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Missing Thermochemical Groups for Large Unsaturated Hydrocarbons: Contrasting Predictions of G2 and CBS-Q

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A total of 12 new thermochemical group additivity values (GAVs) needed to estimate the thermochemistry of large polyunsaturated hydrocarbons are derived from G2 calculations, including the nine missing hydrocarbon group values involving C−H bonds. The CBS-Q method is found to perform very poorly for the calculation of enthalpies of formation of alkynes and systems containing delocalized multiple bonds. The nonsystematic deviations between (i) CBS-Q and experimental values and (ii) CBS-Q and G2 values suggest errors in the CBS-Q extrapolation protocol rather than in the bond-additivity corrections. A few hydrocarbon groups are calculated to have surprisingly different stabilities than the others, and molecules containing these groups would be good targets for future experimental work.

Introduction

Hydrocarbon mixtures will continue to be both the principal chemical feedstock and the principal source of energy worldwide for years to come. Kinetic models of their pyrolysis and combustion chemistry are of great practical importance, and with the rapid improvements in computer-assisted model generation and reactor simulation, quite detailed elementary-step treatments (including hundreds or thousands of species in the reacting mixture) are now possible.[1]

These kinetic models rely on accurate knowledge of the hydrocarbon thermochemistry. However, rarely is the required thermochemical data available from experiment: experimental thermochemical data are available for fewer than 1% of the millions of organic compounds cataloged by Chemical Abstracts Service (CAS), and many of the intermediates thought to be important in the high temperature chemistry of moderately large hydrocarbons have never been detected and do not even have CAS numbers. Fortunately, methods are known for estimating the unknown thermochemical values,[2] and the group-additivity approach of Benson and co-workers has proven extremely accurate and reliable for predicting the thermochemistry of organic compounds, provided the requisite group additivity values (GAVs) are known.[3,4] In this approach, the target molecule is considered to be composed of atom groups, or functional groups, and the sum of the contributions from these groups provides the estimated thermodynamic values of the target molecule. This method is very well suited for predicting the thermochemical values required during computerized kinetic model construction.[5]

Unfortunately, even for hydrocarbons, more than half of the Benson group values remain unknown, severely limiting the range of compounds whose thermochemistry can be accurately predicted. Recently, Cohen[4] has tabulated the best group additivity values available for enthalpies of formation of C/H and C/H/O compounds. The available GAVs based on experimental data do not nearly exhaust all of the possible groups that occur in organic C/H/O compounds. Within the family of C/H compounds alone, the total possible number of hydrogen-containing groups amounts to 25 with three different types of C atoms namely, sp^3 (C), sp^2 (Cd), and sp (Ct). Experimental data are completely lacking for two of the di-substituted alkyl groups and seven of the trisubstituted alkyl groups viz., {C/Ct2/H2}, {C/Ct/Cd/H2}, {C/Ct3/H}, {C/Ct2/C/H}, {C/Ct2/Cd/H}, {C/Cd3/H}, {C/Cd2/Ct/H}, {C/Cd2/C/H}, and {C/Ct/Cd/C/H}. Even fewer data are available for groups containing only carbon atoms; here, we focus on three groups centered on an sp^2 carbon which are missing from Cohen's tabulation but which are required to build models for soot and coke formation from alkanes: {Cd/Ct/Cd}, {Cd/Ct2}, and {Cd/Cd/C}.

The paucity of thermochemical information on molecules containing these groups could suggest that all compounds containing these groups are unimportant. However, it would be extremely risky to assume that just because no thermochemical data is available on a compound it cannot be important. Even rather short-lived intermediates can have important kinetic consequences. When generating kinetic models with a computer, it is good practice to consider each possible species and only discard those found to be numerically insignificant. This determination frequently depends on an estimate of the thermochemistry of the species in question, so knowledge of the thermochemical group values are useful in the model-building procedure even if the compounds with those functional groups turn out to be insignificant.

For the missing groups, the common practice is to estimate an approximate GAV based on the values of similar groups because a close analysis indicates that groups which differ only in the nature of the C substituents (for example, in the set of {C/Cx2/H2}, where the 2 Cx carbons are any combination of C, Cd, and Ct) have approximately the same GAV. This is assumed (by Benson's convention) for groups with three H atoms, and where tested, it has been found to be quite reliable for groups with two H atoms. However, this approximation gets progressively poorer for groups with one or no H atoms. Consequently, application of this rule to estimate the GAV for

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the missing groups is not fully reliable (and it is not possible to test the accuracy of this approximation for completely new groups).

On the other hand, several accurate techniques, e.g., the Gn[6−13] and CBS-n[14−16] series, have been proposed and evaluated in the past decade to predict the thermochemistry of molecules from first-principles calculations. These methods use molecule-independent empirical parameters, and they are parametrized using a test set of relatively small molecules. As evidenced,[17] in the enthalpies of formation of *n*-alkanes of up to 16 carbons and isoalkanes of up to 10 carbons, the calculated heats of formation of large molecule using Gn and CBS-n series could suffer from accumulation of small errors. Nevertheless, it has been shown that one can minimize/cancel the accumulation of such small errors and can improve the agreement with experiment through proper use of isodesmic,[18] isogyric,[19] homodesmotic,[20] or bond separation reaction[21] schemes involving other molecules with similar chemical bonds. These high-level quantum calculations can then be used instead of experimental data to determine the GAVs,[22−23] though one seldom knows if the calculations are sufficiently accurate. Recently, we have demonstrated[5,24−26] the performance of the CBS-Q method in accurately predicting the thermochemical properties of alkanes, alkenes, terminal alkynes, alcohols, acids, aldehydes, ketones, esters, and ethers. We have chosen large molecules in each series, containing up to seven heavy atoms that lie outside the "extended G2 neutral test set" and analyzed the systematic trends, if any, in the predictions. Recently, we also derived[27] nearly 20 GAVs for the molecular family of ketenes using a multivariate linear regression analysis (MVRA). It therefore seems likely that the missing GAVs can be derived from quantum chemical methods, and then group additivity could still be employed as the primary estimation method for the thermochemistry of larger hydrocarbons.

In this paper, we aim to derive the nine missing GAVs for carbons bound to hydrogen and three missing groups for sp^2 carbons needed to compute hydrocarbon thermochemistry, using the G2 level of theory. Many of these groups exist only in molecules containing seven or more carbons, so we could not afford to run high-level calculations on enough molecular systems to do MVRA. Because GAVs derived from a single compound can be subject to large uncertainties, we checked our calculations by comparing the thermochemical properties computed at the G2 and CBS-Q levels of theory. Both levels of theory are known to give very accurate results for many small organics, and they are both extrapolations based on very similar computations, and except in unfavorable cases, one might expect to give very similar values. We have used CBS-Q with great success in several previous publications on thermochemistry and kinetics.[5,24−26] However, CBS-Q has known problems[28,29] in reproducing the experimental heats of formation of 2-butyne and naphthalene, warning that polyunsaturated hydrocarbons may be problematic for CBS-Q.

Theoretical Procedures

Standard ab initio molecular orbital calculations were performed with the Gaussian 98 package.[30] Energies were obtained at the G2 and CBS-Q levels of theory. The G2 level corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on the MP2/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies (ZPE) and making certain assumptions about additivity and appending a small higher-level empirical correction (HLC) to accommodate remaining deficiencies. The main idea in the CBS-Q method is an extrapolation procedure to determine the projected second order (MP2) energy in the limit of a complete basis set. Both methods are known to give very accurate thermochemical values for a variety of small organics.

The total partition function, Q_{tot}, of all species was calculated within the framework of the rigid-rotor-harmonic-oscillator approximation with corrections for internal rotation. The optimized geometrical parameters and the scaled (by 0.91844 for HF/6-31G(d′) and 0.8929 for HF/6-31G(d) level) harmonic vibrational frequencies were used for the calculation of rotational and vibrational partition functions. All torsional motions about the single bonds between polyvalent atoms were treated as hindered internal rotations. The hindrance potential for the internal rotation was obtained at the HF/6-31G(d′) level by optimizing the 3N-7 internal coordinates, except for the specific dihedral angle, which characterizes the torsional motion. This dihedral angle was varied from 0° to 360° in increments of 20 or 30°. The potential energy surface thus obtained was then fitted to a Fourier series $\Sigma_m A_m \cos(m\phi) + B_m \sin(m\phi)$ with $m \leq 17$. Subsequently, the partition function for the hindered rotation was obtained by solving the one-dimensional Schrödinger equation

$$-\frac{h^2}{8\pi^2 I_{\mathrm{hir}}}\frac{\mathrm{d}^2\Psi(\Phi)}{\mathrm{d}\Phi^2} + V(\Phi)\,\Psi(\Phi) = E(\Phi)\,\Psi(\Phi)$$

for the energy eigenvalues with the fitted hindrance potential in the free rotor basis. The reduced moment of inertia for rotation, I_{hir} in the kinetic energy term, was taken as the reduced moment of the two groups about an axis passing through the center of gravity of both the groups. Though I_{hir} is actually a function of ϕ and the vibrational coordinates, in the present work, I_{hir} was fixed at its value for the equilibrium geometry, and the rotating group was assumed to be rigid. The partition function for hindered rotation was evaluated directly from the eigenvalues, whereas the thermodynamic properties H, S, and C_p were calculated[31] from the ensemble energy averages and fluctuations in internal energy, respectively, $\langle E\rangle^2$ and $\langle E^2\rangle$.

Several different schemes were used to convert the theoretically evaluated total energies to the corresponding standard enthalpies of formation, ΔH_f^{298}. This requires relating the calculated ab initio energy of the large molecule of interest to the ab initio energies of a set of smaller species whose experimental heats of formation are well-known. We first used the conventional atomization energy method[32] wherein the theoretical (nonrelativistic) atomization energy at 0 K was used in conjunction with standard experimental ΔH_f^0 values for the atoms and spin−orbit corrections[33,34] to obtain the heats of formation of the species at 0 K. The ΔH_f^{298} values were then obtained using the computed heat capacity curve for the large molecule in combination with literature temperature corrections to the enthalpies of the atoms. The ΔH_f^{298} was further adjusted using the recommended bond-additivity corrections associated with each quantum chemistry method.[34]

Instead of referencing to the separated open-shell atoms, the method of bond-separation reactions[35] uses small closed-shell species as the reference molecules. This leads to improved cancellation of error and avoids the need for bond-additivity corrections. Raghavachari et al.[21] have used this scheme recently with the G2 method to get substantial improvement in the calculated results for large saturated organics. Here, we used methane, ethane, ethylene, and acetylene as the reference molecules for the bond-separation method.

TABLE 1: MP2(full)/6-31G(d) (G2) and MP2(FC)/6-31G(d′) (CBS-Q) Optimized Bond Lengths in Angstroms of the Important Bonds in the Various Systems Investigated in This Work

	C−H		Ct−C		Cd−C		Ct−Ct		Cd═Cd		C−C	
species	G2	CBS-Q	G2	CBS-Q	G2	CBS-Q	G2	CBS-Q	G2	CBS-Q	G2	CBS-Q
$(HCC)_3CH$ (**1**)	1.101	1.104	1.472	1.477			1.218	1.225				
$(HCC)_2CH(CH=CH_2)$ (**2**)	1.101	1.104	1.471	1.477	1.518	1.523	1.219	1.226	1.334	1.341		
$(HCC)_2CHCH_2CH_3$ (**3**)	1.101	1.104	1.468	1.473			1.219	1.226			1.543	1.549
$(CH_2=CH)_3CH$ (**4**)	1.099	1.102			1.506	1.512			1.337	1.343		
$(CH_2=CH)_2CH(CCH)$ (**5**)	1.099	1.101	1.468	1.474	1.509	1.516	1.219	1.227	1.336	1.343		
$(CH_2=CH)_2CHCH_2CH_3$ (**6**)	1.099	1.103			1.502	1.508			1.337	1.344	1.541	1.545
$(HCC)(CH_2=CH)CHEt$ (**7**)	1.099	1.103	1.466	1.472	1.505	1.511	1.219	1.227	1.337	1.343	1.542	1.548
$(HCC)CH_2(CH=CH_2)$ (**8**)	1.098	1.101	1.465	1.471	1.506	1.512	1.219	1.226	1.336	1.342		
$(HCC)_2CH_2$ (**9**)	1.098	1.101	1.466	1.472			1.218	1.225				

TABLE 2: G2 Calculated Thermodynamic Properties Together with the CBS-Q Heats of Formation Obtained Using Atomization Energy Method[a]

	CBS-Q	G2		$C_p(T)$						
species	ΔH_f^{298}	ΔH_f^{298}	S^{298}	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$(HCC)_3CH$ (**1**)	170.1	172.8	80.51	28.23	33.68	37.68	40.76	45.35	48.72	54.01
$(HCC)_2(CH_2=CH)CH$ (**2**)	123.5	128.0	86.22	29.64	36.01	41.03	45.04	51.13	55.61	62.61
$(HCC)_2CHCH_2CH_3$ (**3**)	89.5	95.1	88.01	31.80	39.15	45.18	50.08	57.59	63.09	71.60
$(CH_2=CH)_3CH$ (**4**)	45.1	44.8	92.74	32.29	40.13	47.09	52.98	62.22	69.06	79.66
$(CH_2=CH)_2(HCC)CH$ (**5**)	85.1	85.7	88.47	33.60	40.10	45.56	50.12	57.32	62.74	71.29
$(CH_2=CH)_2CHCH_2CH_3$ (**6**)	13.5	13.5	95.65	35.53	44.21	51.99	58.61	69.01	76.74	88.72
$(HCC)(CH_2=CH)CHEt$ (**7**)	45.0	47.1	90.67	34.94	42.96	49.69	55.26	63.91	70.33	80.36
$(HCC)(CH=CH_2)CH_2$ (**8**)	66.2	65.6	75.94	22.06	27.19	31.52	35.12	40.72	44.89	51.42
$(HCC)_2CH_2$ (**9**)	106.8	107.7	70.77	20.80	25.01	28.31	30.95	35.02	38.06	42.84
$CH_2=C(C_2H)CH_3$ (**10**)	58.2	60.1	73.95	22.63	27.61	31.78	35.26	40.76	44.90	51.41
$CH_2=C(C_2H)(CH=CH_2)$ (**11**)	80.3	82.7	78.35	26.44	33.05	38.02	41.79	47.25	51.21	57.47
$CH_2=C(C_2H)_2$ (**12**)	122.7	126.8	76.45	24.14	29.12	32.86	35.79	40.18	43.40	48.43
$CH_2=C(C_2H)(MeC=CH_2)$ (**13**)	72.9	74.9	85.55	32.70	40.01	45.79	50.46	57.66	63.02	71.46
$MeCH=C(C_2H)(CH=CH_2)$ (**14**)	65.3	74.0	86.18	31.61	39.27	45.44	50.32	57.66	63.05	71.49
$CHMe=C(C_2H)_2$ (**15**)	109.6	118.5	84.86	29.38	35.40	40.31	44.34	50.61	55.24	62.45

[a] ΔH_f^{298} are given in kcal/mol, S^{298} and $C_p(T)$'s are in cal/mol K.

In addition, we also used sets of isodesmic reactions for evaluating more accurate ΔH_f^{298}. Within the constructed isodesmic reactions, most of the reactions are homodesmotic[20] (they conserve the number of bonds of each order between each pair of atom types) as well. By using isodesmic/homodesmotic reactions, one is essentially replacing the generic bond-additivity corrections used in the atomization energy approach with more specific calibrations to chemically similar reference molecules. This approach is known to minimize systematic errors in most methods and to improve the results. The sets of isodesmic/homodesmotic reactions used here provide improved heats of formation when the errors in using the bond-separation reaction approach are large.

If the three different methods for computing the heats of formation give very different results, this is typically interpreted as an indication that the quantum chemistry method is running into problems.

Results and Discussion

The optimized geometries with or without core electron correlation viz., MP2(full)/6-31G(d) in the G2 method and MP2-(Frozen Core)/6-31G(d′) in the CBS-Q method, are very nearly the same (Table 1). The C−H bond length varies up to a maximum of 0.003 Å, whereas the $Ct\equiv Ct$, $Cd=Cd$, C−Cd, C−Ct, and C−C bond lengths vary up to a maximum of 0.007 Å between the two levels. Furthermore, the bond lengths of the common groups in all of the chosen species remain nearly the same suggesting thereby a constant bond strength and transferability of the groups between the molecules.

The calculated thermodynamic properties of the systems at the G2 level are given in Table 2 together with the computed CBS-Q heats of formation. The heats of formation given in this table are derived using the atomization energy method. Because the optimized geometries do not vary between the two levels of treatment, the associated moments of inertia and vibrational frequencies are nearly the same, and consequently, the entropy and $C_p(T)$ values are relatively insensitive to the level of treatment. However, the calculated enthalpy of formations after accounting for appropriate spin−orbit and isodesmic bond-additivity corrections vary significantly with the level of treatment especially for systems with multiple $C\equiv C$ bonds viz., $(HCC)_3CH$ (**1**), $(HCC)_2CHCH=CH_2$ (**2**), $(HCC)_2CHCH_2CH_3$ (**3**), $(HCC)(CH=CH_2)CHCH_2CH_3$ (**7**), $CH_2=C(C_2H)_2$ (**12**), $MeCH=C(C_2H)_2$(**15**), and $MeCH=C(C_2H)(CH=CH_2)$ (**14**). The deviations, do not show any systematic pattern with respect to the number of $C\equiv C$ or $C=C$ bonds.

The recommended bond-additivity corrections (BACs) for G2 and CBS-Q used with the atomization procedure are significantly different and sometimes quite large. These recommended BACs were determined by fitting to a database of examples for each bond type. In doing so, no differentiation was made between a double bond and a delocalized aromatic bond. It is therefore possible that some members of a particular bond type will exhibit larger absolute deviations after applying the BACs than others. Therefore, we devised several isodesmic reactions to understand the anomalous differences in the predicted enthalpy of formations.

The list of isodesmic reactions considered for each molecule is compiled in Table 3 together with the reaction energy at G2 and CBS-Q levels. Except for the reactions in the italicized font in Table 3, the remaining reactions are homodesmotic involving equal numbers of each type of C−C (C−C, $Cd=Cd$, $Ct\equiv Ct$, etc.) and C−H bonds (C−H, Cd−H, Ct−H, etc.,). In this

TABLE 3: Use of Isodesmic Reactions to Calculate the Heats of Formation[a]

isodesmic reactions	ΔH_R(CBS-Q)	ΔH_R(G2)	$\Delta\Delta H_\mathrm{f}$(expt)	ΔH_f(CBS-Q)	ΔH_f(G2)
$\mathrm{(HCC)_3CH}$ (**1**) $\mathrm{+ 2CH_4 \rightarrow 3HCCCH_3}$	−3.05	−5.47	168.4(0.8)	171.42	173.84
$\mathrm{(HCC)_3CH}$ (**1**) $\mathrm{+ 3C_2H_6 \rightarrow 3HCCCH_3 + CH(CH_3)_3}$	−10.92	−13.36	160.6(1.1)	171.54	173.98
$\mathrm{(HCC)_3CH}$ (**1**) $\mathrm{+2C_2H_6+CH_4 \rightarrow 3HCCCH_3 + CH_3CH_2CH_3}$	−5.83	−8.33	165.5(1.0)	171.36	173.86
$\mathrm{(HCC)_2CHCH{=}CH_2}$ (**2**) $\mathrm{+2CH_4 \rightarrow 2HCCCH_3 + CH_2CHCH_3}$	5.36	0.33	129.1(0.7)	123.70	128.73
$(HCC)_2CHCH{=}CH_2$ (**2**) $+3CH_4 \rightarrow 2HCCCH_3 + CH_2{=}CH_2 + CH_3CH_3$	10.85	5.81	134.6(0.9)	123.73	128.77
$\mathrm{(HCC)_2CHCH{=}CH_2}$ (**2**) $\mathrm{+3C_2H_6 \rightarrow 2HCCCH_3 + CH_2CHCH_3 + CH(CH_3)_3}$	−2.51	−7.57	121.3(1.0)	123.82	128.88
$\mathrm{(HCC)_2CHCH{=}CH_2}$ (**2**) $\mathrm{+2C_2H_6+CH_4 \rightarrow 2HCCCH_3 +(CH_3)_2CH_2+CH_2CHCH_3}$	2.58	−2.53	126.2(1.0)	123.64	128.75
$\mathrm{(HCC)_2CHCH_2CH_3}$ (**3**)$\mathrm{+2CH_4 \rightarrow 2HCCCH_3 + CH_3CH_2CH_3}$	8.61	3.26	99.2(0.7)	90.55	95.90
$\mathrm{(HCC)_2CHCH_2CH_3}$ (**3**) $\mathrm{+2C_2H_6+CH_4 \rightarrow 2HCCCH_3 +2\ CH_3CH_2CH_3}$	5.84	0.40	96.3(0.8)	90.48	95.92
$(HCC)_2CHCH_2CH_3$ (**3**) $+ CH_2{=}CH_2 + CH_4 +C_2H_6 \rightarrow CH_2CHCH_3 + CH_3CH_2CH_3 +2\ HCCCH_3$	3.13	−2.40	93.6(1.0)	90.51	96.04
$(CH_2{=}CH)_3CH$ (**4**) $+3CH_4 \rightarrow 3CH_2{=}CH_2 + CH(CH_3)_3$	15.85	14.06	59.25(0.8)	43.40	45.19
$\mathrm{(CH_2{=}CH)_3CH}$ (**4**) $\mathrm{+ 2CH_4 \rightarrow 3\ CH_2CHCH_3}$	7.26	5.50	50.4(0.5)	43.18	44.94
$\mathrm{(CH_2{=}CH)_3CH}$ (**4**) $\mathrm{+ 3C_2H_6 \rightarrow 3\ CH_2CHCH_3 + CH(CH_3)_3}$	−0.61	−2.39	42.7(0.8)	43.30	45.08
$\mathrm{(CH_2{=}CH)_2CH(CCH)}$ (**5**) $\mathrm{+2CH_4 \rightarrow 2CH_2CHCH_3+HCCCH_3}$	5.48	3.58	89.75(0.6)	84.27	86.17
$(CH_2{=}CH)_2CH(CCH)$ (**5**) $+CH_2CH_2+C_2H_6+CH_4 \rightarrow 2CH_2CHCH_3 + HCCCH_3 + CH_2CHCH_3$	−0.01	−1.90	84.2(1.0)	84.24	86.13
$\mathrm{(CH_2{=}CH)_2CHCCH}$ (**5**) $\mathrm{+2C_2H_6+CH_4 \rightarrow 2CH_2CHCH_3+ CH_3CCH + (CH_3)_2CH_2}$	2.70	0.72	86.9(1.1)	84.21	86.19
$\mathrm{(CH_2{=}CH)_2CHCCH}$ (**5**) $\mathrm{+3C_2H_6 \rightarrow 2CH_2CHCH_3+HCCCH_3+CH(CH_3)_3}$	−2.40	−4.31	82.0(1.1)	84.40	86.31
$\mathrm{(CH_2{=}CH)_2CHCH_2CH_3}$ (**6**) $\mathrm{+2CH_4 \rightarrow 2CH_2CHCH_3 + CH_3CH_2CH_3}$	8.16	6.89	20.5(0.7)	12.38	13.65
$\mathrm{(CH_2{=}CH)_2CHCH_2CH_3}$ (**6**) $\mathrm{+2C_2H_6+CH_4 \rightarrow 2CH_2CHCH_3+2CH_3CH_2CH_3}$	5.38	4.03	17.7(0.9)	12.32	13.67
$(CH_2{=}CH)_2CHCH_2CH_3$ (**6**) $+CH_2{=}CH_2+2CH_4 \rightarrow 3CH_2CHCH_3+CH_3CH_3$	5.45	4.27	17.9(1.0)	12.41	13.59
$\mathrm{(CH_2{=}CH)CH(CCH)(CH_2CH_3)}$ (**7**) $\mathrm{+ 2CH_4 \rightarrow CH_2CHCH_3 + HCCCH_3+CH_3CH_2CH_3}$	14.91	12.28	59.85(0.7)	44.94	47.57
$(CH_2{=}CH)CH(CCH)(CH_2CH_3)$ (**7**) $+2CH_4+C_2H_4 \rightarrow 2CH_2CHCH_3 + HCCCH_3+CH_3CH_3$	12.20	9.66	57.2(1.0)	44.97	47.51
$\mathrm{(CH_2{=}CH)CH(CCH)(CH_2CH_3)}$ (**7**) $\mathrm{+CH_4+2C_2H_6 \rightarrow CH_2CHCH_3 + HCCCH_3 + 2CH_3CH_2CH_3}$	12.13	9.42	57.0(0.9)	44.88	47.59
$\mathrm{CH_2(C_2H)(C_2H_3)}$ (**8**) $\mathrm{+ CH_4 \rightarrow HCCCH_3 + CH_2CHCH_3}$	0.94	1.04	66.97(0.5)	66.03	65.93
$\mathrm{CH_2(C_2H)(C_2H_3)}$ (**8**) $\mathrm{+ 2C_2H_6 \rightarrow HCCCH_3 + CH_2CHCH_3 + CH_2(CH_3)_2}$	−1.84	−1.82	64.13(0.5)	65.97	65.95
$\mathrm{CH_2(C_2H)_2}$ (**9**) $\mathrm{+ CH_4 \rightarrow 2HCCCH_3}$	−1.44	−2.04	106.3(0.5)	107.72	108.32
$\mathrm{CH_2(C_2H)_2}$ (**9**) $\mathrm{+ 2CH_3CH_3 \rightarrow 2HCCCH_3 + CH_2(CH_3)_2}$	−4.21	−4.90	103.4(0.8)	107.65	108.34
$CH_2{=}C(C_2H)CH_3$ (**10**) $+CH_4 \rightarrow CH_3CCH+CH_2CHCH_3$	8.95	6.57	67.0(0.5)	58.02	60.40
$\mathrm{CH_2{=}C(C_2H)CH_3}$ (**10**) $\mathrm{+C_2H_6 + CH_2{=}CH_2 \rightarrow 2\ CH_2CHCH_3 + HCCCH_3}$	3.46	1.09	61.45(0.8)	57.99	60.36
$CH_2{=}C(C_2H)(C_2H_3)$ (**11**) $+ 2CH_4 \rightarrow$ $\mathrm{HCCCH_3 + CH_2{=}CH_2 + CH_2CHCH_3}$	17.98	14.29	97.4(0.7)	79.43	83.12
$CH_2{=}C(C_2H)C_2H_3$ (**11**) $+ CH_4 + C_2H_6 \rightarrow$ $\mathrm{HCCCH_3 + 2CH_2CHCH_3}$	12.49	8.86	91.9(0.8)	79.40	83.03
$\mathrm{CH_2{=}C(C_2H)(C_2H_3)}$ (**11**) $\mathrm{+ 2C_2H_6 \rightarrow CH_2{=}C(Me)_2 + HCCCH_3 + CH_2CHCH_3}$	5.96	2.12	85.1(0.8)	79.15	82.99
$\mathrm{CH_2{=}C(C_2H)_2}$ (**12**) $\mathrm{+2C_2H_6 \rightarrow CH_2{=}C(CH_3)_2+2CH_3CCH}$	1.84	−3.00	124.4(0.8)	122.58	127.42
$CH_2{=}C(C_2H)_2$ (**12**) $+ 2CH_4 \rightarrow 2HCCCH_3+CH_2{=}CH_2$	13.86	9.13	136.7(0.7)	122.86	127.59
$CH_2{=}C(C_2H)_2$ (**12**) $+ C_2H_6 +CH_4 \rightarrow$ $\mathrm{CH_2CHCH_3 +2HCCCH_3}$	8.37	3.64	131.2(0.8)	122.83	127.56
$CH_2{=}C(C_2H)(MeCCH_2)$ (**13**) $+ 2CH_4 \rightarrow$ $\mathrm{CH_2{=}CH_2 + HCCCH_3 + CH_2{=}CMe_2}$	16.65	14.07	88.5(0.7)	71.84	75.28
$CH_2{=}C(C_2H)(MeCCH_2)$ (**13**) $+ CH_4 + C_2H_6 \rightarrow$ $\mathrm{CH_2CHCH_3 + CH_2CMe_2 + HCCCH_3}$	11.16	8.65	83.0(0.8)	71.81	75.18
$\mathrm{CH_2{=}C(C_2H)(MeCCH_2)}$ (**13**) $\mathrm{+ 2C_2H_6 + CH_2{=}CH_2 \rightarrow CH_2{=}CMe_2 + HCCMe + 2CH_2CHMe}$	5.67	3.10	77.45	71.78	75.21
$CHMe{=}C(C_2H)(CH{=}CH_2)$ (**14**) $+2CH_4 \rightarrow$ $\mathrm{2MeCHCH_2 + HCCMe}$	25.30	14.41	89.75(0.8)	64.45	74.48
$\mathrm{CHMe{=}C(C_2H)\ (CH{=}CH_2)}$ (**14**) $\mathrm{+CH_2{=}CH_2 + 2C_2H_6 \rightarrow 2CH_2CHMe + HCCMe + CH_2{=}CMe_2}$	13.28	2.24	77.45(1.1)	64.17	74.35
$CHMe{=}C(C_2H)_2$ (**15**) $+ 2CH_4 \rightarrow$ $\mathrm{MeCHCH_2 + 2HCCCH_3}$	19.21	9.85	129.1(0.8)	109.85	119.21
$\mathrm{CHMe{=}C(C_2H)_2}$ (**15**) $\mathrm{+ 2C_2H_6 + CH_2{=}CH_2 \rightarrow MeCHCH_2 + CH_2{=}CMe_2 + 2HCCCH_3}$	7.19	−2.32	116.8(1.1)	109.57	119.08

[a] Reactions an italics are not homodesmotic. The G2 and CBS-Q heats of reaction respectively ΔH_R(G2) and ΔH_R(CBS-Q) and the inferred heats of formation respectively $\Delta H_\mathrm{f}^{298}$(G2) and $\Delta H_\mathrm{f}^{298}$(CBS-Q) of the large molecules. $\Delta\Delta H_\mathrm{f}$(exp) is the total contribution of experimental values on small molecules to the derived heats of formation of the large polyunsaturated molecules. The number in parentheses is the sum of the associated uncertainties in the experimental values. All values in kcal/mol.

collection of isodesmic reactions, we use a set of eight reference molecules CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, C_2H_4, propene, isobutene, and propyne. The experimental heats of formation of these molecules are tabulated in Table 4 together with their absolute energies at the G2 and CBS-Q levels. The experimental values and error bars were taken from the compilation of Pedley[36] et

TABLE 4: CBS-Q and G2 Absolute Energies at 0 K (in au), Thermal Corrections to 298 K (in kcal/mol), and Experimental Heats of Formation at 298 K (in kcal/mol) for the Reference Species Used in the Isodesmic Reactions Given in Tables 3 and 5, and for Some Other Light Hydrocarbons[a]

	CBS-Q energies	G2 energies	therm. corr.	ΔH_f(expt)	ΔH_f(CBS-Q)	ΔH_f(G2)	$\Delta\Delta H_f$(CBS-Q)
CH_4	−40.409582	−40.410891	2.39	−17.9 ± 0.1	−18.05	−17.71	−0.15
CH_3CH_3	−79.629748	−79.630883	2.84	−20.1 ± 0.1	−20.27	−19.91	−0.23
$CH_3CH_2CH_3$	−118.854721	−118.855811	3.52	−25.0 ± 0.1	−25.27	−24.96	−0.25
$(CH_3)_3CH$	−158.083493	−158.084310	4.27	−32.1 ± 0.2	−32.59	−32.19	−0.52
$CH_2{=}CH_2$	−78.415693	−78.415930	2.50	12.5 ± 0.1	13.14	12.63	0.6
$CH_3CH{=}CH_2$	−117.645036	−117.645090	3.22	4.8 ± 0.2	5.43	4.95	0.55
$CH_3CH_2CHCH_2$	−156.870214		4.05	−0.15 ± 0.2	0.45		0.6
$(CH_3)_2C{=}CH_2$	−156.876226		4.05	−4.0 ± 0.2	−3.32		0.72
$CH_2CHCHCH_2$	−155.665680	−155.664270	3.53	26.3 ± 0.2	27.71	26.62	1.42
$(CH_2{=}CH)_2CH_2$	−194.885707		5.14	25.4 ± 0.3	26.73		1.32
HCCH	−77.186245	−77.185740	2.32	54.2 ± 0.2	55.59	54.33	1.39
$HCCCH_3$	−116.422334	−116.419170	3.04	44.2 ± 0.2	43.65	43.97	−0.54
$HCCCH_2CH_3$	−155.646601	−155.643402	3.70	39.5 ± 0.2	39.07	39.35	−0.43
1-pentyne	−194.876495	−194.869074	4.65	34.5 ± 0.5	31.24	34.10	−3.26
$HCCCH(CH_3)_2$	−194.876071	−194.871299	4.50	32.6 ± 0.5	31.38	32.58	−1.22
$HCCC(CH_3)_3$	−234.109182	−234.101450	5.39	25.4 ± 0.3	21.46	24.45	−3.94
$CH_3CCCH_2CH_3$	−194.893389	−194.875589	4.64	30.8 ± 0.5	20.64	30.01	−10.2

[a] ΔH_f(CBS-Q) and ΔH_f(G2) are the calculated heats of formation at 298 K in kcal/mol obtained from the atomization energies. $\Delta\Delta H_f$(CBS-Q) (in kcal/mol) is the deviation of the CBS-Q prediction from experimental data.

al. and from the NIST webbook.[37] Table 4 also includes the calculated ΔH_f^{298} of these species at both levels of theory using the atomization energy method. For these small reference molecules, the agreement between the experimental values and G2 is better than with the CBS-Q results. The $\Delta\Delta H_f$ (CBS-Q) is a measure of deviation from the experimental data. The recommended CBS-Q BAC[34] for C=C is −0.08 kcal/mol/bond. However, from this table, it appears that each double bond requires a correction of about −0.68 kcal/mol. We have added few more dienes in Table 4 for comparison. We believe that the large deviation observed using the atomization energy approach for simple olefins is due to failings of the BAC procedure. Use of isodesmic reactions including double bonds cancels out this error.

It can be seen from Table 3 that, at a chosen level of treatment, different isodesmic reactions give rise to a constant ΔH_f^{298} for the target molecule. For a couple of molecules (**6**, **8**, and **9**), G2 and CBS-Q are in fair agreement on the heat of formation. However, the striking observation is the significantly different prediction for ΔH_f^{298} of alkynes from two different model chemistry methods. The hydrocarbons with two ethynyl (HCC) groups viz., $(HCC)_2CHCH{=}CH_2$ (**2**) and $(HCC)_2CHCH_2CH_3$ (**3**), differ approximately by 5 kcal/mol, whereas the ones with a single ethynyl group, namely, $(CH_2{=}CH)_2CH(CCH)$ (**5**) and $(CH_2{=}CH)CH(CCH)CH_2CH_3$ (**7**), differ approximately by 2.5 kcal/mol from the G2 predictions. In these hydrocarbons, the central CH group prevents the possibility for an extended delocalization. If we extend this analogy, one should expect a deviation of nearly 7.5 kcal/mol for a system with three ethynyl groups. However, in the case of $(HCC)_3CH$ (**1**), the discrepancy is much smaller. Hence, it is not evident whether the large discrepancy between G2 and CBS-Q is systematic and is due to the poor description of a Ct−C single bond. In the case of ene−ynes and ene−diynes, the discrepancy between the two quantum chemistry methods becomes progressively larger with increasing number of ene−yne and yne−yne interactions. The simple $CH_2{=}C(CCH)CH_3$ (**10**) includes a delocalizing interaction between an -ene and an -yne bond and it leads to a mismatch of nearly 2.5 kcal/mol, whereas the ene,-diyne (**12**) consists of two ene−yne interactions, and the deviation amounts to approximately 5.0 kcal/mol. The simple diene−yne $CH_2{=}C(C_2H)CH{=}CH_2$ (**11**) and the internal methyl substituted diene−yne, $CH_2{=}C(C_2H)C(Me){=}CH_2$ (**13**) has one delocalizing ene−yne interaction and a geminal ene−yne interaction, and they give rise to a mismatch of nearly 3.5 kcal/mol. Nevertheless, a very unrealistic mismatch of ∼10 kcal/mol has been observed between the CBS-Q and G2 predictions for terminal methyl substituted diene−yne (**14**) and ene−diyne (**15**).

A unique set of isodesmic reactions is the bond-separation reaction, where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecule containing these same kinds of bonds. Raghavachari et al.[21] have demonstrated that the use of bond-separation reaction with G2 theory leads to a dramatic improvement in the theoretically computed heats of formation. The reference molecules included in this scheme are methane, ethane, ethylene, and acetylene, whose heats of formation are known experimentally to an accuracy of ±0.1 kcal/mol. The bond-separation reactions employed in this study are tabulated in Table 5. As can be seen from Table 4, the experimental ΔH_f^{298} of acetylene (54.2 kcal/mol) is ill predicted at the CBS-Q level (55.6 kcal/mol). The bond-separation method maximizes this ill conditioning in the isodesmic approach. As a result, the discrepancy between G2 and CBS-Q level predictions using the bond-separation approach are larger than that observed in the case of isodesmic reactions of Table 3. At the CBS-Q level, the most accurate theoretical numbers can be taken from the isodesmic cum homodesmotic reactions of Table 3 because (i) the error in the heats of formation of one of the reference molecules used in the bond-separation reaction approach is large and (ii) the recommended bond-additivity correction for a C=C bond used in the atomization energy method introduces large deviations for simple olefins.

As discussed earlier, the cause for the anomalously large and nonsystematic differences between the G2 and CBS-Q predictions of ΔH_f^{298} for some of the larger systems is not clear.

To better understand the discrepancy between these two model chemistries, we expanded our set of alkynes and considered pent-1-yne, 3,3-dimethylbut-1-yne, and pent-2-yne (Table 4) whose experimental ΔH_f^{298} are known. In our earlier work (results recompiled in Table 4), we observed a reasonable agreement between experimental and CBS-Q data for ΔH_f^{298} of the terminal alkynes propyne, but-1-yne, and 3-methylbut-1-yne even though the ΔH_f^{298} of ethyne, the prototypical molecule with a triple bond, was in error by ∼1 kcal/mol. However,

TABLE 5: Use of Bond-Separation Reactions to Calculate the Heats of Formation[a]

isodesmic bond separation reaction	ΔH_R(CBS-Q)	ΔH_R(G2)	$\Delta\Delta H_f$(expt)	ΔH_f(CBS-Q)	ΔH_f(G2)
$(HCC)_3CH\ (\mathbf{1}) + 5CH_4 \rightarrow 3HCCH + 3\ CH_3CH_3$	26.12	19.02	193.0(0.6)	166.9	174.0
$(HCC)_2CH(CH{=}CH_2)\ (\mathbf{2}) + 5CH_4 \rightarrow 2HCCH + CH_2{=}CH_2 + 3\ CH_3CH_3$	30.29	22.13	151.0(1.3)	120.7	128.9
$(HCC)_2CHCH_2CH_3\ (\mathbf{3}) + 5CH_4 \rightarrow 2HCCH + 4\ CH_3CH_3$	30.84	22.44	118.4(1.3)	87.6	96.0
$(CH_2{=}CH)_3CH\ (\mathbf{4}){+}5CH_4 \rightarrow 3C_2H_4 + 3C_2H_6$	23.73	21.95	67.0(1.1)	43.3	45.0
$(HCC)CH(C_2H_3)_2\ (\mathbf{5}){+}\ 5CH_4\ {-}{\rightarrow}\ 2C_2H_4{+}C_2H_2{+}\ 3C_2H_6$	26.18	22.71	109.0(1.2)	82.8	86.3
$CH_3CH_2CH(C_2H_3)_2\ (\mathbf{6}) + 5CH_4 \rightarrow 2C_2H_4 + 4C_2H_6$	21.91	20.72	34.42(1.1)	12.5	13.7
$CH_3CH_2CH(CCH)(C_2H_3)\ (\mathbf{7}){+}\ 5CH_4 \rightarrow 4CH_3CH_3{+}CH_2{=}CH_2{+}HCCH$	32.90	28.78	76.4(1.2)	43.5	47.6
$(C_2H_3)CH_2CCH\ (\mathbf{8})\ {+}3CH_4 \rightarrow C_2H_2 + C_2H_4 + 2C_2H_6$	16.15	14.69	80.7(0.8)	64.6	66.0
$(HCC)_2CH_2\ (\mathbf{9}){+}\ 3CH_4 \rightarrow 2HCCH + 2CH_3CH_3$	18.01	14.28	122.7(0.9)	104.7	108.4
$CH_2{=}C(C_2H)CH_3{+}4CH_4\ (\mathbf{10}){\rightarrow}\ C_2H_2{+}C_2H_4{+}2C_2H_6{+}CH_4$	24.16	20.22	80.7(1.0)	56.5	60.5
$CH_2{=}C(C_2H)(C_2H_3)\ (\mathbf{11}) + 4CH_4 \rightarrow C_2H_2{+}2C_2H_4{+}2C_2H_6$	33.19	27.94	111.1(1.0)	77.9	83.2
$CH_2{=}C(C_2H)_2\ (\mathbf{12}) + 4\ CH_4 \rightarrow C_2H_4\ {+}2C_2H_2{+}\ 2C_2H_6$	33.30	25.49	153.1(1.1)	119.8	127.7
$CH_2{=}C(C_2H)(MeC{=}CH_2)\ (\mathbf{13}) + 5CH_4 \rightarrow 2C_2H_4{+}C_2H_2{+}\ 3C_2H_6$	38.39	34.40	109.0(1.2)	70.61	74.6
$CHMe{=}C(C_2H)(CH{=}CH_2)\ (\mathbf{14}) + 5CH_4 \rightarrow 2C_2H_4{+}C_2H_2{+}\ 3C_2H_6$	46.00	33.53	109.0(1.2)	63.0	75.5
$CHMe{=}C(C_2H)_2\ (\mathbf{15}) + 5CH_4 \rightarrow C_2H_4{+}2C_2H_2{+}\ 3C_2H_6$	44.14	31.66	151.0(1.3)	106.9	119.3

[a] The G2 and CBS-Q heats of reactions respectively ΔH_R(G2) and ΔH_R(CBS-Q), and the inferred heats of formation respectively ΔH_f^{298}(G2) and ΔH_f^{298}(CBS-Q) of the large polyunsaturated molecules. $\Delta\Delta H_f$(expt) is the total contribution of experimental values on small molecules to the derived heats of formation of the large molecules. The number in parentheses is the sum of the associated uncertainties in the experimental values. All values in kcal/mol.

from Table 4, it is clear that the CBS-Q level prediction for pent-2-yne is drastically different (~10.2 kcal/mol) from the experimental value and is moderately off for both the terminal alkynes. We have observed[5,25] earlier that the CBS-Q method over predicts the stability of systems with *tert*-butyl group by ~1.5 kcal/mol (*t*-$BuCH_3$ (CBS-Q −41.57, expt −40.14 kcal/mol); *t*-$BuCH{=}CH_2$ (CBS-Q −15.7 kcal/mol, expt −14.5 kcal/mol); *t*-BuCHO (CBS-Q −60.2 kcal/mol, expt −58.5 kcal/mol); *t*-Bu-C(O)OH (CBS-Q −123.45 kcal/mol, expt −122.0 kcal/mol); *t*-BuOH (CBS-Q −75.9 kcal/mol, expt −74.5 kcal/mol); *t*-BuOMe (CBS-Q −69.4 kcal/mol, expt −67.7 kcal/mol). Even after accounting for this systematic failure, the deviation for 3,3-dimethylbut-1-yne is quite significant. Curtiss et al.[28] earlier observed an anomalous deviation between experimental and theoretical values at the CBS-Q level for 2-butyne and naphthalene. Montgomery et al.[29] attributed this anomaly to basis set near linear dependencies and modified the Gaussian program (Gaussian 98, revision A.7) to allow truncation of the basis set in such situations. Analysis of our outputs using Gaussian 98, revision A.9 and higher, however, do not show any indication of truncation of the basis set (by following the Nbasis and NbsUse variables) except for diene-ynes (**11** and **13**) and ene-diynes (**12** and **15**). In the latter set, one basis function has been eliminated with the default cutoff (10^{-4}), whereas in the former set, the number of basis functions being eliminated corresponds respectively to 3 and 4. There is no indication of near linear dependencies in terminal -ynes. However, similar to but-2-yne, in the case of pent-2-yne, one basis function has been eliminated at the default (10^{-4}) cutoff value. Because experimental ΔH_f^{298} is known for pent-2-yne, we studied the E(CBS2) energy as a function of cutoff using iop(3/59) option. For cutoffs from 10^{-3}−10^{-5}, only one redundant function is eliminated and *E*(CBS2) energy is nearly independent of this cutoff. However, increasing the cutoff to 10^{-2} resulted in removal of eight basis functions causing differences to HF, MP2, and all component energies of CBS-Q and worsened the discrepancy. It appears that the discrepancies we observe are not due to linear dependency.

Preliminary analysis by Hess[38] indicates that part of the problem is instead related to a failure of the orbital localization scheme used in Gaussian for the CBS-Q method. Use of MINPOP instead of the default POP option in CBSExtrapolate keyword seems to overcome this problem, bringing the CBS-Q energy of pent-2-yne into reasonable agreement with experiment. However, switching to MINPOP does not resolve the 9 kcal/mol discrepancy between G2 and CBS-Q for species (**14**). Additional work is needed to understand this error. The present work suggests that caution must be exercised while applying the CBS-Q method to systems with triple bonds and/or delocalized bonds.

It is however immediately obvious from Table 6 that the G2 level prediction is extremely consistent using both types of isodesmic reactions and these differ by less than 1 kcal/mol from the corresponding value obtained using the atomization energy method. Importantly, the G2 predictions for simple alkynes are in very good agreement with the experimental values (Table 4). This provides the rationale for preferring this method in the absence of experimental data. The GAVs of the missing groups are therefore derived from the G2 results in combination with Benson's GAVs for the other groups in each molecule viz., {Cd/H2}, {Cd/H/C}, {Ct/H}, {Ct/C}, {C/C/H3}, {C/C2/H2}, {C/Cd/H3}, {Ct/Cd}, and {Cd/Cd/H}.

The new GAVs based on quantum chemical G2 calculations are tabulated in Table 7 together with Benson's GAVs (in bold face) for some of the similar groups. It is worthwhile to mention that Benson's GAV for {Ct/Cd} group shows an unexpected decrease in C_p value at 500 K. We believe this to be a typographical error and derived the missing groups using Stein and Fahr's recommendations:[39]

group	300K	400K	500K	600K	800K	1000K	1500K	ref
{Ct/Cd}	2.57	3.54	3.50	4.92	5.34	5.50	5.80	Benson
{Ct/Cd}	2.63	3.03	3.42	3.75	4.30	4.71	5.28	Stein and Fahr

Consistent with the rule of similar groups, the three new GAVs centered on sp^2 carbons ({Cd/Ct/C}, {Cd/Ct/Cd}, and {Cd/Ct2}) have nearly the same entropy and enthalpy values as the {Cd/Cd/C} group value of Benson. However, the C_p values differ significantly at low temperatures, possibly because groups with ethynyl substitutents do not have as many associated torsional vibrations as {Cd/Cd/C}. Analysis of the G2 enthalpy values of methyl-substituted dieneynes, namely, $CH_2{=}C(C_2H)(CH{=}CH_2)$ (**11**), $CH_2{=}C(C_2H)(CMe{=}CH_2)$ (**13**), and $CHMe{=}C(C_2H)(CH{=}CH_2)$ (**14**), suggests a cis correction of ~ −0.75 kcal/mol between methyl and ethynyl (CCH) groups. The former two do not exert any cis interactions, whereas the latter (**14**) includes one. This ene-yne-cis nonneighbor correction is in good agreement with the values deduced by Cohen[4] (−0.75 kcal/mol) for the cis interaction between an yne and an alkyl group in Z-3-penten-1-yne and Z-3-decen-1-yne. This value seems to be consistent while going from $CH_2{=}C(C_2H)_2$ (**12**) to $CHMe{=}C(C_2H)_2$ (**15**) which includes one cis interaction.

TABLE 6: Comparison of G2 and CBS-Q Calculated Heats of Formation Using Atomization Energy Method (AE), Isodesmic Reactions (IR; see Table 3), and Isodesmic Bond Separation Reactions (BS; see Table 5)[a]

	ΔH_f^{298}(G2)			ΔH_f^{298}(CBS-Q)		
species	AE	IR	BS	AE	IR	BS
$(HCC)_3CH$ (**1**)	172.8	173.9	174.0	170.1	171.4	166.9
$CH_2{=}CHCH(C_2H)_2$ (**2**)	128.0	128.8	128.9	123.5	123.7	120.7
$(HCC)_2CHCH_2CH_3$ (**3**)	95.1	96.0	96.0	89.5	90.5	87.6
$(CH_2{=}CH)_3CH$ (**4**)	44.8	45.1	45.0	45.1	43.3	43.3
$(CH_2{=}CH)_2CHCCH$ (**5**)	85.7	86.2	86.3	85.1	84.3	82.8
$(C_2H_3)_2CHCH_2CH_3$ (**6**)	13.5	13.6	13.7	13.5	12.4	12.5
$(HCC)(C_2H_3)CHEt$ (**7**)	47.1	47.6	47.6	45.0	44.9	43.5
$HCCCH_2CH{=}CH_2$ (**8**)	65.6	65.9	66.0	66.2	66.0	64.6
$(HCC)_2CH_2$ (**9**)	107.7	108.3	108.4	106.8	107.7	104.7
$CH_2{=}C(CCH)CH_3$ (**10**)	60.1	60.4	60.5	58.2	58.0	56.5
$CH_2{=}C(CCH)(C_2H_3)$ (**11**)	82.7	83.1	83.2	80.3	79.3	77.9
$CH_2{=}C(CCH)_2$ (**12**)	126.8	127.5	127.6	122.7	122.8	119.8
$CH_2{=}C(C_2H)(MeC{=}CH_2)$ (**13**)	74.9	75.2	75.5	72.9	71.8	70.6
$CH_3CH{=}C(C_2H)(C_2H_3)$ (**14**)	74.0	74.4	74.6	65.3	64.3	63.0
$CH_3CH{=}C(C_2H)_2$ (**15**)	118.5	119.1	119.3	109.6	109.7	106.9

[a] ΔH_f^{298}(IR) is the average over all of the isodesmic reactions considered.

TABLE 7: Estimated GAVs for the New Groups as Derived from G2 Calculations on Single Molecules Containing the Group[a]

			$C_p(T)$						
groups	H(298)	S(298)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
Groups Centered on sp^2 Carbons in Conjugated pi Systems									
{Cd/Ct/C}	8.11	−13.02	3.44	4.39	4.96	5.35	5.90	6.19	6.53
{Cd/Ct/Cd}	7.54	−14.65	3.89	5.26	5.98	6.37	6.67	6.78	6.89
{Cd/Ct2}	8.81	−13.51	3.23	4.59	5.41	5.93	6.48	6.74	7.02
{Cd/Cd/C}	8.88	−14.6	4.40	5.37	5.93	6.18	6.50	6.62	6.72
Groups Centered on Secondary sp^3 Carbons									
{C/Ct2/H2}	−0.82	10.04	4.00	6.07	7.71	9.03	10.88	12.30	12.48
{C/Ct/Cd/H2}	−3.49	9.31	4.40	6.33	7.90	9.16	10.93	12.29	13.43
{C/Ct/C/H2}	−4.73	10.30	4.95	6.56	7.93	9.08	10.86	12.19	14.20
{C/Cd/C/H2}	−4.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.36
Groups Centered on Tertiary sp^3 Carbons									
{C/Ct3/H}	10.11	−10.46	3.03	5.27	6.78	7.88	9.14	10.08	8.47
{C/Ct2/Cd/H}	4.73	−11.46	3.58	5.68	7.11	8.12	9.27	10.13	9.44
{C/Ct2/C/H}	1.72	−11.61	3.27	5.32	6.90	8.03	9.33	10.21	9.38
{C/Ct/C2/H}	−1.72	−11.19	3.99	5.61	6.85	7.78	9.10	9.90	11.12
{C/Cd3/H}	0.41	−11.82	4.51	5.96	7.13	7.98	9.06	9.90	11.23
{C/Cd/C2/H}	−1.48	−11.69	4.16	5.91	7.34	8.19	9.46	10.19	11.28
{C/Cd2/Ct/H}	1.88	−13.75	6.68	7.85	8.62	9.16	9.81	10.42	10.49
{C/Ct/Cd/C/H}	−6.90	−13.48	5.55	7.21	8.39	9.17	10.00	10.61	10.51
{C/Cd2/C/H}	−1.10	−13.03	5.28	6.54	7.67	8.48	9.45	10.18	11.24
{C/C3/H}	−1.90	−12.07	4.54	6.00	7.17	8.05	9.31	10.05	11.17

[a] ΔH_f^{298} are given in kcal/mol, S^{298} and $C_p(T)$'s are in cal/mol K. The GAVs in bold face are similar groups developed previously by Benson. The first three GAVs in the table are obtained using the Stein and Fahr values for the {Ct/Cd} group, see text.

As can be seen from Table 7, the rule of similar groups also works pretty well with the secondary groups {C/Ct2/H2} and {C/Ct/Cd/H2}. Except for the enthalpy, their GAVs are very close to the similar known groups {C/Ct/C/H2} and {C/Cd/C/H2}. Moreover, the G2 and CBS-Q values are in good agreement for the secondary groups. The enthalpy GAVs of secondary groups also exhibit some order on successive replacement of an sp^3 carbon substituent by sp^2 and sp carbons:

(i) {C/C2/H2} < {C/C/Cd/H2} < {C/C/Ct/H2} (from Benson's table);

(ii) {C/Cd/C/H2} < {C/Cd2/H2} < {**C/Cd/Ct/H2**} (combined with Benson's table);

(iii) {C/C2/H2} < {C/Cd2/H2} < {**C/Ct2/H2**} (combined with Benson's table). All in all, the computed values for the secondary groups look very reasonable and consistent.

Most of the tertiary groups with 2 or 3 sp carbon substituents have entropies and heat capacities that are similar to the {C/Ct/C2/H} group of Benson. However, the computed enthalpies of the tertiary groups vary over a broad range from −6.90 to +10.11 kcal/mol and follow the order

{C/Ct/Cd/C/H} < {C/C3/H} < {C/C2/Cd/H} <
{C/C2/Ct/H} < {C/Cd2/C/H}< {C/Cd3/H} <
{C/Ct2/C/H} < {C/Cd2/Ct/H} <{C/Ct2/Cd/H} <
{C/Ct3/H}

Similar to the secondary groups, tertiary groups also exhibit some order viz.

{C/C3/H} < {C/C2/Cd/H} < {C/C2/Ct/H}
{C/Cd2/C/H} < {C/Cd3/H} < {C/Cd2/Ct/H}
{C/Ct2/C/H} < {C/Ct2/Cd/H} < {C/Ct3/H}
{C/C3/H} < {C/Cd3/H} < {C/Ct3/H}

which is probably due to the difference in the relative bond strengths of C−C, C−Cd, and C−Ct bonds. Though seven of the 10 tertiary groups have enthalpies in the range of −2 to +2 kcal/mol, the enthalpies of {C/Ct/Cd/C/H} (−6.90), {C/Ct3/H} (10.11), and {C/Ct2/Cd/H} (4.73) lie significantly outside this range. The enthalpy value for the mixed group {C/Ct/Cd/C/H} does not lie on the trend lines established by all of the other tertiary carbon groups and should be reexamined in the future. The computed low temperature heat capacities for the mixed group and for {C/Cd2/Ct/H} are also anomalously large.

The uncertainties in the new group values reported in Table 7 arise from both experimental and theoretical errors. Most of the small species used as references in computing the enthalpies of formation have uncertainties of about 0.1 kcal/mol per carbon atom. Because about 10 carbons are involved in the reactions used to compute the enthalpies, the experimental contribution to the uncertainty in the derived enthalpy group value could be as large as ±1 kcal/mol. However, the errors in both the theoretical and the experimental enthalpies of formation for these small molecules are likely to be systematic because of the way in which they were derived. Because of systematic cancellation in the isodesmic procedure, the true experimental contribution to the uncertainty in the group value is more likely close to 0.1 kcal/mol (the uncertainty in the enthalpy of formation of a C atom). The uncertainty contribution from the G2 calculations is almost certainly larger than 0.1 kcal/mol, but it is extremely difficult to quantify, as most of the systematic errors in the theoretical procedure are expected to cancel in the isodesmic procedure.

In our experience, the calculated entropies and heat capacity group values are quite reliable, usually good to better than 1 cal/mol K. However, two of the tertiary groups have anomalously high low temperature heat capacities as noted above. The heat capacity values for the first three of the tertiary groups in Table 7 drop with increasing temperature above 1000 K, an anomaly also seen in some of Benson's group values; these group values are compensating for other groups whose C_p's are rising too rapidly at high T. We suspect that many of the high temperature heat capacity group values in Benson's table will have to be reexamined and slightly adjusted at some point in the future.

Experimental measurements of the heats of formation of molecules containing the new groups would be extremely valuable as a check on the accuracy of the theoretical calculations. Particularly interesting would be experimental checks on the theoretical enthalpy values for {C/Ct/Cd/C/H}, {C/Ct2/Cd/H}, and {C/Ct3/H}, which are several kcal/mol different from all other values for similar tertiary carbons.

Conclusions

G2 and CBS-Q methods, two of the most reliable quantum chemical methods with average absolute deviation of respectively 1.47 and 1.57 kcal/mol for the 148 enthalpies of G2 test set molecules, were employed to determine the thermochemical properties of systems containing several multiple bonds. Both methods have been used to compute missing thermochemical group values using isodesmic bond-separation and homodesmotic reactions to calculate enthalpies of formation. Though the results obtained from the G2 method are internally consistent, large deviations are observed between the G2 and CBS-Q methods. In the absence of experimental data, an unambiguous decision about which method is better is not possible. However, because of the poor performance of the CBS-Q method even for simple alkynes, we used G2 to derive 12 new thermochemical group values: {C/Ct3/H}, {C/Ct2/Cd/H}, {C/Ct2/C/H}, {C/Cd3/H}, {C/Cd2/Ct/H}, {C/Cd2/C/H}, {C/Ct/Cd/C/H}, {C/Ct2/H2}, {C/Ct/Cd/H2}, {Cd/Ct2}, {Cd/Ct/Cd}, and {Cd/Ct/H}. Most of the new group values fit in well with known trends among thermochemical group values, and are in reasonable agreement with estimates made using rules of thumb. A few groups have substantially different values. The new group values greatly extend the range of hydrocarbons that can be included in detailed kinetic models of pyrolysis and combustion.

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Supporting Information Available: MP2(full)/6-31G(d) optimized geometries, unscaled harmonic vibrational frequencies (in cm^{-1}), and rotational constants (in GHz) of all the species investigated in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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