

# New Additivity Schemes for Hydrocarbon Energies

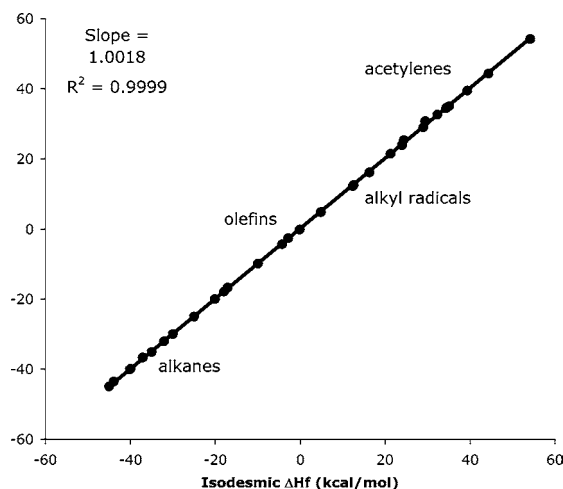
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## ABSTRACT



A new isodesmic additivity scheme based on the energetic relationships among the simplest hydrocarbon molecules reproduces the experimental heats of formation for a broad range of unstrained hydrocarbons with remarkable accuracy. The stabilizations of radicals, double, and triple CC bonds by alkyl substituents (hyperconjugation), as well as the stabilization by 1,3-alkyl group interactions at the same carbon (branching), support conventional interpretations. Statistical data fitting can also be achieved by using only four adjustable parameters.

Decades of meticulous experimental measurements provided accurate thermochemical data for a large number of hydrocarbons.<sup>1</sup> Regularities in these data have been expressed by many quantitative relationships, most notably by the extensive group increment scheme developed and refined by Benson.<sup>2</sup> Assuming additivity, increment values for, e.g., C–(C)(H)<sub>3</sub>, C–(C)<sub>2</sub>(H)<sub>2</sub>, and many other hydrocarbon groups reproduce the known heats of formation<sup>1</sup> ( $\Delta H_f$ ) remarkably well (see the selection in Table 1). Deviations from additivity can be used, for example, to evaluate “strain”, but the main purpose of these increments is predictive, rather than

interpretive. The many increment types required by Benson’s method are evaluated by averaging all the available experimental data. In the present context, Benson’s method requires nine group enthalpy increments for the selection of alkanes, alkenes, and alkynes listed in Table 1, a separate value for methane, and a special treatment for the alkyl radicals.<sup>2</sup>

Recently, Gronert<sup>3</sup> devised a remarkable new additivity scheme, based on fewer parameters and a unified treatment (Scheme 1a), which reproduces the  $\Delta H_f$ ’s of diverse unstrained hydrocarbons, alkanes, alkenes, and alkyl radicals accurately (Table 1). Gronert suggested that this empirical success “does not prove...but makes [his proposal of] geminal repulsion a viable alternative for explaining” the well-established concept of hyperconjugation and the conventional interpretation of the branching effect. We now analyze

(1) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD (<http://webbook.nist.gov>).

(2) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419 and references therein.

(3) Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209.

**Table 1.** Heats of Formation of Gronert's Strain-Free Hydrocarbons as Well as Alkynes (in kcal/mol)<sup>a</sup>

molecule	exptl refs 1 and 7	Benson	Benson deviation	Gronert <sup>b,c</sup>	Gronert deviation	isodesmic	isodesmic deviation
<b>methane</b>	-17.89			-17.3	0.6	-17.89	0.0
<b>ethane</b>	-20.04 ± 0.07	-20.00	0.0	-20.4	0.3	-20.04	0.0
<b>propane</b>	-25.02 ± 0.12	-25.00	0.0	-25.3	0.3	-25.02	0.0
<i>n</i> -butane	-30.03 ± 0.16	-30.00	0.0	-30.2	0.2	-30.00	0.0
<b>isobutane</b>	-32.07 ± 0.15	-32.40	0.3	-31.9	0.2	-32.08	0.0
<i>n</i> -pentane	-35.08 ± 0.14	-35.00	0.1	-35.1	0.0	-34.98	0.1
isopentane <sup>d</sup>	-36.73 ± 0.14	-36.60	0.1	-36.8	0.1	-37.06	0.3
neopentane	-40.14 ± 0.15	-40.10	0.0	-40.3	0.2	-39.98	0.2
<i>n</i> -hexane	-39.96 ± 0.19	-40.00	0.0	-40.0	0.0	-39.96	0.0
<i>n</i> -heptane	-44.89 ± 0.19	-45.00	0.1	(-45.1)	0.2	-44.94	0.1
cyclohexane	-29.43 ± 0.19	-29.30 <sup>e</sup>	0.1	-29.3	0.1	-29.88	0.5
<i>trans</i> -decalin	-43.54 ± 0.55	-44.80	1.3	(-41.8)	2.8	-43.89	0.4
<b>methyl radical</b>	35.05 ± 0.07 <sup>8</sup>			34.9	0.1	35.05	0.0
<b>ethyl radical</b>	29.0 ± 0.4 <sup>8</sup>	28.4	0.0	29.1	0.1	29.00	0.0
<i>n</i> -propyl radical	23.9 ± 0.5	23.4	0.5	24.2	0.3	24.02	0.1
<b>isopropyl radical</b>	21.5 ± 0.4 <sup>8</sup>	21.0	1.0	21.6	0.1	21.29	0.2
<i>sec</i> -butyl radical	16.1 ± 0.5 <sup>8</sup>	16.0	0.0	16.7	0.6	16.31	0.2
<i>tert</i> -butyl radical	12.3 ± 0.4 <sup>8</sup>	11.0	1.3	12.2	0.1	12.40	0.1
cyclohexyl radical	no data	16.0		(17.5)		16.43	
<b>ethene</b>	12.54	12.54	0.0	12.5	0.0	12.54	0.0
<b>propene</b>	4.88	4.82	0.1	4.9	0.0	4.88	0.0
1-butene	-0.15 ± 0.19	-0.18	0.0	0.1	0.3	-0.10	0.1
<i>E</i> -2-butene	-2.58 ± 0.24	-2.90	0.3	-2.6	0.0	-2.78	0.2
<b>2-methylpropene</b>	-4.29 ± 0.26	-3.54	0.8	-4.3	0.0	-4.29	0.0
2-methyl-2-butene	-9.92 ± 0.21	-10.12	0.2	-10.1	0.2	-10.25 <sup>f</sup>	0.3
tetramethylethylene	-16.80 ± 0.36	-17.42	0.6	(-21.6)	4.8	-17.06 <sup>f</sup>	0.3
<b>acetylene</b>	54.19 ± 0.19	54.20	0.0			54.19	0.0
<b>propyne</b>	44.32 ± 0.21	44.40	0.1			44.32	0.0
1-butyne	39.48 ± 0.21	39.66	0.2			39.34	0.2
2-butyne	34.68 ± 0.24	34.60	0.1			34.45	0.2
1-pentyne	34.50 ± 0.50	34.67	0.2			34.36	0.1
2-pentyne	30.80 ± 0.50	29.86	0.9			29.47	1.3
3-methyl-1-butyne	32.60 ± 0.50	32.86	0.3			32.28	0.3
3,3-dimethyl-1-butyne	25.36	25.72	0.4			24.38	1.0

<sup>a</sup> Molecules shown in bold font were used to derive the isodesmic parameters and attenuation coefficients employed in Scheme 2 and Table 2. <sup>b</sup> Data given by Gronert (ref 3) or (in parentheses) derived here from his scheme. <sup>c</sup> Acetylenes were not considered by Gronert. <sup>d</sup> Isopentane is strained, but the gauche interaction is ignored. <sup>e</sup> Benson's 0.7 kcal/mol strain correction was included. <sup>f</sup> Including 2.03 kcal/mol cis strain corrections. See text.

Gronert's treatment in detail and show that the simpler Scheme 1b, with a single, *attractive* geminal term, is able to reproduce the same set of experimental data satisfactorily. Our second treatment, Scheme 2, based on conventional reasoning, performs equally well.

**Scheme 1.** (a) Gronert's Method for Evaluating Alkane, Cycloalkane, Alkene, and Alkyl Radical Heats of Formation. (b) Four-Parameter Simplification Employing Experimental H and C Data<sup>a</sup>

$$\Delta H_f = n_{C-C}E_{C-C} + n_{C=C}E_{C=C} + n_{C-H}E_{C-H} + n_{C-C-C}E_{C-C-C} + n_{C-C-H}E_{C-C-H} + n_{H-C-H}E_{H-C-H} - f(C,H)$$

a) Gronert's evaluation (including CH and CH<sub>2</sub>):  $f(C,H) = (170.6 + E_C)n_C + 52.1 n_H$ ;  $E_{C-C} = -146.0$ ,  $E_{C=C} = -66.2$ ,  $E_{C-H} = -124.2$ ,  $E_{C-C-C} = 10.2$ ,  $E_{C-C-H} = 9.3$ ,  $E_{H-C-H} = 6.6$ , and  $E_C = 60.7$  kcal/mol.

b) Four-parameter simplification (excluding CH and CH<sub>2</sub>):  $f(C,H) = (170.6 n_C + 52.1 n_H)$ ,  $E_{C-C} = -85.59$ ,  $E_{C-H} = -96.07$ ,  $E_{C-C-C} = -64.34$ ,  $E_{H-C-H} = -1.97$

<sup>a</sup> See Supporting Information Tables SI-2 and SI-17.

Gronert's Scheme 1a is easy to use in practice. It depends on the number of each kind of bond (two-atom terms) and the 1,3-geminal combination (three-atom terms). The H atom  $\Delta H_f$  value of 52.1 kcal/mol, used in the one-atom  $f(C,H)$  term, is the only directly employed experimental value. In contrast, Gronert did not employ the experimental  $\Delta H_f$  value of 170.6 kcal/mol for the C atom but increased its value to 231.3 kcal/mol by adding 60.7 kcal/mol (the bond dissociation energy of the excited C–H quartet state). Gronert then derived his C–C, C=C, and C–H bond energies arbitrarily by statistical fitting; the resulting values are very far from

**Scheme 2.** Generalized Isodesmic Method for Calculating Heats of Formation of Unstrained Alkanes, Alkenes, Alkynes, and Alkyl Radicals (in kcal/mol)<sup>a</sup>

$$\Delta H_f = \text{base} - 2.15n(\text{CH}_2) - 1.3\text{CCC branching attraction} - \text{hyperconjugation}$$

<sup>a</sup> See the text and the parameters in Table 2 for details of the applications and the evaluations.

conventional estimates (see discussion below). The values of these bond energies are artificially *assumed to be the same for all hydrocarbons* (independent of carbon hybridization, etc.) and serve to decrease the total energy.

Three additional statistically derived CCC, CCH, and HCH three-atom geminal interaction terms increase the energy. These terms *depend only on the number of each type of geminal unit and are independent of the actual structure*.

To summarize, Scheme 1a achieves its diversity of application and accuracy by employing the fixed values of seven arbitrarily derived terms. The value for  $f(\text{C})$  is set ad hoc, and the values of the other terms are determined empirically as best fit averages of the experimental hydrocarbon heats of formation shown in Table 1. Only  $f(\text{H})$  is based directly on the experimental  $\Delta H_f$  value.

Gronert conceded that his derived C–C and C–H bond energy values are far larger than those commonly accepted in the literature. For instance, the conventional average C–H bond energy (BE) of methane (99.2 kcal/mol) is one-fourth the experimental atomization energy (396.9 kcal/mol). Gronert's C–H value is 124.2 kcal/mol. Assuming that ethane has the same C–H BE as methane (an assumption Gronert adopts), the experimentally based C–C BE of ethane is 78.5 kcal/mol.<sup>4</sup> The experimental CC bond dissociation energy (BDE) of ethane into two methyl radicals is 91.4 kcal/mol. Gronert's 146.0 kcal/mol C–C value is much larger than both the ethane BE and BDE and has no independent support. As the one-atom and two-atom terms in Scheme 1a result in  $\Delta H_f$ 's that are far too negative, Gronert compensates for the gross overestimation by "repulsive" (positive) 1,3 geminal C–C–C, C–C–H, and H–C–H terms, which are adjusted to give the best overall data fit. His 1,3 "repulsion" concept was then employed to challenge hyperconjugation as well as the conventional interpretation of the stabilization of branched alkanes as a net attractive effect; e.g., isobutane and neopentane are usually interpreted as having a greater number of net attractive interactions among 1,3-groups than their less stable *n*-alkane isomers.

While Gronert appreciated statisticians' warnings that good correlations do not necessarily establish causal relationships,<sup>5</sup> some may interpret the quantitative success of his treatment to be the chief evidence favoring his iconoclastic interpretation of branching and his contest of hyperconjugation. We argue that Gronert's overestimation of bond energies masks the stabilizing influence of hyperconjugation and branching. Indeed, we have found that many different values of the Gronert terms give satisfactory to excellent  $\Delta H_f$  estimates, when compared with experiment. Supporting Information Table SI-2 summarizes some of the alternative parameter sets we have devised by statistical data fitting<sup>6</sup> (details are given in the Supporting Information Comments to Table SI-2 and in Tables SI-3–SI-17), many showing good correlation with experiment. We use the experimental  $\Delta H_f$ 's for C and H atoms; this results in CH and CC bond energies close to the conventional estimates. When the exceptional <sup>4</sup>CH excited state and the <sup>3</sup>CH<sub>2</sub> molecules are removed from the set, data fitting for the remaining 22 alkanes, alkenes, and free radicals is achieved remarkably well *with only four*

*adjustable parameters*, the minimum number chemically plausible (see Scheme 1b and Supporting Information Table SI-17). In contrast to Scheme 1a, the adjustable two atom C–H, C–C, and C=C terms in Scheme 1b *overestimate* the magnitude of  $\Delta H_f$ , but only modestly. This is corrected by the single three-atom HCH term, which (in contrast to Scheme 1a) is *negative* (i.e., *attractive*). In operation, Schemes 1a and 1b are mathematically equivalent! The –1.8 kcal/mol 2HCC → CCC + HCH difference (Scheme 1a) matches the –1.97 kcal/mol HCH term of Scheme 1b. This helps explain why the latter simplifications works so well (Supporting Information Table SI-17). *However, no significance can be attached to the values obtained from all such empirical fitting schemes.* (Also see Supporting Information Comments.)

We now propose a new approach to an additivity scheme, which makes use of conventional considerations and does not require data fitting (Scheme 2).

Our new isodesmic additivity method (Scheme 2) for a wider set of hydrocarbons including alkynes (Table 1) is based almost entirely on experimental data for the simplest molecules (methane, ethane, propane, ethene, propene, ethyne, propyne, as well as the methyl and ethyl radicals). Scheme 2 reproduces the heats of formation of hydrocarbons with accuracies equal to Gronert's Scheme 1a *without using data averaging*. All the 1,3-interactions in our scheme are stabilizing (rather than destabilizing) and provide *support for the conventional concepts of branching and hyperconjugation*. The only adjustable parameters arise in Scheme 2 from the reasonable assumption that the magnitude of stabilizing effects at a given carbon are attenuated when more than one substituent contributes.

The  $\Delta H_f$ 's (in kcal/mol) of the molecules chosen as the appropriate base (methane (–17.89), ethene (+12.54), ethyne (+54.19), and the methyl radical (+35.05)) are elaborated by the formal addition of one or more [CH<sub>2</sub>] units. The –2.15 [CH<sub>2</sub>] increment in Scheme 2 (the difference in the heats of formation of CH<sub>4</sub> (–17.89) and C<sub>2</sub>H<sub>6</sub> (–20.04), reaction 1, Table 2) is employed universally in our method for each additional [CH<sub>2</sub>] unit in larger unstrained molecules. Like all the values used in Scheme 2 and Table 2, it is *not* derived by averaging.

Table 2 summarizes the derivation and the parameters employed in our Scheme 2. The parameters are based on the five bond separation energies of eqs 1–5 and a uniform attenuation treatment.

However, the [CH<sub>2</sub>] incorporation that extends ethane to propane introduces a new type of 1,3-CCC interaction not present in methane or ethane. If there were a linear progression from methane and ethane, the  $\Delta H_f$  of propane would

(4) Exner, K.; Schleyer, P. v. R. *J. Phys. Chem. A* **2001**, *105*, 3407.

(5) For example, correlations have been found in some European countries between human birth rates and stork populations. We have found many other numerical combinations of values that give good results when employed in a similar treatment (data fitting employed the Excel program).

(6) (a) Schleyer, P. v. R. *Abstracts of Papers*, 229th National Meeting of the American Chemical Society, San Diego, CA, March 13–17, 2005; American Chemical Society: Washington, DC, 2005. (b) Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R., to be submitted.

**Table 2.** Parameters Employed in Scheme 2<sup>a</sup>

reaction	energy	attenuation	interaction
1) C <sub>2</sub> H <sub>6</sub> - CH <sub>4</sub> → [CH <sub>2</sub> ] <sup>b</sup>	2.15	none	
2) C <sub>3</sub> H <sub>8</sub> + CH <sub>4</sub> → 2C <sub>2</sub> H <sub>6</sub>	2.83	(0.955) <sup>N-1 c</sup>	1,3-CCC branching
3) C <sub>2</sub> H <sub>5</sub> · + CH <sub>4</sub> → C <sub>2</sub> H <sub>6</sub> + CH <sub>3</sub> ·	3.90	(0.85) <sup>N-1 d</sup>	alkyl radical HC
4) propene + CH <sub>4</sub> → C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub>	5.51	(0.88) <sup>N-1 e</sup>	alkene HC
5) propyne + CH <sub>4</sub> → C <sub>2</sub> H <sub>6</sub> + CH <sub>4</sub>	7.72	none	alkyne HC

<sup>a</sup> Experimental  $\Delta H_f$  data (in kcal/mol) were used for their evaluation.

<sup>b</sup> Value of the [CH<sub>2</sub>] unit to be added to the base. The methane-bound -15.74 [H<sub>2</sub>] unit (via [CH<sub>2</sub>] + [H<sub>2</sub>] = CH<sub>4</sub>) is used to correct for the stoichiometric differences of polycycles. <sup>c</sup> Derived from the difference per 1,3-CCC in propane and isobutane. <sup>d</sup> Derived from the difference per hyperconjugation (HC) in the ethyl and isopropyl radicals. <sup>e</sup> Derived from the difference per hyperconjugation (HC) in propene and 2-methylpropene.

be  $-20.04 - 2.15 = -22.19$  kcal/mol. Instead, its experimental  $\Delta H_f$  (-25.02) is  $-2.83$  kcal/mol more negative (reaction 2, Table 2). This  $-2.83$  *net attraction* value is employed universally as the 1,3-CCC term in Scheme 2 not only to other unstrained straight chain and cyclic hydrocarbons but also to all situations not involving branching or hyperconjugation. Examples are the 1,3-CCC methyl–methyl interactions in 2-methylpropene and in the isopropyl radical. Contrary to Gronert's geminal terms, our 1,3-CCC interactions based on propane *reduce* the total energy and are *net stabilizing*.<sup>7</sup>

**Branching and Attenuation.** Chain branching results in multiple 1,3-interactions at the same carbon. Three 1,3-CCC interactions are present in isobutane and in the *tert*-butyl radical. Six 1,3-CCC interactions are present in neopentane. Attenuation effects, which are common in chemistry, occur: the second (and subsequent) substituent stabilizes less effectively than the first. The  $-2.83$  kcal/mol 1,3-CCC stabilization value is attenuated somewhat in branched molecules. This attenuation can be expressed by a single term,  $(0.955)^{N-1}$ , which employs a coefficient *based on isobutane, the smallest branched chain alkane*, and an exponent,  $N-1$ , where  $N$  is the number of 1,3-CCC interactions at the same carbon. Note that the 0.955 attenuation coefficient gives excellent agreement for neopentane, the most highly branched example in Table 1.

**Hyperconjugation in Alkenes, Alkynes, and Alkyl Radicals.** Alkyl substituents stabilize unsaturated functional groups by electron donation. Such “hyperconjugative” interactions (last term, Scheme 2) are evaluated simply from the BSE eqs 3–5 in Table 2. Thus, the alkyl group stabilization is 5.51 kcal/mol for an alkene (based on propene), 7.72 kcal/mol for an alkyne (based on propyne), and 3.90 kcal/mol for an alkyl radical (based on the ethyl radical) due to hyperconjugation. (Note that “hyperconjugation”, as defined here (Table 2), includes all the 1,3-CCC interactions involving the two unsaturated carbons. Consequently, the  $-2.83$  kcal/mol branching term is NOT applied in such instances.) However, attenuation is present, as two (or more) alkyl groups attached to the same carbon are not

as effective as the first. The attenuation terms are  $(0.88)^{N-1}$  for alkenes (based on isobutene) and  $(0.85)^{N-1}$  for alkyl radicals (based on isopropyl).

Because of its cis interaction, 2-methyl-2-butene, included by Gronert, is not strain free. A 2.03 kcal/mol strain correction is deduced from our treatment. Applying this correction twice to tetramethylethylene results in a good isodesmic value, in contrast to Gronert's method (Table 1).

**Method of Application.** In practice, Scheme 2 is evaluated quite simply by using the parameters in Table 2. The  $\Delta H_f$  of a hydrocarbon is computed from its appropriate base, its stoichiometry, and its connectivity. Details for the derivation of each hydrocarbon  $\Delta H_f$  in Table 1 are given in Supporting Information Table SI-1 in simplified form, with separate entries depending on the number of 1,3-CCC interactions.

**Cyclic Molecules.** The same approach applies to unstrained acyclic, cyclic, and polycyclic alkanes, but the variations in stoichiometry must be taken into account. The C<sub>n</sub>H<sub>2n+2</sub> alkanes are based on methane ( $\Delta H_f = -17.89$ ), but the C<sub>n</sub>H<sub>2n</sub> cycloalkanes have two fewer H's for the same number of carbons and need no base. Instead, the  $-2.15$  kcal/mol value for each [CH<sub>2</sub>] unit is used directly, e.g., six times for cyclohexane. The  $-2.83$  term is employed six times as well, as there are six 1,3-CCC interactions around the six-membered ring. The resulting  $-29.88$   $\Delta H_f$  estimate matches the experimental value of  $-29.43 \pm 0.19$  kcal/mol. The  $\Delta H_f$  evaluation of C<sub>n</sub>H<sub>2n-2</sub> bicycloalkanes employs the 15.74 kcal/mol [H<sub>2</sub>] unit as the base (see Table 2, footnote a). Our  $-43.89$  estimate for *trans*-decalin (Table 1) agrees better with experiment ( $\Delta H_f = -43.54 \pm 0.55$ ) than the  $-41.8$  value calculated using Gronert's scheme. The splendid overall performance of our isodesmic method is illustrated in the abstract figure.

Gronert's Scheme 1a also gives good results. It employs seven adjusted parameters, but these are ad hoc and are derived by data averaging. If CH and CH<sub>2</sub> are removed from Gronert's data set, our simplified data-fitting Scheme 1b requires only four adjusted parameters to give satisfactory results. Our alternative treatment, Scheme 2, is based on the well-established theoretical concepts of branching, hyperconjugation, and attenuation and depends only on the energetic relationships among the simplest hydrocarbon molecules. The parameters are not averaged and are applied universally to reproduce experimental heats of formation for acyclic and cyclic alkanes, alkyl free radicals, alkenes, and alkynes very accurately (Table 1 and abstract figure).

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**Supporting Information Available:** Details of the Scheme 2 derivations of heats of formation for the compounds listed in Table 1 are given in Table SI-1. Tables summarizing our alternative data fitting schemes are given in Tables SI-2–SI-17 along with detailed comments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(7) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.