JOC Article

Choice of Bond Dissociation Enthalpies on Which To Base the Stabilization Energies of Simple Radicals: DH(R−H) Is Preferred Because DH(R−Me) and DH(R−R) Are Perturbed by Changes in Chain Branching

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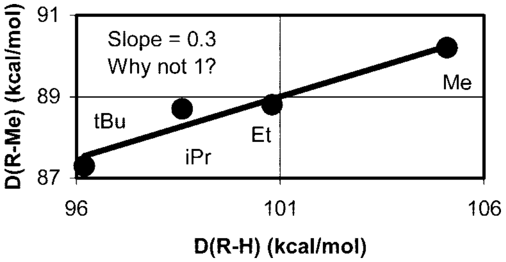

The relative stabilization energies of radicals, SE(R•), along the simple series methyl/ethyl/isopropyl/*tert*-butyl are known to vary in spread and even direction dependent on which dissociation enthalpies, DH(R−X), are used for their definition. Using a highly electronegative X is recognized as unwise, but it is not clear that using X = Me or X = R itself might not be preferred over the almost universal use of X = H. The enthalpies of formal isomerization of C_4 radical pairs that vary only in the substitution pattern at the radical center but not in carbon skeleton confirm that X = H is indeed the better choice. Comparisons in the context of recent predictive models for alkane and radical stability indicate that, while relative DH(R−H) values highlight the desired difference in substitution pattern at the radical center, relative DH(R−Me) values are perturbed by differences in skeletal branching or protobranching which are well-known to affect thermochemistry. As a result, SE(R•) values derived from relative DH(R−Me) values are consistently too small. The same pattern is illustrated for *prim*, *sec*, and *tert* allylic and benzylic radicals (larger SE(R•)) and for the parent vinyl, phenyl, and ethynyl radicals (negative SE(R•)).

Introduction and Thesis

The definition of bond dissociation enthalpy, DH(R−X), is given in eq 1.[1−14] A common definition of radical stabilization energy [$SE_X(R\bullet)$], relative to methyl, is given in eq 2, where the subscript "X" indicates the R−X series used for the DH(R−X) values.

$$R{-}X \rightarrow R\bullet + X\bullet \quad DH(R{-}X) = \Delta_f H(R\bullet) + \Delta_f H(X\bullet) - \Delta_f H(R{-}X) \quad (1)$$

$$SE_X(R\bullet) = [DH(Me{-}X) - DH(R{-}X)] \quad (2)$$

From the earliest studies of radical thermochemistry and relative reactivity,[15,16] it became conventional wisdom that the

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[1] All $\Delta_f H$ values herein, and the derived DH(R−X) values, are for the gaseous standard state at 298 K. The "compromise" values chosen for alkanes and alkyl radicals (refs 2−14) are listed in the Supporting Information.

[2] Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. I.

[3] *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P. J.; Mallard, W. G. Eds.; National Institute of Standards and Technology: Gaithersburg, MD, June 2005 (http://webbook.nist.gov).

[4] Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411.

[5] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

[6] (a) Wodrich, M. D.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 2135. (b) Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R. *Chem. Eur. J.* **2007**, *13*, 7731.

[7] (a) Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209 (correction p 9560). (b) Gronert, S. *J. Org. Chem.* **2006**, *71*, 7045. (c) Gronert, S. *Org. Lett.* **2007**, *9*, 2211.

[8] Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, 2007.

[9] (a) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255. (b) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

[10] (a) Janochek, R.; Rossi, M. J. *Int. J. Chem. Kinet.* **2002**, *34*, 550. (b) Janochek, R.; Rossi, M. J. *Int. J. Chem. Kinet.* **2004**, *36*, 661.

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TABLE 1. Recommended DH(R−X) and, in Parentheses, $SE_X(R\bullet)$ Values (kcal/mol) as a Function of R and X

R	X = H[a]	X = Me[a]	X = Cl[b]	X = OH[b]	X = F[c]
methyl	105.1 (0.0)	90.2 (0.0)	83.7 (0.0)	93.0 (0.0)	110.0 (0.0)
ethyl	100.8 (4.3)	88.8 (1.4)[d]	83.7 (0.0)	93.6 (−0.6)	111.7 (−1.7)
isopropyl	98.6 (6.5)	88.7 (1.5)[d]	84.5 (−0.8)	95.6 (−2.6)	115.5 (−5.5)
tert-butyl	96.2 (8.9)	87.3 (2.9)[d]	84.0 (−0.3)	95.7 (−2.7)	118.5 (−8.5)
allyl	88.1 (17.0)	76.1 (14.1)	71.2 (12.5)	79.4 (13.6)	
1-methylallyl[e]	86.2 (18.9)	75.6 (14.6)	73.9 (9.8)		
1,1-dimethylallyl[e]	83.9 (21.2)	74.9 (15.3)			
benzyl	89.7 (15.4)	77.6 (12.6)	74.1 (9.6)	81.1 (11.9)	98.7 (11.3)
1-phenylethyl	87.0 (18.1)	76.1 (14.1)			
cumyl	86.1 (19.0)	75.5 (14.7)			
phenyl	113.1 (−8.0)	103.9 (−13.7)	96.8 (−13.1)	112.7 (−19.7)	125.6 (−15.6)
vinyl	111.0 (−5.9)	101.6 (−11.4)	95.1 (−11.4)	110.9 (−17.9)	123.7 (−13.7)
ethynyl	120.8 (−15.7)	113.8 (−23.6)	10.1 (−17.3)		124.6 (−14.6)

[a] Based on $\Delta_f H$ values in Table S-1, Supporting Information. [b] Based on $\Delta_f H(R\bullet)$ from Table S-1, Supporting Information and $\Delta_f H(R-X)$ from ref 3 except $\Delta_f H(HO\bullet)$ = 8.9 kcal/mol from ref 17; values for lower three blocks are less certain because of fewer thermochemical data. [c] From DH compilation in ref 8; again values for lower two blocks are less certain because of fewer thermochemical data. [d] The $S_R(R\bullet)$ values are 1.4, 1.7, and 3.4 kcal/mol, respectively. [e] Referenced to terminal olefin.

"stability" of simple alkyl radicals increases in the order methyl < *prim* < *sec* < *tert*. The major evidence typically cited to support and *quantify* this conclusion is the decrease in DH(R−H) of alkanes as methyl substituents are progressively added to methane. Thus for X = H in eq 2, we obtain the steadily increasing values of $SE_H(R\bullet)$ shown at the top of column 2 of Table 1 for the standard methyl/ethyl/isopropyl/*tert*-butyl series. These lead to generic values of ΔSE_H(*sec* − *prim*) = 2.2 and ΔSE_H(*tert* − *sec*) = 2.4 kcal/mol; (these are not likely different within experimental error). Since hydrogen transfer between radical centers is a ubiquitous feature of radical chemistry, considering structure−reactivity relationships (e.g., the Evans−Polanyi relationship) in the context of DH(R−H) values is very natural.

However, it is now well recognized that $SE_X(R\bullet)$ is dependent on the chemical identity of X and any approach to search for *absolute* SE(R•) values based on relative DH(R−X) values is inherently flawed because added substituents influence the stability of R−X as well as that of R•, as shown in eq 1, with the balance dependent on the nature of X.[7a,15,18−21] This ambiguity is illustrated at the top of columns 3−6 of Table 1 where X is varied widely.[22] These trends and dependences on X were reproduced in high-level calculations.[21] Thus if one chose to use X = Me instead of X = H, one would deduce the same stability order for the alkyl radicals but with considerably muted absolute values of $SE_{Me}(R\bullet)$ (top of column 3 of Table 1) and of the differences ΔSE_{Me}(*sec* − *prim*) = 0.1, and ΔSE_{Me}(*tert* − *sec*) = 1.4 kcal/mol. If one chose X = Cl, one would deduce little differentiation in stability among the radicals; if one chose X = OH, or in the extreme, X = F, one would deduce the reverse order of stability, i.e., negative $SE_X(R\bullet)$ values for the more highly alkylated radicals.

In the context of the Pauling electronegativity relationship (eq 3)[23] which attempts to quantify the added stabilization of a covalent A−B bond by polar $A^{\delta+}-B^{\delta-}$ resonance structures as the electronegativity difference, $\Delta\chi$, between A and B increases, one should immediately distrust $SE_X(R\bullet)$ values based on such electronegative X as Cl, OH, or F because of significant differential stability effects in RX arising from $R^{\delta+}-X^{\delta-}$ contributors. The usual preference to use $SE_H(R\bullet)$ values is thus obvious because of the relatively nonpolar nature of the R−H bond (small $\Delta\chi$). However, the R−Me bond may well be even less polarized than the R−H bond.[7c] In fact in the context of the Pauling equation, Matsunaga, Rogers, and Zavitsas[20b] proposed that a more proper approach toward SE(R•) values would involve DH values of symmetrical R−R radical precursors for which $\Delta\chi \equiv 0$. Their proposal thus uses the "average" expressed in eq 4, where we have appended the subscript "R" to distinguish $SE_R(R\bullet)$ based on DH(R−R) from the very similar $SE_{Me}(R\bullet)$ based on D(R−Me). Note that eq 4 allows empirical predictions of D(R−R) compared with D(Me-Me) just as eq 2 with X = H allows empirical predictions of D(R−H) compared with R(Me-H). (To address the known destabilization of R−R bonds in sterically crowded cases,[24] they used adjusted "strain-free" values of $DH(R-R)_{sf}$ for *i*-Pr-*i*-Pr and *t*-Bu-*t*-Bu which they derived with the assumption that strain relief during dissociation would not be significant for R−Me and R-OH.[25]).

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(11) Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757.

(12) Tsang, W. In *Energetics of Organic Free Radicals*; Martinho Simoes, J. A.; Greenberg, A.; Liebman, J. F., Eds.; Blackie Academic and Professional: London, 1996.

(13) Agapito, F.; Nunes, P. M.; Costa Cabral, B. J.; Borges dos Santos, R. M.; Martinho Simoes, J. A. *J. Org. Chem.* **2007**, *72*, 8770.

(14) (a) Muralha, V. S. F.; Borges dos Santos, R. M.; Martinho Simoes, J. A. *J. Phys. Chem. A* **2004**, *108*, 936. (b) Golovin, A. V.; Takhistov, V. V. *J. Mol. Struct.* **2004**, *701*, 57.

(15) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 49−53.

(16) Pryor, W. A. *Free Radicals*; McGraw-Hill: New York, 1966.

(17) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; Srinivasan, N. K.; Su, M.-C.; Sutherland, J. W.; Michael, J. V. *J. Phys. Chem. A* **2006**, *110*, 6592.

(18) Ruchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830.

(19) Nicholas, A. M. d. P.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1850.

(20) (a) Zavitsas, A. A. *J. Chem. Educ.* **2001**, *78*, 417. (b) Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158. (c) See Zavitsas, A. A.; Matsunaga, N.; Rogers, D. W. *J. Phys. Chem A* **2008**, *112*, 5734. for additional discussion of the use of empirical models and the ambiguities in definitions and reference states for hyperconjugation and geminal interactions; this model however does not treat radicals.

(21) (a) Coote, M. L.; Pross, A.; Radom, L. *Org. Lett.* **2003**, *5*, 4689. (b) Izgorodina, E. I.; Coote, M. L.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 7558.

(22) For a similar tabular summary, see ref 12.

(23) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed.;Cornell University Press: Ithaca, NY, 1960.

(24) (a) Ruchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429. (b) Ruchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem.* **1985**, *130*, 1. (c) Welle, F. M.; Beckhaus, H.-D.; Ruchardt, C. *J. Org. Chem.* **1997**, *62*, 552. (d) Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Ruchardt, C. *J. Org. Chem.* **1998**, *63*, 1935.

(25) Note that this assumption is not consistent with the importance of 1,3-interactions implicit in the other models (refs 6 and 7) considered herein.

$$\mathrm{DH(A{-}B)} = [\mathrm{DH(A{-}A)} + \mathrm{DH(B{-}B)}]/2 + 23(\Delta\chi)^2 \quad (3)$$

$$\mathrm{SE_R(R\bullet)} = [\mathrm{DH(Me{-}Me)} - \mathrm{D(R{-}R)_{sf}}]/2 \quad (4)$$

Equation 4 leads to $\mathrm{SE_R(Et\bullet)} = 1.4$, $\mathrm{SE_R}(i\text{-}\mathrm{Pr\bullet}) = 1.7$, and $\mathrm{SE_R}(t\text{-}\mathrm{Bu\bullet}) = 3.4$ kcal/mol,[26] values much closer to $\mathrm{SE_{Me}(R\bullet)}$ than to $\mathrm{SE_H(R\bullet)}$ (Table 1). In summary, we must ask why the $\mathrm{SE_H(R\bullet)}$ and the $\mathrm{SE_{Me}(R\bullet)}$ (or $\mathrm{SE_R(R\bullet)}$) values are as different as they are (Table 1) (since we would estimate the experimental error as ≤ 0.5 kcal/mol, they are almost surely different) and which one is preferable to describe the relative "stabilities" of simple hydrocarbyl radicals.

Comparisons along the methyl/ethyl/isopropyl/*tert*-butyl series will always be plagued with issues of defining a proper reference state because of the differences in carbon number. Therefore we defer them temporarily and focus on comparisons of radical "stabilities" based on absolute $\Delta_f H(\mathrm{R\bullet})$ values for radicals[27] that have different substitution patterns at the radical center but are otherwise *skeletally* identical. For example, to compare the relative stabilities of a typical *prim* and *sec* radical,[28] one would derive ΔH values for the formal "isomerization" equilibria shown in eqs 5 or 6 that depend only on absolute $\Delta_f H(\mathrm{R\bullet})$ values rather than any DH(R−X) values. (All ΔH values appended to equations are based on the $\Delta_f H$ values in Table S-1, Supporting Information.)

$$\mathrm{CH_3CH_2CH_2\bullet} \rightleftharpoons \mathrm{CH_3CH{\bullet}CH_3} \qquad \Delta H = (21.5 - 23.9) = -2.4 \text{ kcal/mol} \quad (5)$$

$$\mathrm{CH_3CH_2CH_2CH_2\bullet} \rightleftharpoons \mathrm{CH_3CH_2CH{\bullet}CH_3} \qquad \Delta H = (16.2 - 18.9) = -2.7 \text{ kcal/mol} \quad (6)$$

On this basis the ΔSE(*sec* − *prim*) value derived from the $\mathrm{SE_H(R\bullet)}$ values in Table 1 (2.2 kcal/mol) appears in fact to be more valid than that derived from $\mathrm{SE_{Me}(R\bullet)}$ (0.1 kcal/mol) or from $\mathrm{SE_R(R\bullet)}$ (0.3 kcal/mol). Analogously, to compare the relative stabilities of a typical *prim* and *tert* radical, one could (mistakenly) use eq 7.

$$\mathrm{CH_3CH_2CH_2CH_2\bullet} \rightleftharpoons \mathrm{(CH_3)_3C\bullet} \qquad \Delta H = (12.0 - 18.9) = -6.9 \text{ kcal/mol} \quad (7)$$

However, its ΔH difference is surprisingly large even when compared with that derived from the $\mathrm{SE_H(R\bullet)}$ values in Table 1 (4.6 kcal/mol) and indeed it almost surely is because not only the substitution pattern at the radical center but also the degree of skeletal branching changes in eq 7. The more proper comparison would be eq 8 *within* the branched $\mathrm{C_4}$ skeleton which gives a ΔSE(*tert* − *prim*) value again much closer to that derived from the $\mathrm{SE_H(R\bullet)}$ values in Table 1 (4.6 kcal/mol) than that derived from $\mathrm{SE_{Me}(R\bullet)}$ (1.5 kcal/mol) or from $\mathrm{SE_R(R\bullet)}$ (2.0 kcal/mol).

$$\mathrm{(CH_3)_2CHCH_2\bullet} \rightleftharpoons \mathrm{(CH_3)_3C\bullet} \qquad \Delta H = (12.0 - 16.8) = -4.8 \text{ kcal/mol} \quad (8)$$

The importance of preserving the degree of branching in such comparisons is nicely illustrated by considering eq 9

$$\mathrm{CH_3CH_2CH_2CH_2\bullet} \rightleftharpoons \mathrm{(CH_3)_2CHCH_2\bullet} \qquad \Delta H = (16.8 - 18.9) = -2.1 \text{ kcal/mol} \quad (9)$$

that connects the two isomeric *prim* $\mathrm{C_4}$ radicals. Why, in this direct comparison, does isobutyl appear to be $\approx$2 kcal/mol more stable than *n*-butyl, even though both are *prim* radicals? Almost surely the reason is that the skeletal structure has not been held constant in eq 9. In fact the exothermicity of the *n*-butyl/isobutyl radical equilibrium in eq 9 is identical to that for the parent alkanes in eq 10.

$$\mathrm{CH_3CH_2CH_2CH_3} \rightleftharpoons \mathrm{(CH_3)_2CHCH_3} \qquad \Delta H = (-32.1 + 30.0) = -2.1 \text{ kcal/mol} \quad (10)$$

Both cases are consistent with the well-known stabilizing effect of branching in alkanes (see Table S-1, Supporting Information, and below) without requiring any significant difference associated with the radical center. In summary, eqs 6−9 indicate that the $\mathrm{C_4}$ radicals fall in the stability order *n*-butyl $\approx$ isobutyl < *s*-butyl < *tert*-butyl with increments of $\approx$2.5 kcal/mol between the latter pairs, a conclusion reached independent of any DH(R−X) values. Thus the magnitude of the *prim* < *sec* < *tert* stability ordering is in fact *more consistent with that conventionally derived from DH(R−H) rather than D(R−Me) or D(R−R) values*.

Expanding on this suggestive evidence in eqs 6−9, we will now demonstrate more systematically that the reason for this assertion is that $\mathrm{SE_{Me}(R\bullet)}$ values for the methyl/ethyl/isopropyl/*tert*-butyl series are invariably contaminated by enthalpic differences arising from changes in carbon skeleton compared with the $\mathrm{SE_H(R\bullet)}$ values. We do this by using recent models[6a,7a,b] for predicting $\Delta_f H$ values for simple unstrained alkanes and alkyl radicals.

Application of Models to the Methyl/Ethyl/Isopropyl/*tert*-Butyl Stability Order

Numerous models have been developed to predict $\Delta_f H$ values for organic molecules based on additive parameters that describe the contributions of various structural groups. These are largely empirical with the parameters being derived from statistical fitting to selected training sets of molecules. The most used is the Benson group additivity (GA) scheme,[29] $\Delta_f H = \sum_i n_i H_i$, where n_i is the number of occurrences of a given structural "group" which contributes an enthalpy increment H_i. A "group" consists of a central atom type and the various atom types bonded directly to it. The H_i parameters are derived from best fits to experimental data, and no physical significance is assigned to them. We shall return to the GA model below. However, there has been a recent resurgence of interest in formulating models[6a,7a,b] based implicitly, if not explicitly, on physical structural postulates, and we begin with two of these which differ considerably. We do not enter the controversy and make no judgment concerning how well either of these models corresponds to physical reality, but we simply apply them empirically to the issue under consideration herein.

The Wodrich−Schleyer Model. Wodrich and Schleyer[6a] recently proposed an additive model for simple unstrained hydrocarbons and radicals based on specific assumptions about the quantitative effects of structural features on $\Delta_f H$, in particular 1,3-interactions[6b] and hyperconjugation, and the H_i parameters were derived from experimental ΔH data for specific isodesmic reactions rather than empirical data fitting. The version relevant here is eq 11.

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(26) These values have been adjusted slightly based on the DH values used herein, as shown in the Supporting Information.

(27) Although such values are of course often derived from eq 1, the use of experimental values of $\Delta_f H(\mathrm{R{-}X})$ and $\Delta_f H(\mathrm{X\bullet})$ in the calculation should avoid the complications from varying X demonstrated in Table 1 (see ref 9).

(28) We consider herein only enthalpic differences, not free-energy differences.

(29) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976. (b) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419. (c) Reference 4. (d) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

$$\Delta_f H = H_{\text{base}} + n_{\text{extraC}}H_{\text{extraC}} + \sum_{\text{all C-C-C units}} [N(H_{\text{CCC}})(F_{\text{CCC}})^{N-1}] + N'(H_{\text{HC,rad}})(F_{\text{HC,rad}})N'^{-1} \quad (11)$$

H_{base} is taken as $\Delta_f H$ of the simplest parent for each series: −17.89 kcal/mol for methane and 35.05 kcal/mol for methyl.[30] A stabilization of $H_{\text{extraC}} = -2.15$ kcal/mol is applied for each additional carbon atom of either series ($n_{\text{extraC}} = n_C - 1$), where $H_{\text{extraC}} \equiv \Delta_f H(\text{ethane}) - \Delta_f H(\text{methane})$. A further net *stabilization* of $H_{\text{CCC}} = -2.83$ kcal/mol is applied for each 1,3 C−C−C unit in either series, including the radical center, where $H_{\text{CCC}} \equiv \Delta_f H(\text{propane}) + \Delta_f H(\text{methane}) - 2\Delta_f H(\text{ethane})$. This term represents the "protobranching" stabilization[31,32] concept recently propounded by the Schleyer and Houk groups.[6b] In the simple model, the same H_{CCC} parameter is used for sp^3- or sp^2-hybridized carbon-based groups, and no effect is proposed for a C−C−H or H−C−H unit (compare with the Gronert model below). However, if there are multiple (N in total) C−C−C interactions at a *single* carbon, i.e., actual branching rather than protobranching, H_{CCC} for that carbon is attenuated by a factor of $(F_{\text{CCC}})^{N\text{-}1}$, where $F_{\text{CCC}} = 0.955$ is derived from $\Delta_f H$(isobutane) compared with $\Delta_f H$(propane). Thus for a methyl carbon, the 1,3-interaction term does not exist; for each methylene carbon (n_{sec} in total), it is simply −2.83 kcal/mol; for each methine carbon (n_{tert} in total), it is $3(-2.83)(0.955)^2 = -7.74$ kcal/mol; and for each quaternary carbon (n_{quat} in total), it is $6(-2.83)(0.955)^5 = -13.49$ kcal.mol. Finally for the alkyl radicals only, a stabilization of $H_{\text{HC,rad}} = -3.90$ kcal/mol is applied for each hyperconjugative interaction of the unpaired electron with an adjacent alkyl group, where $H_{\text{HC,rad}} \equiv \Delta_f H(\text{ethyl}) + \Delta_f H(\text{methane}) - \Delta_f H(\text{ethane}) - \Delta_f H(\text{methyl})$. If there are multiple (N' in total) hyperconjugative interactions possible for a radical center, an attenuation factor of $F_{\text{HC,rad}} = 0.85$ is applied, derived from $\Delta_f H$(isopropyl) compared with $\Delta_f H$(ethyl). Thus for methyl, the hyperconjugation term does not exist; for a *prim* radical ($n_{\text{rad,prim}} = 1$), it is simply −3.90 kcal/mol; for a *sec* radical ($n_{\text{rad,sec}} = 1$), it is $2(-3.90)(0.85) = -6.63$ kcal/mol; and for a *tert* radical ($n_{\text{rad,tert}} = 1$), it is $3(-3.90)(0.85)^2] = -8.45$ kcal/mol. Equation 11 with these specific parameters inserted becomes eq 12.

$$\Delta_f H = -17.89{*}[35.05{**}] - n_{\text{extraC}}(2.15) - n_{\text{sec}}(2.83) - n_{\text{tert}}(7.74) - n_{\text{quat}}(13.49) - n_{\text{rad,prim}}(3.90) - n_{\text{rad,sec}}(6.63) - n_{\text{rad,tert}}(8.45) \quad (12)$$

where * indicates values for alkanes and ** indicates values for alkyl radicals. Wodrich and Schleyer[6a] demonstrated excellent agreement with experimental data for several small alkanes and alkyl radicals. As a simple test set to evaluate the performance of their model for our purposes, we used the nine alkanes methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane,[33] neopentane, and *n*-hexane and the nine alkyl radicals methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *s*-butyl, isobutyl, *tert*-butyl, and neopentyl. The deviations ($\Delta_f H_{\text{exp}} - \Delta_f H_{\text{model}}$) are given as "*m*/*n*" where "*m*" is the mean deviation (MD) and "*n*" is the mean unsigned deviation (MUD). From eq 12, they were −0.09/0.11, −0.15/0.21, and −0.12/0.16 for the alkanes, alkyl radicals, and their combination, respectively, probably all within experimental error. Our nonlinear least-squares[34] best fit for these specific 18 data points led to only trivial changes in the parameters ($H_{\text{extraC}} = -2.09$, $H_{\text{CCC}} = -2.94$, $F_{\text{CCC}} = 0.955$, $H_{\text{HC,rad}} = -3.98$, and $F_{\text{HC,rad}} = 0.849$) and deviations of −0.01/0.09, −0.01/0.11, and −0.01/0.10, respectively.

We now apply this model to the SE$_\text{H}$(R•) and SE$_\text{Me}$(R•) values defined above. For the simplest example of SE$_\text{H}$(Et•), we compare the processes: $CH_3CH_2{-}H \rightarrow CH_3CH_2\bullet + H\bullet$ and $CH_3{-}H \rightarrow CH_3\bullet + H\bullet$. Subtracting gives the *composite* eq 13 whose ΔH is the desired SE$_\text{H}$(Et•) (see Table 1).

$$CH_3CH_2\bullet + CH_4 \rightleftharpoons CH_3CH_3 + CH_3\bullet \qquad \Delta H = SE_H(\text{Et}\bullet) = 4.3 \quad (13)$$

Assignment of the Wodrich−Schleyer *n* coefficients of eq 12 to each species in eq 13 shows that the *only* nonzero Δn is $\Delta n_{\text{rad,prim}} = -1$ (the implicit $\Delta n_{\text{rad,methyl}} = +1$ is inherent in the H_{base} term); the thus predicted $\Delta H_{13} = -H_{\text{rad,prim}} = 3.9$ kcal/mol is in good agreement with the experimental value. To obtain the parallel SE$_\text{Me}$(Et•) value, we compare the processes: $CH_3CH_2{-}CH_3 \rightarrow CH_3CH_2\bullet + CH_3\bullet$ and $CH_3{-}CH_3 \rightarrow CH_3\bullet + CH_3\bullet$; subtraction gives the composite eq 14 which appears superficially similar to eq 13 but is 2.9 kcal/mol less endothermic, i.e., SE$_\text{Me}$(Et•) < SE$_\text{H}$(Et•) (see Table 1).

$$CH_3CH_2\bullet + CH_3CH_3 \rightleftharpoons CH_3CH_2CH_3 + CH_3\bullet \qquad \Delta H = SE_{Me}(\text{Et}\bullet) = 1.4 \quad (14)$$

In this case in addition to $\Delta n_{\text{rad,prim}} = -1$, we also have $\Delta n_{\text{sec}} = 1$; the thus predicted $\Delta H_{14} = (-H_{\text{rad,prim}} + H_{\text{sec}}) = (3.90 - 2.83) = 1.1$ kcal/mol is again in good agreement. Thus the Wodrich−Schleyer model reveals that composite eq 14 involves not only the desired conversion of ethyl to methyl but is contaminated by the gain of a stabilizing protobranch in propane. Hence it is less endothermic than expected from differences in radical stability alone. In fact, subtracting eq 13 from 14 gives eq 15 from which all radicals have disappeared and which is simply the Schleyer−Houk[6b] defining reaction for forming a protobranch.

$$2\,CH_3CH_3 \rightleftharpoons CH_4 + CH_3CH_2CH_3 \qquad \Delta H = -2.9 \quad (15)$$

We apply the same protocol to compare the stability of isopropyl with methyl in composite eqs 16 and 17.

$$CH_3CH\bullet CH_3 + CH_4 \rightleftharpoons CH_3CH_2CH_3 + CH_3\bullet \qquad \Delta H = SE_H(i\text{-Pr}\bullet) = 6.5 \quad (16)$$

$$CH_3CH\bullet CH_3 + CH_3CH_3 \rightleftharpoons (CH_3)_2CHCH_3 + CH_3\bullet \qquad \Delta H = SE_{Me}(i\text{-Pr}\bullet) = 1.5 \quad (17)$$

For eq 16, the change is the desired $\Delta n_{\text{rad,sec}} = -1$ ($\Delta n_{\text{sec}} = 0$), and ΔH_{16} is thus predicted to be $-H_{\text{rad,sec}} = 6.6$ kcal/mol. For eq 17, we have in addition $\Delta n_{\text{sec}} = -1$ and $\Delta n_{\text{tert}} = 1$, and ΔH_{17} is thus predicted to be $(-H_{\text{rad,sec}} - H_{\text{sec}} + H_{\text{tert}}) = (6.63 + 2.83 - 7.74) = 1.7$ kcal/mol. In this case we thus see further perturbation from C−C−C interactions in the composite eq 17 that defines SE$_\text{Me}$(*i*-Pr•) as the destabilizing loss of a protobranch

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[30] Although the $\Delta_f H$ values used herein (Table S-1, Supporting Information) are slightly different that those used by Wodrich and Schleyer, we have not attempted to adjust their H_i parameters.

[31] Protobranching is defined in ref 6b as "the net stabilizing 1,3-alkyl−alkyl interactions (the net attractive composite of carbon and hydrogen interactions) existing in normal, branched, and most cycloalkanes but not in methane and ethane. [It] is a net favorable composite of attractions (larger) and repulsions (smaller)."

[32] Wilson, E. K. *Chem. Eng. News* **2008**, *86* (8), 39.

[33] A correction of −0.8 kcal/mol was applied to account for its obligatory 1,4 gauche interaction that is not addressed in the model.

[34] Program by Pezzullo, J. C. http://statpages.org/nonlin.html accessed June, 2008.

in isopropyl is overwhelmed by the stabilizing gain of a real methine branch in isobutane.

Finally, we apply the same protocol to compare the stability of *tert*-butyl with methyl in composite eqs 18 and 19.

$$(CH_3)_3C\bullet + CH_4 \rightleftharpoons (CH_3)_2CHCH_3 + CH_3\bullet \qquad \Delta H = SE_H(\text{t-Bu}\bullet) = 8.9 \qquad (18)$$

$$(CH_3)_3C\bullet + CH_3CH_3 \rightleftharpoons (CH_3)_3CCH_3 + CH_3\bullet \qquad \Delta H = SE_{Me}(\text{t-Bu}\bullet) = 2.9 \qquad (19)$$

For eq 18, the change is the desired $\Delta n_{rad,tert} = -1$ ($\Delta n_{tert} = 0$), and ΔH_{18} is thus predicted to be $-H_{rad,tert} = 8.5$ kcal/mol. For eq 19, we have in addition $n_{tert} = -1$ and $\Delta n_{quat} = 1$, and ΔH_{19} is thus predicted to be $(-H_{rad,tert} - H_{tert} + H_{quat}) = (8.45 + 7.74 - 13.49) = 2.7$ kcal/mol. In this case we see an even more complex perturbation from C−C−C interactions as the destabilizing loss of the real methine branch in *tert*-butyl is overwhelmed by the stabilizing gain of a double branch in neopentane.

In summary, in each case the composite reference reaction to obtain $SE_H(R\bullet)$ based on DH(R−H) involves only changes in the degree of alkylation of the radical while that to obtain $SE_{Me}(R\bullet)$ based on DH(R−Me) is contaminated by additional changes in the degree of branching and/or protobranching. This provides the systematic rationale for the thesis outlined above that the former approach more nearly reproduces experimental data based on radical "isomerizations." Note that, while this conclusion is nicely illustrated in the context of the Wodrich−Schleyer model,[6a] it does *not* depend on the model's specific assumptions concerning the effects of structural features on stability being physically correct, because the stabilizing effects of branching in alkanes are well-known based only on experimental $\Delta_f H$ values (see Table S-1, Supporting Information).

The Gronert Model. The Wodrich−Schleyer model[6a] was in part a response to another recent model from Gronert[7a,b] which is built on diametrically opposed structural assumptions. Whereas the dominant reason normally presented for the alkyl radical stability order is the increased opportunity for stabilization of the unpaired electron by hyperconjugation, as the Wodrich−Schleyer model assumes, Gronert argued that stabilization of radicals by hyperconjugation is energetically minimal.[7c] He proposed instead that the stability order results from *differential* steric strain relief as a function of differing alkyl substitution patterns. Central to his model is the proposal that 1,3 C−C, C−H, and H−H geminal interactions are all *repulsive* and destabilizing,[32] albeit to different extents, both in the radical and especially in its precursor alkane. In contrast, the Wodrich−Schleyer model assigns a stabilizing role to every C−C−C protobranch.[20c] The two models thus differ fundamentally in whether the net balance between steric repulsions and dispersion attractions from electron correlation is repulsive or attractive for 1,3-interactions.[35] Although Gronert assigned the parameters in the model by a best fit to a training data set of small alkanes and alkyl radicals, and although he carefully noted that "[mathematical] correlation does not necessarily imply causation," he suggests that the success of the model strongly implies a correspondence with physical reality.

The model and assigned parameters applicable to alkanes and alkyl radicals are given by eq 20.[37a]

$$\begin{aligned}\Delta_f H = {} & n_{CC}H_{CC} + n_{CH}H_{CH} + n_{CCC}H_{CCC} + n_{CCH}H_{CCH} + n_{HCH}H_{HCH} + (170.6 + H_C)n_C + 52.1n_H \\ = {} & -146.0n_{CC} - 124.2n_{CH} + 10.2n_{CCC} + 9.3n_{CCH} + 6.6n_{HCH} + (170.6 + 60.7)n_C + 52.1n_H \\ = {} & -146.0n_{CC} - 72.1n_{CH} + 10.2n_{CCC} + 9.3n_{CCH} + 6.6n_{HCH} + 231.3n_C \end{aligned} \qquad (20)$$

Because $n_{CH} \equiv n_H$ for hydrocarbons, two terms can be combined as shown. The model is based on three underlying assumptions: (1) the 1,2-bonding interactions H_{CC} and H_{CH} are independent of skeletal structure and carbon hybridization state, (2) the geminal 1,3-interactions H_{CCC}, H_{CCH}, and H_{HCH} are net repulsive, and (3) hyperconjugation makes no significant contribution to radical stabilization. Because the first five terms produce an atomization energy, a sixth term *f*(C,H) was added to convert to a $\Delta_f H$ value. Because of an ambiguity of which ground-state to choose for the carbon atom for polyradicals,[37] *f*(C,H) was expressed as $(170.6 + H_C)n_C + 52.1n_H$, where H_C was treated as an additional adjustable parameter and the numerical factors are $\Delta_f H(C)$[38] and $\Delta_f H(H)$, respectively. Empirical data fitting to a training set of small alkanes and alkyl radicals gave the H_i parameters shown in eq 20, and the author suggested that their values were likely supportive of the underlying assumptions. Thus while the (inherently negative) H_{CC} and H_{CH} parameters are notably larger than typically encountered for "intrinsic" C−C and C−H bond energies,[40] such enhanced values are inherent to the model because they are partially offset by the (significantly positive) 1,3-interaction parameters to give realistic $\Delta_f H$ values. A unique simplifying feature of the model is that it requires *no additional terms* to treat alkyl radicals beyond those required for alkanes, because the same coefficients for the 1,3-interactions are used at a radical center as at a saturated carbon. Thus breaking a C−H bond to form a radical simply decreases n_{CH} by one and decreases the number of 1,3-interactions from six per alkane carbon to three per radical center (the unpaired electron is not considered as a "substituent"), as summarized in Table 2.

For the same test set that we used above to evaluate the performance of the Wodrich−Schleyer model,[6a] the deviations from predictions from eq 20 were 0.19/0.39, −0.17/0.26, and −0.01/0.32 for the alkanes, alkyl radicals, and their combination, respectively, compared with −0.09/0.11, −0.15/0.21, and −0.12/0.16 for eq 12. Thus both models appear to be empirically reliable, although based on totally conflicting assumptions.

For composite eqs 13−14, 16−17, and 18−19, we applied the same protocol of examining the effects of the Δn values in the Gronert model[7a,b] on the predicted $\Delta_f H$ values that were

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(35) Although both simplified models treat the methyl (or alkyl) group involved in a 1,3-interaction as a "hard-sphere," the interactions are of course composites among more than one non-bonded atom pair. To illustrate, consider some interatomic distances about the central carbon in the MM3-minimized (ref 36) staggered structure for propane. While the closest 1,3 H−H interaction is simply between two hydrogen atoms at 1.79 Å (well within their combined van der Waal's radii of 2.4 Å), the 1,3 Me−H interaction features two 1,3 H−C interactions at 2.18 Å, and the 1,3 Me−Me interaction features a 1,3 C−C interaction at 2.55 Å, two 1,4 C−H interactions at 2.83 Å, and two 1,5 H−H interactions at 2.65 Å.

(36) PCMODEL, Ver 9.00.0, 2004, Serena Software.

(37) Gronert also included the polyradicals $^3CH_2$ and ^4CH which we do not consider herein.

(38) The generally accepted value is in fact 171.3 kcal/mol (ref 39); we have not corrected this discrepancy which will be offset by an equal difference in the derived H_C.

(39) Chase, M. W. NIST-JANAF Thermochemical Tables, 4th ed. *J. Phys. Chem. Ref. Data, Monogr. 9* **1998**, 1.

(40) (a) Exner, K.; Schleyer, P. v. R. *J. Phys. Chem. A* **2001**, *105*, 3407. (b) Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529.

TABLE 2. Numbers of Geminal Repulsion Terms as a Function of Carbon Type in the Gronert Model[a]

carbon type	n_{CCC}	n_{CCH}	n_{HCH}
methane	0	0	6
methyl carbon	0	3	3
methylene carbon	1	4	1
methine carbon	3	3	0
quaternary carbon	6	0	0
methyl radical	0	0	3
prim radical	0	2	1
sec radical	1	2	0
tert radical	3	0	0

[a] References 7a and 7b.

used above for the Wodrich−Schleyer model[6a] (even though there is no explicit recognition of differences in radical stability in the Gronert model). The Gronert coefficient differences for composite eqs 13, 16, and 18 based on DH(R−H) are $\Delta n_{CCH} = 1$ and $\Delta n_{HCH} = -1$, $\Delta n_{CCH} = 2$ and $\Delta n_{HCH} = -2$, and $\Delta n_{CCH} = 3$ and $\Delta n_{HCH} = -3$, respectively, so that $\Delta H = SE_H(R\bullet)$ is predicted to be multiples of $(H_{CCH} - H_{HCH})$, i.e., 2.7, 5.4, and 8.1 kcal/mol, respectively. In other words, the Gronert model reproduces the methyl/ethyl/isopropyl/*tert*-butyl increasing stability order and the general magnitude of the stability differences but with no selectivity between each pair (cf. Table 1). The analogous coefficient differences for composite eqs 14, 17, and 19 based on DH(R−Me) are $\Delta n_{CCC} = 1$ and $\Delta n_{CCH} = -1$, $\Delta n_{CCC} = 2$ and $\Delta n_{CCH} = -2$, and $\Delta n_{CCC} = 3$ and $\Delta n_{CCH} = -3$, respectively, so that $\Delta H = SE_{Me}(R\bullet)$ is predicted to be multiples of $(H_{CCC} - H_{CCH}) = 0.9$, 1.8, and 2.7 kcal/mol, respectively (cf. Table 1). Hence again a smaller spread is predicted for $SE_{Me}(R\bullet)$ than for $SE_H(R\bullet)$, and the difference can again be traced to differences in branching.

Wodrich and Schleyer[6a] demonstrated that the fitted set of six H_i parameters used by Gronert[7a] was not unique for the subset of alkanes and monoalkyl radicals, and several alternate sets of parameters were presented which gave comparable fits for the data we are considering herein. In an extreme case that they highlighted, setting H_C, H_{CCC}, and H_{CCH} in the Gronert scheme to zero led to "best fit" values for the remaining parameters of $H_{C-C} = -85.59$, $H_{C-H} = -96.07$, and $H_{H-C-H} = -1.97$ kcal/mol. Although these authors recognized that such parameter assignment is an exercise in empirical curve fitting, they still could not resist the observations that the intrinsic C−C and C−H bond energies in this alternate assignment were more "normal"[40] than those used by Gronert (because the counterbalancing repulsive 1,3-interaction terms disappeared) and especially that H_{HCH} was slightly negative, i.e., attractive and stabilizing. Yet no matter what interpretation for 1,3-interaction terms is accepted, it appears unusual to us that the H−C−H interaction would be nonzero, regardless of sign, while the C−C−C and C−C−H interactions were zero. In our hands, dependent on which linear least-squares program[41,42] we used for fitting, we could achieve MD ≈ 0 for our 18-compound test set with wildly different, and physically unrealistic, parameter sets (see Supporting Information for discussion of a collinearity in the n_i values for alkanes and alkyl radicals). Yet even with these nonunique parameters, the ΔH values for eqs 13, 16, and 18 vs 14, 17, and 19, as outlined above, remain very similar. With any parameter set, it can be seen that to successfully predict the greater stability of branched compared with linear alkanes it is critical that the inequality, $H_{CCH} > (H_{CCC} + H_{HCH})/2$, be maintained.

The Group Additivity Model. We finally applied the venerable empirical GA model. (A mapping of the Wodrich−Schleyer parameters and the Gronert parameters onto the Benson parameters is shown in the Supporting Information.) For the alkanes involved in composite eqs 13−18, we used the original Benson group values[29a] of $C(C)(H)_3 = -10.20$, $C(C)_2(H)_2 = -4.93$, $C(C)_3(H) = -1.90$, and $C(C)_4 = 0.50$ kcal/mol. In addition, to consider methane which Benson did not address, we defined a singular $C(H)_4 = \Delta_f H(\text{methane}) = -17.9$ kcal/mol. The group's values for radical centers were modified from the Benson values, which are now outdated because of updated $\Delta_f H$ values for simple radicals; to reproduce the DH(R−H) values in Table 1, we chose $C\bullet(H)_3 = 35.1$, $C\bullet(C)(H)_2 = 38.9$, $C\bullet(C)_2(H) = 41.9$, and $C\bullet(C)_3 = 42.6$ kcal/mol. Benson[29] distinguished between a $C(C)_x(H)_{4-x}$ group and a $C(C\bullet)(C)_{x-1}(H)_{4-x}$ group. However the differences were very small and, in the spirit of the approximate models considered above in which the hybridization state of an adjacent carbon was ignored, we used the $C(C)_x(H)_{4-x}$ group for both structural situations. The estimated values for the composite reaction enthalpies for calculating $SE_H(R\bullet)$, i.e., ΔH_{13}, ΔH_{16}, and ΔH_{18} were 4.3, 6.5, and 8.9 kcal/mol, respectively; of course, this perfect agreement with the $SE_H(R\bullet)$ values in Table 1 is assured by our method of choosing the radical group values. Of more interest are the parallel estimated values for the composite reaction enthalpies for calculating $SE_{Me}(R\bullet)$, i.e., ΔH_{14}, ΔH_{17}, and ΔH_{19} which were again systematically smaller: 1.9, 1.8, and 3.7 kcal/mol, respectively. Expressed in group terms, $(\Delta H_{14} - \Delta H_{13}) = -2.4$ kcal/mol, i.e., the difference between the composite equations based on DH(R−Me) and on DH(R−H), corresponds to $[C(H)_4 + C(C)_2(H)_2 - 2\ C(C)(H)_3]$. Analogously, $(\Delta H_{17} - \Delta H_{16}) = -4.7$ kcal/mol and corresponds to $[C(H)_4 + C(C)_3(H) - C(C)(H)_3 - C(C)_2(H)_2]$, while $(\Delta H_{19} - \Delta H_{18}) = -5.2$ kcal/mol and corresponds to $[C(H)_4 + C(C)_4 - C(C)(H)_3 - C(C)_3(H)]$. These differences are in qualitative, if not quantitative, agreement with the data at the top of columns 2 and 3 of Table 1 and are based on group values that have been used successfully for years to estimate the stabilization of alkanes by branching. Note that these groups contain a trend that the *increments* between members of the $C(C)_x(H)_{4-x}$ group values become increasingly smaller as x increases. Specifically the fact that the quantity $2\ C(C)(H)_3$ is more positive than the sum $[C(H)_4 + C(C)_2(H)_2]$ leads to the exothermicity of the defining protobranching reaction: 2 ethane → propane + methane; the fact that the quantity $2\ C(C)_2(H)_2$ is more positive than the sum $[C(C)(H)_3 + C(C)_3(H)]$ leads to the exothermicity of the branching reaction: n-butane → isobutane; and the fact that the sum $[C(C)_2(H)_2 + C(C)_3(H)]$ is more positive than the sum $[C(C)(H)_3 + C(C)_4]$ leads to the exothermicity of the double branching reaction: isopentane → neopentane. Hence the GA values also indicate that eqs 14, 17, and 19 are contaminated by effects of branching compared with eqs 13, 16, and 18.

Application of Models to the C_4 Radical Isomerizations

We now return from the standard methyl/ethyl/isopropyl/*tert*-butyl series to the simpler case of radical "isomerizations" which

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(41) "LINEST" function in Microsoft Excel with $b = 0$. The presence of a collinearity is signaled by a 0.00 ± 0.00 output for one of the parameters.

(42) Program at http://www3.sympatico.ca/mcomeau/webpublic/javapage/reg/reg.htm accessed June, 2008.

TABLE 3. Predictions of ΔH Values (kcal/mol) for C_4 Radical Isomerizations

reaction	exp[a]	Wodrich−Schleyer model	Gronert model	group additivity
n-butyl ⇌ *sec*-butyl	−2.7	−2.7	−2.7	−2.2
isobutyl ⇌ *tert*-butyl	−4.8	−4.6	−5.4	−5.0

[a] From Table S-1, Supporting Information.

achieve simple repositioning of the radical center without other skeletal change, as illustrated in eqs 6 and 8 for the C_4 series which is the smallest carbon number that allows *prim*, *sec*, and *tert* radicals. The experimental ΔH values are compared in Table 3 with those predicted by the models. The increments of ≈2.5 kcal/mol between the three radical classes are closely reproduced, in spite of the totally different assumptions of the models. The Wodrich−Schleyer model[6a] explicitly attributes the trend to increasing stabilization by hyperconjugation in the radical by adding β-C−H bonds. The Gronert model[7a,b] implicitly attributes the trend to decreasing destabilization by replacing 1,3 C−C−H interactions with less unfavorable 1,3 H−C−H interactions. The GA model of course is purely empirical and makes no mechanistic assumptions. We take no position here but simply note some relevant recent data[7c,43] and calculations, especially treatments of 1,3-interactions which appear to be highly sensitive to electron correlation.[6b,7b,44−49]

Other Radicals

The constant-skeleton "isomerization" approach to compare radical stabilities is not available for other than simple alkyl radicals because of limitations in accuracy of $\Delta_f H$ data. However, values of $SE_H(R\bullet)$ and $SE_{Me}(R\bullet)$ determined in the same fashion from composite equations that are the difference between DH(R−H) and DH(R−Me) are shown in the lower portion of Table 1.

Resonance-Stabilized Radicals. For the progression along the allylic radical series, the relevant equations are the pairs 21 and 22, 23 and 24, and 25 and 26.[50]

$$\text{allyl }(\mathbf{1}) + CH_4 \rightarrow CH_2{=}CHCH_3 + CH_3\bullet \qquad SE_H(\mathbf{1}) = 17.0 \qquad (21)$$

$$\mathbf{1} + CH_3CH_3 \rightarrow CH_2{=}CHCH_2CH_3 + CH_3\bullet \qquad SE_{Me}(\mathbf{1}) = 14.1 \qquad (22)$$

$$\text{1-methylallyl }(\mathbf{2}) + CH_4 \rightarrow CH_2{=}CHCH_2CH_3 + CH_3\bullet \qquad SE_H(\mathbf{2}) = 18.9 \qquad (23)$$

$$\mathbf{2} + CH_3CH_3 \rightarrow CH_2{=}CHCH(CH_3)_2 + CH_3\bullet \qquad SE_{Me}(\mathbf{2}) = 14.6 \qquad (24)$$

$$\text{1, 1-dimethylallyl }(\mathbf{3}) + CH_4 \rightarrow CH_2{=}CHCH(CH_3)_2 + CH_3\bullet \qquad SE_H(\mathbf{3}) = 21.2 \qquad (25)$$

$$\mathbf{3} + CH_3CH_3 \rightarrow CH_2{=}CHC(CH_3)_3 + CH_3\bullet \qquad SE_{Me}(\mathbf{3}) = 15.3 \qquad (26)$$

In each case the stabilization energy deduced from eqs 21, 23, and 25 is somewhat greater than that deduced from eqs 22, 24, and 26; specifically, $[SE_H(R\bullet) - SE_{Me}(R\bullet)]$ for allyl (**1**), 1-methylallyl (**2**), and 1,1-dimethylallyl (**3**) is 2.9, 4.3, and 5.9 kcal/mol, respectively.[51] Similarly the Δ(SE) values between the *sec*-allylic **2** and *prim*-allylic **1** and between the *tert*-allylic **3** and *sec*-allylic **2** are larger when based on $(SE)_H(R\bullet)$ (1.9 and 2.3 kcal/mol, respectively) than when based on $(SE)_{Me}(R\bullet)$ (0.5 and 0.7 kcal/mol, respectively). Although neither the Wodrich−Schleyer[6a] nor the Gronert model[7a,b] was elaborated for resonance-stabilized radicals, the same pattern can be seen as for the alkyl radicals, i.e., the composite equations based on DH(R−H) involve no change in branching or protobranching while those based on DH(R−Me) each do. Thus no matter how "branching" or "protobranching" is counted in the radical species, it is obvious that the reference olefin on the right-hand side has an additional branch or protobranch in the second of each pair of equations.

A parallel treatment for the benzylic radical series is shown in composite eqs 27—32, and the trends and conclusions are identical.

$$PhCH_2\bullet\ (\mathbf{4}) + CH_4 \rightarrow PhCH_3 + CH_3\bullet \qquad SE_H(\mathbf{4}) = 15.4 \qquad (27)$$

$$\mathbf{4} + CH_3CH_3 \rightarrow PhCH_2CH_3 + CH_3\bullet \qquad SE_{Me}(\mathbf{4}) = 12.6 \qquad (28)$$

$$PhCH\bullet CH_3(\mathbf{5}) + CH_4 \rightarrow PhCH_2CH_3 + CH_3\bullet \qquad SE_H(\mathbf{5}) = 18.1 \qquad (29)$$

$$\mathbf{5} + CH_3CH_3 \rightarrow PhCH(CH_3)_2 + CH_3\bullet \qquad SE_{Me}(\mathbf{5}) = 14.1 \qquad (30)$$

$$PhC\bullet(CH_3)_2\ (\mathbf{6}) + CH_4 \rightarrow PhCH(CH_3)_2 + CH_3\bullet \qquad SE_H(\mathbf{6_H}) = 19.0 \qquad (31)$$

$$\mathbf{6} + CH_3CH_3 \rightarrow PhC(CH_3)_3 + CH_3\bullet \qquad SE_{Me}(\mathbf{6}) = 14.7 \qquad (32)$$

The Δ(SE) values between the *sec*-benzylic **5** and *prim*-benzylic **4** and between the *tert*-benzylic **6** and *sec*-benzylic **5** are again marginally larger when based on $SE_H(R\bullet)$ (2.7 and 0.9 kcal/mol, respectively) than when based on $SE_{Me}(R\bullet)$ (1.5 and 0.6 kcal/mol, respectively).We note a larger difference between **5** and **6** (3.0 kcal/mol) in a recent compilation[24d] derived from the kinetic method of the Ruchardt group,[24] and $\Delta_f H(\mathbf{6})$ appears to remain somewhat uncertain.[8,14a,24d]

Radicals at Unsaturated Centers. Finally we apply the same protocol to the "unstable" vinyl, phenyl, and ethynyl radicals, for which eq 2 leads to negative SE(R•) values compared with methyl. The composite eqs 33 and 34 for vinyl radical (**7**) indicate $SE_H(\mathbf{7}) = -5.9$ but $SE_{Me}(\mathbf{7}) = -11.4$ kcal/mol; hence

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(43) Ingold, K. U.; DiLabio, G. A. *Org. Lett.* **2006**, *8*, 5923.

(44) Grimme, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4460.

(45) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 3631.

(46) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(47) Mitoraj, M.; Zhu, H.; Michalak, A.; Ziegler, T. *J. Org. Chem.* **2006**, *71*, 9208.

(48) Matta, C. F.; Castillo, N.; Boyd, R. J. *J. Chem. Phys.* **2006**, *125*, 204103.

(49) Fernandez, I.; Frenking, G. *Chem. Eur. J.* **2006**, *12*, 3617.

(50) For the latter two pairs there is an ambiguity whether the terminal or internal olefin is the precursor state. We illustrate the former, but the trends are the same for the latter, although of course the values of ΔH differ by the differences of $\Delta_f H$ of the olefins; cf. ref 13.

(51) Although we do not explicitly show the details for the corresponding differences for propargylic radicals because the thermochemical data base is less sure, the analogous differences for propargyl, 1-methylpropargyl, and 1,1-dimethylpropargyl are similar: 2.5, 4.7, and 4.9 kcal/mol.

the *directionality* of the difference is the same as for the stabilized radicals discussed above in that $SE_{Me}(R\bullet)$ is now more negative (i.e., still less positive).

$$CH_2{=}CH\bullet(\mathbf{7}) + CH_4 \rightarrow CH_2{=}CH_2 + CH_3\bullet \quad SE_H(\mathbf{7}) = -5.9 \tag{33}$$

$$\mathbf{7} + CH_3CH_3 \rightarrow CH_2{=}CHCH_3 + CH_3\bullet \quad SE_{Me}(\mathbf{7}) = -11.4 \tag{34}$$

Equation 34 is more exothermic and more contaminated by factors other than radical stability, than eq 33 because it involves not only the gain of a possible protobranch but also especially the gain of hypercongugation in propene that is not present in ethylene; in the Wodrich−Schleyer model,[6a] these effects are combined in a single $H_{HC,olefin} = -5.51$ kcal/mol term. The parallel situation for phenyl (**8**) is shown in eqs 35 and 36 and for ethynyl (**9**) in eqs 37 and 38.[52]

$$C_6H_5\bullet\ (\mathbf{8}) + CH_4 \rightarrow C_6H_6 + CH_3\bullet \qquad SE_H(\mathbf{8}) = -8.0 \tag{35}$$

$$\mathbf{8} + CH_3CH_3 \rightarrow C_6H_5CH_3 + CH_3\bullet \qquad SE_{Me}(\mathbf{8}) = -13.7 \tag{36}$$

$$HC{\equiv}C\bullet\ (\mathbf{9}) + CH_4 \rightarrow HC{\equiv}CH + CH_3\bullet \qquad SE_H(\mathbf{9}) = -15.7 \tag{37}$$

$$\mathbf{9} + CH_3CH_3 \rightarrow HC{\equiv}CCH_3 + CH_3\bullet \quad SE_{Me}(\mathbf{9}) = -23.6 \tag{38}$$

Thus in summary, basing the stabilization energies of radicals on the time-honored practice of comparing D(R−H) values, rather than D(R−Me), D(R−R), or some other D(R−X) values, appears empirically justified until some more precise formulation is developed.

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Supporting Information Available: Table S-1 contains Δ_fH values and sources for the species considered herein. Fine-tuning of the $SE_R(R\bullet)$ values from Matsunaga, Rogers, and Zavitsas[20b] for self-consistency with the thermochemical values used herein is detailed. A collinearity in the coefficients of the Gronert model for alkanes and alkyl radicals is identified. Mapping the Wodrich−Schleyer parameters[6a] and the Gronert parameters[7a] onto the Benson parameters[29a] is shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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[52] The Δ_fH value for ethynyl is controversial; we accept the recent revised value from ref 14, see Table S-1, Supporting Information.