-1-enyl (**3**), and cycloprop-2-enyl (**4**) radicals. Our extrapolations incorporate explicit computations as large as cc-pV6Z ROHF, cc-pV6Z MP2 or ZAPT2, cc-pV5Z CCSD and CCSD(T), cc-pVTZ CCSDT, and cc-pVDZ CCSDT(Q). Separate focal point analyses of core correlation effects employed computations through the cc-pCVQZ CCSD(T) level. Zero-point vibrational energies were determined via VPT2 with ANO4321 CCSD(T) harmonic frequencies appended with anharmonicities from ANO4321 MP2 quartic force fields. The DBOC and scalar relativistic effects were also accounted for with correlated electronic structure methods. Our approach is very similar and competitive with the HEAT 345-(Q) protocol, which for a standard test suite of small molecules yields atomization energies with errors no larger than 0.17 kcal mol^{-1}.[78] The key methodological improvement in both the HEAT 345-(Q) protocol and the focal point scheme employed here is the use of CCSDT(Q) computations[61] to account perturbatively for connected quadruple excitations in coupled-cluster theory. Accordingly, the realm of subchemical accuracy (near 0.1 kcal mol^{-1}) in computational thermochemistry has been reached here for systems with three heavy atoms and three or four hydrogens. Heretofore, only a very limited number of ab initio studies[31,32] have achieved this target accuracy for systems at least as large as those investigated here, but the prospects for burgeoning high-accuracy computational thermochemistry are good.

By means of isodesmic reactions involving methyl, methane, acetylene, ethylene, and ethane, we determine $\Delta_f H_0^\circ$(allene) = 47.41, $\Delta_f H_0^\circ$(propyne) = 46.33, $\Delta_f H_0^\circ$(propargyl) = 84.76, $\Delta_f H_0^\circ$(1-propynyl) = 126.60, $\Delta_f H_0^\circ$(cycloprop-1-enyl) = 126.28, and $\Delta_f H_0^\circ$(cycloprop-2-enyl) = 117.36 kcal mol^{-1}. By comparison, use of our ab initio data in a direct atomization energy approach gives $\Delta_f H_0^\circ = 47.20$, 46.14, and 84.48 kcal mol^{-1} for allene, propyne, and propargyl, respectively. On the basis of this comparison, the existing standardizations for the HEAT 345-(Q) method,[78] and the small inconsistencies observed here among various thermochemical routes, we estimate the errors in our recommended enthalpies of formation to be no larger than 0.3 kcal mol^{-1}. However, there is recent evidence that $\Delta_f H_0^\circ$ of the gaseous carbon atom should be revised upward by about 0.1 kcal mol^{-1},[113] a shift that would alter virtually the entire thermochemical database of hydrocarbon compounds and would generally have a cumulative effect as the number of carbon atoms increases. Any future changes that might be necessitated in the enthalpies of formation for our reference compounds (Table 3) can be applied readily to our present recommendations based on the pure theoretical results underlying them.[114]

Immediate results of our thermochemical recommendations are the C−H bond dissociation energies of propyne and allene: D_0(HCCCH$_2$−H) = 90.1, D_0(H−CCCH$_3$) = 131.9, and D_0(H$_2$CCCH−H) = 89.0 kcal mol^{-1}. Our recommended enthalpies of formation are the most reliable values available for the C$_3$H$_3$ isomers considered here and should be incorporated into detailed kinetic models of soot formation. Additionally, the computed energy of allene relative to propyne is a suitable benchmark against which DFT methods can be tested, since this system poses a difficulty for many popular DFT functionals.[102]

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Supporting Information Available: Focal point tables of the core correlation effect on the propyne/allene energy separation, the relative energies of C$_3$H$_3$ isomers, and the energies for reactions 1 and 6−9; ANO4321 ROCCSD(T) vibrational frequencies for allene, propyne, and C$_3$H$_3$ isomers **1**−**4**; focal point analysis of the methyl C−H bond energy of propyne. This material is available free of charge via the Internet at http://pub.acs.org.

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