Ab Initio Calculations of Carbon-Containing Species and Comparison with Group Additivity Results. Part II. C_4 Species

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The thermochemistry of 34 C_4 compounds and radicals related to combustion processes have been calculated using the ab initio G3B3 method. The results have been compared to group additivity results and literature values if available. Three different group additivity programs were used, and results concerning the comparison are given.

Introduction

This is the second in a series of papers where molecules and radicals of C_3 to C_6 species important in combustion reactions are investigated. The first paper[1] was dedicated to 26 C_5 species.

It became customary by most general thermochemical users to think that all the thermochemical information and data are available from experimental sources, or that, in those cases where no experimental data are available, they can be easily estimated by group additivity methods, such as those developed by Sidney Benson[2] and his students.

The thermochemical data—mainly enthalpies of formation, Gibbs energies, entropies, heat capacities, and equilibrium constants—have been published in many compendia in tabulated forms and also in polynomial forms. During the past 20 years several estimating programs that use Benson's group additivity method have been written[3−5] and extensively used. Internet databases have also appeared.[6−9]

The C_4 molecules and radicals play an important role in the kinetics of combustion of current automotive and aviation fuels. In all modeling and simulations of combustion of gasoline, kerosene, and diesel oils, these species are present in significant abundances. Since experimental data for the stable C_4 molecules and radicals are very scarce or completely nonexistent, most of the data up to recent times were estimated using the Benson group additivity method[2] as available in several popular programs.[3−5]

The additivity estimates are widely used in programs that automatically design kinetic combustion schemes. Although very popular, Benson's additivity method has significant limitations. In particular, its accuracy for species where no experimental values exist is known to be in the range of ± (10 to 20) $kJ \cdot mol^{-1}$. Its estimates of cyclic compounds are problematic. The method is not sensitive in many cases to the geometrical conformation of the estimated species, and therefore, similar isomers often have the same predicted value, for example, the two configurations of *o*-chlorophenol, etc. It cannot always estimate the neighboring influence of large atoms such as Cl, Br, or O, and there are not enough data to calculate many carbon compounds including N, F, Cl, Br, S, and other atoms. In the domain of radicals the accuracy of predictions by the group additivity method is particularly unclear, and the thermochemistry of many crucially important radicals is still being disputed. This method sometimes estimates different values for (canonical) resonance forms that have the same value.

Only relatively recently have high-accuracy ab initio electronic structure methods become conveniently available in program suites such as Gaussian[10] that can be run on commodity off-the-shelf computers, thus gradually replacing the group additivity method.

In the present study, 34 C_4 compounds and radicals have been computed. This is part of a big effort to replace low-quality thermochemical data in a popular database devoted mainly to species used in combustion processes.[8] The main "properties" these species had in common was lack of experimental or computational spectroscopic information (i.e., vibrations, moments of inertia, and enthalpies of formation), and these values were calculated in the database by extrapolating C_p additivity group values, available mainly up to 1000 K. These additivity group data were in many cases extrapolated themselves from a more restricted temperature range. Thus, the data of these species were considered of low reliability, specifically at temperature ranges pertinent to combustion processes (see ref 8). The species were recalculated using the composite ab initio G3//B3LYP (also known as G3B3) method and the results compared with the former group additivity estimates to assess the strong and the weak points of the group additivity method.

Ab Initio Calculations and Additivity Estimates

New high-quality and low-error computational methods are available presently, such as the W2, W3, and W4 methods. Unfortunately, these methods are available in their inventor's laboratory, are presently restricted to MOLPRO packages,[11] and are relatively expensive in computer time and memory. Only a modified W1 method is implemented in the Gaussian 03 program suite,[10] but its results are not necessarily better than those of other methods probably because it is the predecessor of the W*n* method series. Among the other methods that are available commercially, the most accurate and time economic method is G3//B3LYP. To be able to compare data among themselves, the atomization method was chosen since using isodesmic or isogyric reactions means using different reactions for every species. The G3//B3LYP calculations were performed following the scheme of Baboul et al.[12] and using the Gaussian 03 program suite. The input to Gaussian was prepared using Chem3D[13] to draw the species. The Chem3D structure was sequentially relaxed to a minimum energy conformation by

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Table 1. Experimental Enthalpies of Formation, $\Delta_f H^\circ_0$, of the Gas Atoms and Thermal Energy Contents, $H^\circ_{298.15} - H^\circ_0$, of Elements in their Standard States[15,16]

atom	$\Delta_f H^\circ_0$ kJ·mol^{-1}	$H^\circ_{298.15} - H^\circ_0$ kJ·mol^{-1}
H	216.035	4.234
C	711.194	1.050
N	470.818	4.335
O	246.795	4.340
F	79.38	6.518
Cl	119.621	4.591

molecular mechanics, PM3, and AM1 methods as implemented in the MOPAC 2000 package.[14] These input coordinates were run with the Gaussian package, where the G3B3 composite sequence of Baboul et al.[12] was called explicitly, rather than by invoking the built-in G3B3 keyword. Hence, the initial geometry provided by the MOPAC 2000[14] package was optimized, and the vibrational frequencies were computed at the B3LYP/6-31G(d) level (and scaled by 0.96). This was followed by single-point energies at the QCISD(T,E4T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3Large levels. The Gaussian output was subsequently mined by a custom-written script, which collects all the relevant computed quantities, applies the higher level corrections for paired and unpaired electrons, adds the scaled zero-point energy, subtracts the relevant atomic energies (corrected using the atomic higher level corrections and the atomic spin−orbit splittings), and provides a computational summary that conveniently includes the final enthalpy of formation of the target species at 0 K and at 298 K. The experimental enthalpies of formation, $\Delta_f H^\circ_0$, of the gas atoms used by the above-mentioned script (needed to recover the enthalpy of formation of the target species at 0 K from the computed atomization enthalpy at 0 K), together with the "per atom" thermal energy contents, $H^\circ_{298.15} - H^\circ_0$, of the elements in their reference states (needed to convert the enthalpy of formation of the target species from (0 to 298.15) K) are listed in Table 1.

The transition from $\Delta_f H^\circ_0$ to $\Delta_f H^\circ_{298.15}$ is performed according to the following equations:

$$\Delta_f H^\circ_0(\mathrm{C_4Cl_2,calcd}) = 4\Delta_f H^\circ_0(\mathrm{C(g),exptl}) + 2\Delta_f H^\circ_0(\mathrm{Cl(g),exptl}) - \{4(H^\circ_0(\mathrm{C,\ calcd}) + 2H^\circ_0(\mathrm{Cl,\ calcd}) - H^\circ_0(\mathrm{C_4Cl_2,\ calcd})\} \quad (1)$$

$$\Delta_f H^\circ_{298.15}(\mathrm{C_4Cl_2,calcd}) = \Delta_f H^\circ_0(\mathrm{C_4Cl_2,calcd}) + \{H^\circ_{298.15} - H^\circ_0\}(\mathrm{C_4Cl_2,calcd}) - 4\{H^\circ_{298.15} - H^\circ_0\}(\mathrm{C(ref),exptl}) - 2\{H^\circ_{298.15} - H^\circ_0\}(\mathrm{Cl(ref),exptl}) \quad (2)$$

where $H^\circ_0(\mathrm{C_4Cl_2,\ calcd})$ is the computed electronic energy of C_4Cl_2 with the inclusion of molecular higher level corrections and the scaled zero-point energy (for molecules) and the atomic higher level corrections and spin−orbit splittings (for atoms).

The G3B3 method[12] gives results which are effectively at the QCISD(T,Full)/G3Large level (atomization), assuming that the various contributions are indeed additive. In practical terms, the estimated uncertainty of the resulting enthalpy of formation at 298 K is 8 kJ·mol^{-1}, where the latter roughly approximates the 95 % confidence limit customary in thermochemistry and is estimated by taking twice the value of the mean absolute error of the method, which is ~4 kJ·mol^{-1}.

The additivity estimates were quoted using the value approximations made by Stein's NIST No. 25 program.[3] Where NIST No. 25 (also known as NIST 94) failed, estimates made with the THERM program[4] of Ritter and Bozzelli and with the Muller et al. THERGAS program[5] were used. Because the THERM and THERGAS programs use an input for group data very similar to or exactly the same as that of NIST 94, it was not useful to try it in cases where a NIST 94 result was obtained, because the results are identical. However, because THERGAS includes slightly improved methods where group data are not available, it was used in these cases.

Results

The G3B3 enthalpies of formation at 298 K as calculated by the G3B3 method and the enthalpy of formation at 0 K obtained from the NASA PAC99 program[17] for 34 C_4 species are listed in Table 2. In the G3B3 method, the atomic higher level corrections are fitted and benchmarked[15] to experimental values, most of them obtained at 298.15 K. It was therefore argued that the values of the enthalpy of formation at 298.15 K should be preferred over the values at 0 K.

As mentioned earlier, the enthalpy of formation at 0 K was also calculated by the G3B3 postcalculation script. However, we preferred to use the values obtained by the NASA PAC99 program to fit with the rest of the data available in the mentioned thermochemical database.[8] The differences between the two values (the G3B3 value and the NASA PAC99 value) is on the order of up to ± 1 kJ·mol^{-1}, considerably lower than the accuracy of the G3B3 method, which is ± 8 kJ·mol^{-1}.

The enthalpies of formation at 298 K from additivity programs used in the past for these species are also quoted. In addition, literature values are quoted, if they exist. The original error estimation of the referred source is given as a ± value. Most of these are estimations based on Benson's group additivity method. When needed, the literature values given at 0 K were converted to values at 298 K using enthalpy increments computed with the NASA PAC99 program.[17] This program calculates the conversions as explained above by eqs 1 and 2 from a database for all elements called EFDATA that uses the same values listed in Table 1. The NASA program[17] is used to provide data and polynomials for the mentioned combustion thermochemistry database,[8] which includes all the thermochemical information as a function of temperature, i.e., the heat content, C_p, the enthalpy, $H_T - H_{298}$, the entropy, S, the Gibbs energy, G, the enthalpy of formation, $\Delta_f H$, and the equilibrium constant, K_c. In Table 2 the entropy at 298 K obtained by the PAC99 program is also listed.

Individual Compounds

C_4Cl_2, Dichlorodiacetylene, ClC≡CC≡CCl, $\Delta_f H^\circ_{298}$ = 453.6 kJ·mol^{-1}. The enthalpy of formation of this compound is not mentioned in the literature. The NIST 94[3] estimate $\Delta_f H^\circ_{298}$ = 363.2 kJ·mol^{-1} is 90 kJ·mol^{-1} below the G3B3-calculated value.

C_4F_2, Difluorodiacetylene, FC≡CC≡CF, $\Delta_f H^\circ_{298}$ = 215.3 kJ·mol^{-1}. The enthalpy of formation of this compound is not mentioned in the literature, nor can it be calculated using NIST 94. The value obtained with THERGAS (Yoneda's method)[5] seems completely irrelevant, $\Delta_f H^\circ_{298}$ = 77.72 kJ·mol^{-1}, ~137 kJ·mol^{-1} below the G3B3 value.

$C_4H_2N_2$, trans-Dicyanoethylene, t-NCCH=CHCN, $\Delta_f H^\circ_{298}$ = 331 kJ·mol^{-1}. The enthalpy of formation of this compound was published by Boyd et al.[18] as $\Delta_f H^\circ_{298}$ = (340 ± 3) kJ·mol^{-1}, 9 kJ·mol^{-1} higher than the G3B3 calculations. The NIST 94[3] estimate is $\Delta_f H^\circ_{298}$ = 313.0 kJ·mol^{-1}, 18 kJ·mol^{-1} below the G3B3-calculated value.

Table 2. Enthalpies of Formation, $\Delta_f H^\circ_{298}$, of the G3B3 Method, the Derived $\Delta_f H^\circ_0$, the Group Additivity Values at 298 K, the Literature Values with References, and Entropies Derived from the G3B3 Method

	$\Delta_f H^\circ_{298}$	$\Delta_f H^\circ_0$	$\Delta_f H^\circ_{298}$(NIST 94)	$\Delta_f H^\circ_{298}$(lit.)		S_{298}
species	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	ref	$J \cdot mol^{-1} \cdot K^{-1}$
C_4Cl_2, $ClC{\equiv}CC{\equiv}CCl$	453.6	447.2	363.2			319.21
C_4F_2, $FC{\equiv}CC{\equiv}CF$	215.3	210.2	77.72^c			294.68
$C_4H_2N_2$, *t*-$NCCH{\equiv}CHCN$	331	334.8	313.0	340 ± 3^g	18^d	309
C_4H_3, (*E*)-$*CH{=}CHC{\equiv}CH$	543.1	545.7	531.0	547.3 at 0 K	19^d	281.77
				547.3	20^e	
				549.7	21,^{e} G3	
				527	21,^{e} MC	
				539.4 ± 8	27a^e	
C_4H_3, $CH_2{=}C*C{\equiv}CH$	501.8	502.0	540.06^b	497.7 at 0 K	19^d	305.37
				499.15	20^e	
				505.8	21,^{e} G3	
				499.5	21,^{e} MC	
				501.8 ± 8	27a^e	
C_4H_4, $CH_2{=}CHC{\equiv}CH$	287.9	294.7	289.4	295 at 0 K	19^d	277.32
				295	22^e	
				305.4	23^f	
				315.0 at 0 K	24^d	
				283.3 ± 8	27a^e	
C_4H_4O, $CH_2{=}CHCH{=}C{=}O$	22.7	32	82.7^b	7.6	25^e	309.17
			6.24^c	16.7	26^f	
C_4H_5, $CH_2{=}CHCH{=}CH*$	363.3	373.4	350.7	359.7	21,^{e} G3	303.59
				364.4 ± 8	27b^e	
C_4H_5, $CH_2{=}CHC*{=}CH_2$	315.2	325.4	345.5^b	313.3 ± 8	27b^e	290.12
C_4H_5, $*CH_2CH{=}C{=}CH_2$	315.2	325.3	312.2	resonant form of previous species	27b^e	
			291.3^b			
C_4H_5, $HCC*CHCH_3$	318.4	327.9	215.4	316.53 ± 8	27b^e	293.84
				295.0 ± 9.2	28,^{e} GA	
C_4H_5, CH_3CCCH_2*	306.085	314.86	305.85	304.5	27b	300.78
				293.7	28,^{e} GA	
C_4H_6, $CH_3C{\equiv}CCH_3$	146.3	159.4	145.3	142.8 ± 8	27b^e	291.91
				145.1	29^d	
				146.3	23^f	
				145.8 ± 0.8	30^e	
C_4H_6, $CH_2{=}CHCH{=}CH_2$	110.8	125.1	109.1	105.8 ± 8	27b^e	293.33
				111.9 ± 1	31^d	
				108.8 ± 0.8	29^d	
				110.0 ± 0.8	32^f	
C_4H_6, $CH_2{=}C{=}CHCH_3$	161.3	175.4	162.6	157.3	27b^e	290.99
				162.2 ± 0.6	29^d	
$C_4H_6Cl_2$, $CHCl{=}CHCH_2CH_2Cl$	−51.9	−34.6	−54.1	−58.2	33^e	386.08
$C_4H_6Cl_2$, $CH_2{=}CHCHClCH_2Cl$	−53.6	−36.1	−36.8	−69.0	33^e	379.4
C_4H_7O, $CH_3CH*COCH_3$	−76	−57.7	−20.6^a			344.66
C_4H_7O, $H_2C{=}C(CH_3)CH_2O*$	55.7	75.4	51.7^a			334.26
C_4H_8O, $CH_2{=}C(CH_3)CH_2OH$	−161.1	−137.3	−165.6	−159.0	26^f	316.18
C_4H_8O, *trans*-2,3-dimethyloxirane	−137.7	−113.0		−129.7	26^f	303.78
C_4H_8O, ethyloxirane	−116	−91.1		−117.2	26^f	316.5
C_4H_9, $CH_3CH_2CH_2CH_2*$	81.8	105.9	79.7	66.5	34^d	307.63
				75.3	26^f	
				78.0	35^e	
				77.8 ± 2.1	36^e	
C_4H_9, $CH_3CH*CH_2CH_3$	70.2	94.9	65.4	70.3 ± 8	27b^e	327.42
				69.0 ± 4.2	37^d	
				69.0 ± 2	38^d	
				67.8 ± 2.1	36^e	
C_4H_9, $CH_3CH(CH_3)CH_2*$	73.8	97.9	70.4	70.3 ± 8	27b^e	304.66
				70.0 ± 4.2	37^d	
				70.0 ± 2	38^d	
C_4H_9, $(CH_3)_3C*$	55.0	79.7	50.3	55.3	27c^e	323.39
				52.04	37^d	
				48 ± 3	38^d	
C_4H_9O, $CH_3CH_2CH_2CH_2O*$	−56.3	−29.0	−58.15			349.13
C_4H_9O, $(CH_3)_2CHCH_2O*$	−65.07	−36.7	−67.7			319.04
C_4H_9O, $CH_3CH(O*)CH_2CH_3$	−69.84	−43.1	−73.2			327.06
C_4H_9O, $(CH_3)_3CO*$	−86.9	−60.4	−92.0	−85.2 ± 8	27b^e	309.19
C_4H_9O, $C_2H_5OCH_2CH_2*$	−44.09	−18.83	−51.0^b			366.75
C_4H_9O, $C_2H_5OCH*CH_3$	−74.7	−49.96	−69.3			370.67
$C_4H_{10}N_2$, 1,4-piperazine	32.06	70.65	20.0^b	25.1 ± 0.8	26^f	301.19
				25 ± 6.3	39^e	
$C_4H_{10}O$, $C_2H_5OC_2H_5$	−254.95	−224.5	−250.0	−251.5 ± 0.4	32^f	345.73
				−252.2 ± 0.79	40^d	

[a] THERM.[4] [b] THERGAS,[5] Benson's method. [c] THERGAS,[5] Yoneda's method. [d] Experimental value. [e] Theoretically calculated value. [f] Review. [g] Original error estimate.

C_4H_3, (E)-trans-1-Buten-3-yn-1-yl Radical, (E)-*CH=CHC≡CH, $\Delta_fH^\circ_{298} = 543.1$ kJ·mol^{-1}. The (*Z*)-*cis* form has a very close energy. The C_4H_3 radicals are very important since they are precursors of aromatic ring closures and thus formation of soot compounds largely known as PAHs or are products of aromatic ring decomposition. There are no direct or indirect experimental measurements of the heat of formation of C_4H_3 radicals, and only calculated values exist basically from Wheeler et al.,[19] Klippenstein and Miller,[20] and Krokidis et al.[21] Wheeler et al. obtained $\Delta_fH^\circ_0 = 547.3$ kJ·mol^{-1} on the basis of systematic extrapolation of ab initio energies. Klippenstein and Miller obtained $\Delta_fH^\circ_{298} = 547.3$ kJ·mol^{-1} using the quartic configuration interaction of single and double excitations (and triple excitations added perturbatively) (QCISD(T)) method. In the older paper of Krokodidis et al., $\Delta_fH^\circ_{298} = 549.7$ kJ·mol^{-1} for their G3 calculation, while their Monte Carlo calculation gives $\Delta_fH^\circ_{298} = 527$ kJ·mol^{-1}. Comparing these with the G3B3 value positions our value 4 kJ·mol^{-1} below Wheeler's[19] supposed accurate value and Klippenstein's[20] very similar result. In a very recent publication, Rossi,[27a] using the G3MP2B3 method, obtained $\Delta_fH^\circ_{298} = (539.4 \pm 8)$ kJ·mol^{-1}, that is, ∼4 kJ·mol^{-1} below the G3B3 value, well within the error limit of both methods. The NIST 94[3] value for this radical is $\Delta_fH^\circ_{298} = 531.0$ kJ·mol^{-1}, 12 kJ·mol^{-1} lower than the G3B3 value and 16 kJ·mol^{-1} lower than the Wheeler calculation.

C_4H_3, 1-Buten-3-yn-2-yl Radical, CH_2=C*C≡CH, $\Delta_fH^\circ_{298} = 501.8$ kJ·mol^{-1}. This radical is in resonance with the 1-allenyl radical CH_2=C=C=CH*, and they therefore have the same values. This radical considered together with the former conformer has as well no experimental determinations. Wheeler et al.[19] give a value of $\Delta_fH^\circ_0 = 497.7$ kJ·mol^{-1} for their method (see the previous radical), and Klippenstein and Miller[20] have a value of $\Delta_fH^\circ_{298} = 499.15$ kJ·mol^{-1}. Krokodidis et al.[21] give approximately the same value for their Monte Carlo calculation. $\Delta_fH^\circ_{298} = 499.5$ kJ·mol^{-1}, while their G3 value is $\Delta_fH^\circ_{298} = 505.8$ kJ·mol^{-1}. Our value using G3B3 is between (2 and 3) kJ·mol^{-1} higher than the Wheeler or Klippenstein value. Recently, Rossi[27a] reported his G3MP2B3 value of $\Delta_fH^\circ_{298} = 501.8$ kJ·mol^{-1}. This species could not be calculated by the NIST 94[3] program. The THERGAS[5] value $\Delta_fH^\circ_{298} = 540.06$ kJ·mol^{-1} is 40 kJ·mol^{-1} above the G3B3 value. However, for the 1-allenyl resonant form, it calculated $\Delta_fH^\circ_{298} = 578.9$ kJ·mol^{-1}, i.e., 77 kJ·mol^{-1} above the G3B3 value.

C_4H_4, 1-Buten-3-yne, CH_2=CHC≡CH, $\Delta_fH^\circ_{298} = 287.9$ kJ·mol^{-1}. This stable molecule has some old experimental heat of formation values. Roth et al.[22] found $\Delta_fH^\circ_{298} = 295$ kJ·mol^{-1}, Stull et al.[23] preferred $\Delta_fH^\circ_{298} = 305.4$ kJ·mol^{-1}, and Thornberg[24] gave $\Delta_fH_0 = 315.0$ kJ·mol^{-1}. The calculation of Wheeler[19] for C_4H_4 gives $\Delta_fH^\circ_0 = 295$ kJ·mol^{-1}, just 0.3 kJ·mol^{-1} above the G3B3-calculated value at 0 K. Recently, Rossi[27a] reported a G3MP2B3 value of $\Delta_fH^\circ_{298} = 283.3$ kJ·mol^{-1}, 4.5 kJ·mol^{-1} below the G3B3 value. The NIST 94[3] $\Delta_fH^\circ_{298} = 289.4$ kJ·mol^{-1} is just 1.5 kJ·mol^{-1} above the G3B3 value.

C_4H_4O, Vinylketene, CH_2=CHCH=C=O, $\Delta_fH^\circ_{298} = 22.7$ kJ·mol^{-1}. This compound was published by Zhong and Bozzelli,[25] and they propose an unacceptable value of $\Delta_fH^\circ_{298} = 7.6$ kJ·mol^{-1}, 15 kJ·mol^{-1} below the G3B3 calculation, while Lias et al.[26] give $\Delta_fH^\circ_{298} = 16.7$ kJ·mol^{-1}, 6 kJ·mol^{-1} below the G3B3 calculation. It is inferred therefore that any group additivity that Zhong and Bozzeli[25] have estimated on the basis of this calculation may be wrong. The compound could not be calculated using NIST 94.[3] The THERGAS[5] estimate was $\Delta_fH^\circ_{298} = 88.7$ kJ·mol^{-1}, 66 kJ·mol^{-1} above the G3B3 value.

C_4H_5, 1,3-Butadien-1-yl Radical, CH_2=CHCH=CH*, $\Delta_fH^\circ_{298} = 363.3$ kJ·mol^{-1}. Krokidis and Frenklach[21] have calculated using the G3 method $\Delta_fH^\circ_{298} = 359.7$ kJ·mol^{-1}, just 3.6 kJ·mol^{-1} below the G3B3 calculation. Janoschek and Ross[27b] using the G3MP2B3 method obtained a value very similar to ours, $\Delta_fH^\circ_{298} = 364.4$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_fH^\circ_{298} = 350.7$ kJ·mol^{-1}, 13.4 kJ·mol^{-1} below the G3B3 value. At the same time THERGAS[5] estimated $\Delta_fH^\circ_{298} = 291.3$ kJ·mol^{-1}.

C_4H_5, 1,3-Butadien-2-yl Radical, CH_2=CHC*=CH_2, $\Delta_fH^\circ_{298} = 315.2$ kJ·mol^{-1}. This radical isomer was published by Janoschek and Rossi[27b] using the G3MP2B3 method and resulted in $\Delta_fH^\circ_{298} = 313.3$ kJ·mol^{-1}. This radical cannot be estimated using NIST 94.[3] The THERGAS[5] estimated value is $\Delta_fH^\circ_{298} = 345.5$ kJ·mol^{-1}, about 30 kJ·mol^{-1} above the G3B3 value.

C_4H_5, 1,2-Butadien-4-yl Radical, *CH_2CH=C=CH_2, $\Delta_fH^\circ_{298} = 315.2$ kJ·mol^{-1}. The G3B3 results are exactly like those of the previous 1,3-butadien-2-yl radical because these two radicals are in resonance. NIST 94[3] gives a value for this species, and the estimate is $\Delta_fH^\circ_{298} = 312.2$ kJ·mol^{-1}, 3 kJ·mol^{-1} below the G3B3-calculated value.

C_4H_5, 1-Butyn-2-yl Radical, HC≡C*$CHCH_3$, $\Delta_fH^\circ_{298} = 318.4$ kJ·mol^{-1}. This radical was published by McMillan and Golden,[28] $\Delta_fH^\circ_{298} = (295.0 \pm 9.2)$ kJ·mol^{-1}, 23 kJ·mol^{-1} below the G3B3 value, and by Janoschek and Rossi,[27b] $\Delta_fH^\circ_{298} = 316.5$ kJ·mol^{-1}, just 2 kJ·mol^{-1} below the G3B3 value. The molecule could not be estimated by NIST 94[3] and THERGAS.[5]

C_4H_5, 2-Butyn-1-yl Radical, CH_3C≡CCH_2*, $\Delta_fH^\circ_{298} = 306.1$ kJ·mol^{-1}. This radical was published by McMillan and Golden,[28] $\Delta_fH^\circ_{298} = 293.7$ kJ·mol^{-1}, ∼12 kJ·mol^{-1} below the estimated value. The given value is a transition-state calculation by the G3B3 method, because no minimum was detected, but the G3MP2B3 method used by Janoschek and Rossi[27b] yielded $\Delta_fH^\circ_{298} = 304.5$ kJ·mol^{-1}. The NIST 94[3] value is $\Delta_fH^\circ_{298} = 305.9$ kJ·mol^{-1}.

C_4H_6, 2-Butyne (Dimethylacetylene), CH_3C≡CCH_3, $\Delta_fH^\circ_{298} = 146.3$ kJ·mol^{-1}. The enthalpy of formation of dimethylacetylene was first published by Prosen et al.[29] as $\Delta_fH^\circ_{298} = 145.1$ kJ·mol^{-1}, and then Stull, Westrum, and Sinke[23] published $\Delta_fH^\circ_{298} = 146.3$ kJ·mol^{-1}, exactly the same as the G3B3-calculated value. The similar G3MP2B3 method used by Janoschek and Rossi[27b] gave $\Delta_fH^\circ_{298} = 142.8$ kJ·mol^{-1}, and the ATcT[30] value is given as $\Delta_fH^\circ_{298} = (145.8 \pm 0.8)$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_fH^\circ_{298} = 145.3$ kJ·mol^{-1}.

C_4H_6, 1,3-Butadiene, CH_2=CHCH=CH_2, $\Delta_fH^\circ_{298} = 110.8$ kJ·mol^{-1}. The enthalpy of formation of 1,3-butadiene was published by Prosen and Rossini in 1946,[31] $\Delta_fH^\circ_{298} = (111.9 \pm 1)$ kJ·mol^{-1}, and then by Prosen et al.,[29] $\Delta_fH^\circ_{298} = (108.8 \pm 0.8)$ kJ·mol^{-1}. It is also given by Pedley and Rylance[32] as $\Delta_fH^\circ_{298} = (110.0 \pm 0)$ kJ·mol^{-1}. Janoschek and Rossi[27b] used G3MP2B3 values and obtained $\Delta_fH^\circ_{298} = 105.8$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_fH^\circ_{298} = 109.1$ kJ·mol^{-1}, about 1.5 kJ·mol^{-1} below the G3B3 value.

C_4H_6, 1,2-Butadiene, CH_2=C=$CHCH_3$, $\Delta_fH^\circ_{298} = 161.3$ kJ·mol^{-1}. This species was published by Prosen, Maron, and Rossini in 1951[29] as $\Delta_fH^\circ_{298} = (162.2 \pm 0.6)$ kJ·mol^{-1}, just 0.9 kJ·mol^{-1} above the G3B3 calculation. Janoschek and Rossi[27a] using the G3MP2B3 method obtained $\Delta_fH^\circ_{298} = 157.3$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_fH^\circ_{298} = 192.6$ kJ·mol^{-1}, ∼31 kJ·mol^{-1} above the G3B3 value.

$C_4H_6Cl_2$, 1,4-Dichloro-1-butene, CHCl=$CHCH_2CH_2$Cl, $\Delta_fH^\circ_{298} = -51.9$ kJ·mol^{-1}. There are no thermochemical publications regarding this compound except for the group additivity estimation made by Weismann and Benson[33] with $\Delta_f H^\circ_{298} = -58.2$ kJ·mol^{-1}, 6.3 kJ·mol^{-1} lower than the G3B3-calculated value.

$C_4H_6Cl_2$, 3,4-Dichloro-1-butene, $CH_2{=}CHCHClCH_2Cl$, $\Delta_f H^\circ_{298} = -53.6$ kJ·mol^{-1}. There are no thermochemical publications regarding this compound except for the group additivity estimation made by Weismann and Benson[33] with $\Delta_f H^\circ_{298} = -60.0$ kJ·mol^{-1}, 6.4 kJ·mol^{-1} lower than the G3B3-calculated value.

C_4H_7O, 2-Butanon-3-yl Radical, $CH_3CH{*}COCH_3$, $\Delta_f H^\circ_{298} = -76.$ kJ·mol^{-1}. This radical is not mentioned in the literature. It was calculated using the THERM[4] program, and the result is $\Delta_f H^\circ_{298} = -20.6$ kJ·mol^{-1}, about 55 kJ·mol^{-1} above the G3B3 value.

C_4H_7O, 2-Methylallyloxy Radical, $H_2C{=}C(CH_3)CH_2O{*}$, $\Delta_f H^\circ_{298} = 55.7$ kJ·mol^{-1}. This radical is not mentioned in the literature. It was calculated using the THERM[4] program, and the result is $\Delta_f H^\circ_{298} = 51$ kJ·mol^{-1}, 4 kJ·mol^{-1} below the G3B3 value.

C_4H_8O, 2-Methylallyl Alcohol, $CH_2{=}C(CH_3)CH_2OH$, $\Delta_f H^\circ_{298} = -161.1$ kJ·mol^{-1}. This compound was published by Lias et al.[26] as $\Delta_f H^\circ_{298} = -159.0$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = -165.6$ kJ·mol^{-1}, ~4.5 kJ·mol^{-1} below the G3B3 calculation.

C_4H_8O, trans-2,3-Dimethyloxirane, $\Delta_f H^\circ_{298} = -137.7$ kJ·mol^{-1}. Dimethyloxirane (dimethylethylene oxide) was estimated and published by Lias et al.[26] as $\Delta_f H^\circ_{298} = -129.7$ kJ·mol^{-1}, ~8 kJ·mol^{-1} above the G3B3 value. This compound cannot be estimated by the group additivity method because of the oxirane ring.

C_4H_8O, Ethyloxirane, $\Delta_f H^\circ_{298} = -116.0$ kJ·mol^{-1}. Ethyloxirane (ethylethylene oxide) was estimated and published by Lias et al.[26] as $\Delta_f H^\circ_{298} = -117.2$ kJ·mol^{-1}, just 1.2 kJ·mol^{-1} below the G3B3-calculated value. This compound cannot be estimated by the group additivity method because of the oxirane ring.

C_4H_9, n-Butyl Radical, $CH_3CH_2CH_2CH_2{*}$, $\Delta_f H^\circ_{298} = 81.8$ kJ·mol^{-1}. This is the simplest butyl radical. Its thermochemistry was first published by TRC[34] in 1984 with $\Delta_f H^\circ_{298} = 66.5$ kJ·mol^{-1}. Lias et al.[26] estimated it as $\Delta_f H^\circ_{298} = 75.3$ kJ·mol^{-1}. Kromkin et al.[35] estimates $\Delta_f H^\circ_{298} = 78.0$ kJ·mol^{-1}. Luo[36] quotes $\Delta_f H^\circ_{298} = (77.8 \pm 2.1)$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = 79.7$ kJ·mol^{-1}, ~2 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9, sec-Butyl Radical (Butan-2-yl Radical), $CH_3CH{*}CH_2CH_3$, $\Delta_f H^\circ_{298} = 70.2$ kJ·mol^{-1}. The secondary butyl radical was estimated by W. Tsang[37] on the basis of his kinetic measurements as $\Delta_f H^\circ_{298} = (69.0 \pm 4.2)$ kJ·mol^{-1} In 1996,[38] he repeated this estimate with a lower error bar of ± 2 kJ·mol^{-1}. Kromkin et al.[35] give the same value. Janoschek and Rossi[27b] using the G3MP2B3 method obtained $\Delta_f H^\circ_{298} = 70.3$ kJ·mol^{-1}. Luo[36] quotes $\Delta_f H^\circ_{298} = (67.8 \pm 2.1)$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = 65.4$ kJ·mol^{-1}, ~5 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9, Isobutyl Radical (2-Methylpropan-1-yl Radical), $CH_3CH(CH_3)CH_2{*}$, $\Delta_f H^\circ_{298} = 73.8$ kJ·mol^{-1}. The isobutyl radical was estimated by W. Tsang[37] on the basis of his kinetic measurements as $\Delta_f H^\circ_{298} = (70.0 \pm 4.2)$ kJ·mol^{-1}. In 1996,[38] he repeated this estimate with a lower error bar of ± 2 kJ·mol^{-1}. Janoschek and Rossi[27b] using G3MP2B3 found $\Delta_f H^\circ_{298} = 70.3$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = 70.4$ kJ·mol^{-1}, ~3.5 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9, tert-Butyl Radical $(CH_3)_3C{*}$, $\Delta_f H^\circ_{298} = 55.0$ kJ·mol^{-1}. The *tert*-butyl radical was estimated by W. Tsang[37] on the basis of his kinetic measurements as $\Delta_f H^\circ_{298} = 52.4$ kJ·mol^{-1}. In 1996,[38] he changed this estimate to $\Delta_f H^\circ_{298} = (48 \pm 3)$ kJ·mol^{-1}. Janoschek and Rossi[27c] using the similar G3MP2B3 method found $\Delta_f H^\circ_{298} = 55.3$ kJ·mol^{-1}. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = 50.3$ kJ·mol^{-1}, 4.7 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9O, n-Butoxy Radical, $CH_3CH_2CH_2CH_2O{*}$, $\Delta_f H^\circ_{298} = -56.3$ kJ·mol^{-1}. The *n*-butoxy radical is not mentioned in the thermochemical literature. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = -58.15$ kJ·mol^{-1}, ~2 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9O, Isobutoxy Radical, $(CH_3)_2CHCH_2O{*}$, $\Delta_f H^\circ_{298} = -65.1$ kJ·mol^{-1}. The isobutoxy radical is not mentioned in the thermochemical literature. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = -67.7$ kJ·mol^{-1}, about 2.5 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9O, sec-Butoxy Radical, $CH_3CH(O{*})CH_2CH_3$, $\Delta_f H^\circ_{298} = -68.8$ kJ·mol^{-1}. The *sec*-butoxy radical is not mentioned in the thermochemical literature. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = -73.2$ kJ·mol^{-1}, 4.4 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9O, tert-Butoxyl Radical $(CH_3)_3CO{*}$, $\Delta_f H^\circ_{298} = -86.92$ kJ·mol^{-1}. The *tert*-butoxy radical was calculated by Janoschek and Rossi[27b] using the similar G3MP2B3 method, and $\Delta_f H^\circ_{298} = -85.2$ kJ·mol^{-1} was obtained. The NIST 94[3] estimate is $\Delta_f H^\circ_{298} = -92.0$ kJ·mol^{-1}, about 5 kJ·mol^{-1} below the G3B3 calculation.

C_4H_9O, Diethyl Ether α-Radical (2-Ethoxyethyl Radical), $C_2H_5OCH_2CH_2{*}$, $\Delta_f H^\circ_{298} = -44.098$ kJ·mol^{-1}. This radical is not mentioned in the literature and could not be estimated by NIST 94[3] as opposed to the other radical; see below. The THERGAS[5] estimated value is $\Delta_f H^\circ_{298} = (-51.0 \pm 0.4)$ kJ·mol^{-1}, 7 kJ·mol^{-1} below the G3B3 value.

C_4H_9O, Diethyl Ether β-Radical (1-Ethoxyethyl Radical), $C_2H_5OCH{*}CH_3$, $\Delta_f H^\circ_{298} = -74.7$ kJ·mol^{-1}. This radical is also not mentioned in the literature, but it could be estimated by NIST 94,[3] giving $\Delta_f H^\circ_{298} = -69.3$ kJ·mol^{-1}, 5.4 kJ·mol^{-1} above the G3B3 value.

$C_4H_{10}N_2$, 1,4-Piperazine, $\Delta_f H^\circ_{298} = 32.06$ kJ·mol^{-1}. This compound was estimated by group additivity with THERGAS[5] and resulted in $\Delta_f H^\circ_{298} = 20.0$ kJ·mol^{-1}, 12 kJ·mol^{-1} lower than the G3B3 value. It was published by An and Zhang et al. in 1981[39] as $\Delta_f H^\circ_{298} = (25 \pm 6.3)$ kJ·mol^{-1} and by Lias et al. in 1988[26] as $\Delta_f H^\circ_{298} = (25.1 \pm 0.8)$ kJ·mol^{-1}, both 7 kJ·mol^{-1} lower than our calculation.

$C_4H_{10}O$, Diethyl Ether, $C_2H_5OC_2H_5$, $\Delta_f H^\circ_{298} = -254.95$ kJ·mol^{-1}. This compound was estimated by NIST 94[3] as $\Delta_f H^\circ_{298} = -250.0$ kJ·mol^{-1}. The experimental value was obtained by Pilcher and Skinner[40] as $\Delta_f H^\circ_{298} = (-252.2 \pm 0.8)$ kJ·mol^{-1} and estimated by Pedley and Rylance[32] as $\Delta_f H^\circ_{298} = (-251.5 \pm 0.4)$ kJ·mol^{-1}.

Discussion

One of the problems when dealing with comparison of ab initio calculations with the group additivity method is the error attributed to each method. The error of the G3B3 method is approximately ± 8 kJ·mol^{-1}. This value is based on a benchmark that includes mainly small molecules and radicals. It is argued that this error may be bigger when the size of the molecules increases as in the present study. Therefore, this paper should serve as an additional benchmark for the method comparing it to Benson's additivity or other methods or experimental values that will become available. The present study shows that ± 8 kJ·mol^{-1} is reasonable even at higher molecular sizes.

In recent publications Rossi[27a] and Janoschek and Rossi[27b,c] have reported calculations of several of the listed species using the G3MP2B3 method, which is of the same family as the G3B3 method used in this study (uses the same scaling factor of 0.96). The differences as expected are in the range of ± (1 to 5) kJ·mol^{-1}. The G3MP2B3 method contains one inferior step compared to the G3B3 method, but on the basis of the present study it is not possible to say which of the methods gives results closer to the experimental values since the experimental values themselves (if they exist) are not very accurate.

Another point of reference should be the dichlorodiacetylene and difluorodiacetylene molecules listed at the top of the C_4 compound list. In the first molecule a 90 kJ·mol^{-1} difference is observed between the NIST 94[3] estimate and the G3B3 method value. This discrepancy is expected because the data available to the NIST 94[3] program for the strained molecule have a high uncertainty connected to them. It is enough to see that in the case of C_2Cl_2, dichloroacetylene, the JANAF[16] value, $\Delta_f H°_{298} = (209.6 \pm 42)$ kJ·mol^{-1}, has a 42 kJ·mol^{-1} error while the newer estimate of Manion[41] also has a large uncertainty value, $\Delta_f H°_{298} = (226.6 \pm 14)$ kJ·mol^{-1}. In the case of difluorodiacetylene, NIST 94[3] has no estimate and THERGAS[5] cannot estimate a value using the Benson method. It can calculate a Yoneda[42] estimate 137 kJ·mol^{-1} lower than the G3B3 calculation. This value is completely erroneous since the Yoneda method included in THERGAS replaces the Cl atoms in the molecule with CH_3 groups (according to the THERGAS manual). Thus, the estimation methods of THERGAS by which it differs from NIST 94 and specifically Yoneda's method[42] are not good.

When checking the 34 results, one notices that 2 were calculated by Weisman and Benson[33] (the two $C_4H_6Cl_2$ isomers) but their values are different from estimates obtained with NIST 94.[3] Nine species could not be estimated using NIST 94,[3] and seven were calculated using the THERM[4] and THERGAS[5] programs. The oxirane species could not be calculated with any of the programs. On one hand, these seven species are not enough to compare the two competitors[4,5] with the NIST 94 program, but on the other hand, since all three programs use the same additivity groups, it is clear that they should give exactly the same results as NIST 94 where this program does work.

The NIST 94[3] estimates were modestly consistent with the G3B3 results, with an average difference of |12.2| kJ·mol^{-1}. It is remarked that 18 out of 24 estimates were lower than the G3B3 estimates. Only two species ($C_4H_6Cl_2$) were calculated using THERM.[4] The result for one radical is 4 kJ·mol^{-1} lower than the G3B3 result, but the second is 56 kJ·mol^{-1} higher. The results with THERGAS[5] gave an average of |47.4| kJ·mol^{-1} where two out of the six values are lower than the G3B3 estimate.

The calculations using THERM[4] are the most prone to subjective errors, because THERM—as opposed to the other two group additivity programs—does not analyze the molecule to find the group contributions. Rather, it allows complete freedom (and hence potentially a high degree of arbitrariness) in specifying the groups involved, and thus, the results are not necessarily unique. On the other hand, it includes groups for ring stabilization and additional groups developed by Bozzelli and his students. Unfortunately, the values of these groups are being changed and there is no text to describe the symbols used in some of the groups. The radicals in THERM are calculated by assuming a breakage of a H bond from the parent molecule, as opposed to radical group contributions in the NIST program. The programs that automatically assign the group contributions, such as NIST 94 and THERGAS, give results accurate on average to 12.5 kJ·mol^{-1} for NIST 94. This is still an acceptable accuracy for most combustion kinetics applications. However, problems arise when the leading program, NIST 94,[3] cannot provide an estimate. Only in a very limited number of such cases THERGAS[5] can help, and this help is not clear. For example, when dealing with resonant species, the programs have no means to identify resonance, and therefore assign very different heat of formations to different resonant forms. Two examples are listed in this study: the resonance of the C_4H_3 species, $CH_2{=}C^*C{\equiv}CH \rightleftharpoons CH_2{=}C{=}C{=}CH^*$, where THERGAS[5] estimated values of $\Delta_f H°_{298}$ = (540.06 and 578.9) kJ·mol^{-1}, respectively (see Table 2 and the section "Individual Compounds"), and the case of the C_4H_5 species, $CH_2{=}CHC^*{=}CH_2 \rightleftharpoons {}^*CH_2CH{=}C{=}CH_2$, for which THERGAS[5] estimated $\Delta_f H°_{298}$ = (345.5 and 293.1) kJ·mol^{-1}, respectively. At the same time NIST 94[3] could estimate only one or neither of the resonant forms, and its estimate was within 3 kJ·mol^{-1} of the G3B3 calculation.

As mentioned, the estimates using THERM critically hinge on the level of expertise of the user, because the program does not analyze the molecule and/or restrict the user's actions, making it extremely uncertain to use by nonspecialists.

Though the group additivity method is in many respects becoming anachronistic as the ab initio computing capabilities constantly expand toward larger and larger species, the main impetus to still use additivity schemes is the possibility to automatically build kinetic schemes for the reactions of big molecules. However, given the inherent uncertainty of extrapolation toward large species where few data exist, this is exactly the area where the additivity method should not be used in an indiscriminate manner.

The thermochemistry of the 34 species reported in this paper is available on the Web[8] in standard NASA seven- term polynomial form, together with the full set of calculated vibrations, moments of inertia, and internal moments of inertia as well as estimated internal rotation barriers. The polynomials were calculated using the Gordon and McBride NASA program.[17] Nonscaled B3LYP/6-31G(d) vibrations were used (because they fit better the experimental IR peak positions than the scaled ones). Additionally, the calculated moments of inertia and reduced moments of internal rotation as well as estimated rotation barrier energies were used. The enthalpy of formation at 298 K calculated by the B3LYP method (Table 2) was included in the calculation.

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Supporting Information Available:

Table 3 giving the moments of inertia and reduced internal moments of inertia of the 34 molecules and also the unscaled computed vibrations as obtained from the B3LYP/6-31G(d) program. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Burcat, A. Ab-Initio Calculations of Carbon Containing Species and Comparison with Group Additivity Results. Part I. C_5 Species. *Int. J. Chem. Kinet.* **2007**, *39*, 620–628.

(2) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(3) Stein, S. E. *NIST Structures & Properties*, version 2.0; Computerized Database 25; National Institute of Standards and Technology: Gaithersburg, MD, 1994.

(4) Ritter, E. R.; Bozzelli, J. W. THERM: Thermodynamic Property Estimation for Gas Phase Radicals and Molecules. Presented at the 12th International CODATA Conference, July 1990.

(5) Muller, C.; Michel, V.; Scacchi, G.; Chatome, G. M. THERGAS: A Computer Program for the Evaluation of Thermochemical Data of Molecules and Free Radicals in the Gas Phase. *J. Chim. Phys. Phys.-Chim. Biol.* **1995**, 1154–1178.

(6) Afeefy, H. Y.; Liebmann, J. F.; Stein, S. E. In *NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2008; http://webbook.nist.gov/chemistry.

(7) NASA Anonymous Thermochemical Database compiled by Bonnie McBride, last updated in 2002; http://cea.grc.nasa.gov.

(8) Burcat, A.; Ruscic, B. *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables*; ANL Report 05/20 and TAE Report 960; Argonne Nat. Lab.: Argonne, IL, 2005; available in print and at ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/, 2008; mirrored at http://garfield.chem.elte.hu/Burcat/burcat.html.

(9) Allendorf, M. High Temperature Gas Phase Thermochemical Database, 2008; http://www.ca.sandia.gov/HiTempThermo/index.html.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(11) MOLPRO is a package of ab initio programs designed by H.-J. Werner and P. J. Knowles. The authors are H.-J. Werner, P. J. Knowles, M. Schütz, R. Lindh, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson, University College Cardiff Consultants Ltd., Wales, U.K.

(12) Baboul, A. G.; Curtis, L. A.; Redfem, P. C.; Raghavachari, K. Gaussian-3 theory using density functional geometries and zero point energies. *J. Chem. Phys.* **1999**, *110*, 7650.

(13) Chem3D is a "CambrigeSoft" program for molecular modeling and display with semiempirical calculations built in.

(14) Stewart, J. J. P. *MOPAC 7 Manual*; Fujitsu Ltd.: Tokyo, 1993.

(15) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assesment of Gaussian-2 and Density Functional Theories for Computation of Enthalpies of Formation. *J. Chem. Phys.* **1997**, *106*, 1063–1079.

(16) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. The JANAF Thermochemical Tables, 3rd Edition. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(17) McBride, B. J.; Gordon, S. *Computer Program for Calculating and Fitting Thermodynamic Functions*; NASA RP 1271; National Aeronautics and Space Administration: Washington, DC, 1992.

(18) Boyd, R. H.; Guha, K. R.; Wuthrich, R. Thermochemistry of Cyanocarbons. II. The Heats of Combustion of Pyridinium Dicyanomethylide, Malononitrile, and Fumaronitrile. *J. Phys. Chem.* **1967**, *71*, 2187–2191.

(19) Wheeler, S. E.; Allen, W. D.; Schaefer, H. F. Thermochemistry of Disputed Soot Formation Intermediates C_4H_3 and C_4H_5. *J. Chem. Phys.* **2004**, *121*, 8800–8813.

(20) Klippenstein, S. J.; Miller, J. A. The Addition of Hydrogen Atoms to Diacetylene and the Heats of Formation of i-C_4H_3 and n-C_4H_3. *J. Phys. Chem. A* **2005**, *109*, 4285–4302.

(21) Krokidis, X.; Moriarty, N. W.; Lester, W. A., Jr.; Frenklach, M. A Quantum Monte Carlo Study of Energy Differences in C_4H_3 and C_4H_5 Isomers. *Int. J. Chem. Kinet.* **2001**, *33*, 808–828.

(22) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H. W.; Boese, R. Die Berechnung von Resonanzenergien; das MM2ERW-Kraftfeld. *Chem. Ber.* **1991**, *124*, 2499–2521.

(23) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(24) Torenberg, A. *Spectrochim. Acta, A* **1989**, *36*, 975.

(25) Zhong, X.; Bozzelli, J. Thermochemical and Kinetic Analysis of the H, OH, HO_2, O and O_2 Association Reactions with Cyclopentadienyl Radical. *J. Phys. Chem. A* **1998**, *102*, 3537–3555.

(26) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(27) (a) Rossi, M. Thermochemical Properties from ab Initio Calculations: π- and σ-Free Radicals of Importance in Soot formation: $^{\bullet}C_3H_3$ (Propargyl), $^{\bullet}C_4H_3$, $^{\bullet}C_{13}H_9$ (Phenalenyl), $^{\bullet}C_6H_5$ (Phenyl), $^{\bullet}C_{10}H_7$ (Naphthyl), $^{\bullet}C_{14}H_9$ (Anthryl), $^{\bullet}C_{14}H_9$ (Phenanthryl), $^{\bullet}C_{16}H_9$ (Pyrenyl), $^{\bullet}C_{12}H_7$ (Acenaphthyl), and $^{\bullet}C_{12}H_9$ (Biphenylyl). *Int. J. Chem. Kinet.* **2008**, *40*, 395–415. (b) Janoschek, R.; Rossi, M. Thermochemical Properties from G3MP2B3 Calculations, Set-2 Free Radicals with Special Consideration $CH_2{=}CH\text{-}C^*{=}CH_2$ Cyclo C_5H_5, $^*CH_2OOH$, HO-*CO and HC(O)O*. *Int. J. Chem Kinet.* **2004**, *36*, 661–686. (c) Janoschek, R.; Rossi, M. Thermochemical Properties of Free Radicals from G3MP2B3 Calculations. *Int. J. Chem Kinet.* **2002**, *34*, 550–560.

(28) McMillen, D. F.; Golden, D. M. Hydrocarbon Bond Dissociation Energies. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(29) Prosen, E. J.; Maron, F. W.; Rossini, F. D. Heat of Isomerization of the Two Butadienes. *J. Res. Natl. Bur. Stand. (U.S.)* **1951**, *46*, 106–112.

(30) Ruscic, B. ATcT A. *Active Thermochemical Tables*; unpublished results, 2005; values reported only in ref 8.

(31) Prosen, E. J.; Rossini, F. D. Heats of Formation and Combustion of 1,3-Butadiene and Styrene. *J. Res. Natl. Bur. Stand. (U.S.)* **1945**, *34*, 59–63.

(32) Pedley J. B.; Rylance. *Thermochemical Data and Structure of Organic Compounds*; University of Sussex: Brighton, U.K., 1977.

(33) Weissman, M.; Benson, S. W. Mechanism of Soot Initiation in Methane Systems. *Prog. Energy Combust. Sci.* **1989**, *15*, 273.

(34) *TRC Thermodynamic Tables—Hydrocarbons*; published as loose leaf sheets by the Thermodynamic Research Center, Texas A&M University, College Station, TX; presently NIST-TRC, Boulder, CO.

(35) Khromkin, E. A.; Tumanov, V. E.; Denisov, E. T. Calculation of C-H Bond Dissociation Energies and Reactivity in Radical Abstraction Reactions. *Nefttchimia* **2002**, *42*, 3.

(36) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2005.

(37) Tsang, W. Chemical Kinetic Data-Base for Combustion Chemistry. Part 4. Isobutane. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1–68.

(38) Tsang, W. In *Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals*; Martinho Simoes, J. A., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic and Professional: London, 1996; pp 22−58.

(39) An, X.-W.; Zhang, Z.-L.; Wang, S.-N.; Yan, J.-Q.; Hu, R.-H. Investigation on Bond Energies: The Heat of Combustion of Hippuric Acid, Piperazine and Azacycloheptane. *Acta Chim. Sin.* **1981**, *39*, 485–492.

(40) Pilcher, G.; Skinner, H. A.; Pell, A. S.; Pope, A. E. Measurements of Heats of Combustion by Flame Calorimetry. Part 1.—Diethyl Ether, Ethyl Vinyl Ether and Divinyl Ether. *Trans. Faraday Soc.* **1963**, *59*, 316–330.

(41) Manion, J. A. Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons. *J. Phys. Chem. Ref. Data* **2003**, *31*, 123–172.

(42) Yoneda, Y. CHEMOGRAM a computer program package for chemical logic. Part 3. An estimation of the thermodynamic properties of organic compounds with a ring of cyclopentane, cyclohexane, benzene, or napthalene. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1297–1314.

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