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Shortcomings of Basing Radical Stabilization Energies on Bond Dissociation Energies of Alkyl Groups to Hydrogen

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R-R'	BDE by SE_H	BDE (exp.)
CH_3CH_2-CH_2CH_3	81.6	87.4 ± 0.7
CH_3-$CH(CH_3)_2$	83.6	89.9 ± 0.5
$(CH_3)_2CH$-$CH{=}CH_2$	89.6	99.9 ± 1.1
CH_3CH_2-Ph	93.9	101.5 ± 2.1
$PhCH_2$-$CH_2CH{=}CH_2$	57.1	62.9 ± 1.2

Stabilization energies (SE_H) of carbon radicals ($R^{\bullet}$) are traditionally defined as the difference between the bond dissociation energy (BDE) of $CH_3{-}H$, as a reference point, and of R−H. The term "stabilization energy" implies that it is an intrinsic property of the radical and a quantitative measure of stability. Applicable only to carbon-centered radicals, SE_H stabilization energies are not transferable and cannot be used to estimate carbon−carbon BDE[R−R′], symmetrical BDE[R−R], or any other BDE[R−X]. SE_H values by themselves are neither an intrinsic property nor a quantitative measure of stability. There is available an alternative that is not limited only to carbon−carbon and carbon−hydrogen bonds, does not depend on any one particular molecule or BDE as a reference point, and is accurate with several hundred different types of bonds.

Introduction

There is a great deal of chemical literature regarding radical stabilization energies, but the subject continues to attract interest. Despite much work on the topic, differences of opinion remain about the interpretation of experimental findings and about the specific reference state to which radical stabilization energies should be compared.

The traditional and widely used definition of carbon radical stabilization energies is eq 1, where BDE denotes the bond dissociation energy and $R^{\bullet}$ is a carbon-centered radical.[1]

$$SE_H[R^{\bullet}] = BDE[CH_3-H] - BDE[R-H] \qquad (1)$$

There is a warning that this definition constitutes a "superficial treatment" reflecting only qualitative trends.[2] It is occasionally noted that carbon radical stabilization energies obtained from R−H bond differences are "crudely defined".[3] Anything called the stabilization energy of the radical, however defined, should be an intrinsic property of the species. One should expect that such values would be transferable to bonds other than those from which they were derived. After some problems with the rationale of using eq 1 appeared,[4] later editions of some of the textbooks mentioned[1] eliminated eq 1 in discussion of radical reactivity and stabilization.

Recently in this journal, Poutsma[5] examined the current situation and used eq 1 to obtain SE_H values and compared their performance relative to an alternative eq 2, which we had proposed.[6] In eq 2, $A^{\bullet}$ denotes *any* atom or group, not only carbon-centered radicals.

$$SE_A[A^{\bullet}] = \frac{1}{2}(BDE[CH_3-CH_3] - BDE[A-A]) \qquad (2)$$

SE_H values obtained by eq 1 were reported[5] to be 4.3 kcal mol^{-1} for primary (1°) alkyl radicals (exemplified by ethyl),

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[1] Some random examples: (a) Solomons, T. W. G.; Fryhle, C. B. *Organic Chemistry*, 8th ed.; Wiley: Hoboken, NJ, 2004. (b) Wade, L. G., Jr. *Organic Chemistry*, 5th ed.; Pearson Education: Upper Saddle River, NJ, 2003. (c) McMurry, J. *Organic Chemistry*, 4th ed.; Brooks/Cole: Pacific Grove, CA, 1996. (d) Carey, F. A.; Guiliano, R. M. *Organic Chemistry*, 8th ed.; McGraw-Hill: New York, 2008. (e) Campos, L. M.; Dang, H.; Ng, D.; Yang, Z.; Martinez, H. L.; Garcia-Garibay, M. A. *J. Org. Chem.* **2002**, *67*, 3728. (f) Menon, A. S.; Radom, L. *J. Phys. Chem. A* **2008**, *112*, 13225. (g) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2010**, *6*, 107.

[2] Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 51−52.

[3] Simmie, J. M.; Curran, H. J. *J. Phys. Chem. A* **2009**, *113*, 5128.

[4] Zavitsas, A. A. *J. Chem. Educ.* **2001**, *78*, 417.

[5] Poutsma, M. L. *J. Org. Chem.* **2008**, *73*, 8921.

[6] Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158.

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6.5 for secondary (2°) (isopropyl), 8.9 for tertiary (3°) (*tert*-butyl), 15.4 for benzyl, 17.0 for allyl, −5.9 for vinyl, and −8.0 for phenyl. Negative values indicate radicals less stable than methyl.

SE_A values by eq 2 were reported to be 1.1 kcal mol^{-1} for 1° alkyl radicals (ethyl), 1.4 for 2° (isopropyl), 3.7 for 3° (*tert*-butyl), 11.7 for benzyl, 14.3 for allyl, −11.6 for vinyl, and −13.1 for phenyl.[6] Other examples are $SE_A[Cl^\bullet] = 15.9$, $SE_A[HO^\bullet] = 19.4$, and $SE_A[H_2N^\bullet] = 11.4$ (see also below). Gas-phase heats of formation, Δ_fH at 298 K, of the NIST database[7] were used for consistency.[6]

The comparison of the two sets led to the claim that SE_H values are "preferable" to, and "more valid" than, those of SE_A.[5] The claim was based on the fact that differences in SE_H values, $\Delta(SE_H)$, are better than $\Delta(SE_A)$ in matching differences in the heats of formation of skeletally identical 1°, 2°, and 3° alkyl radicals, $\Delta(\Delta_fH)$. Using various sources of experimental BDE and Δ_fH values, only slightly different from ours, the following $\Delta(\Delta_fH)$ were reported for the radicals.[5]

$$\begin{aligned}\Delta_fH[\text{propyl}] - \Delta_fH[\text{isopropyl}] &= 23.9 - 21.5\\ &= 2.4\ (2° \text{ vs } 1°) \qquad (3)\end{aligned}$$

$$\begin{aligned}\Delta_fH[n\text{-butyl}] - \Delta_fH[sec\text{-butyl}] &= 18.9 - 16.2\\ &= 2.7\ (2° \text{ vs } 1°) \qquad (4)\end{aligned}$$

$$\begin{aligned}\Delta_fH[\text{isobutyl}] - \Delta_fH[tert\text{-butyl}] &= 16.8 - 12.0\\ &= 4.8\ (3° \text{ vs } 1°) \qquad (5)\end{aligned}$$

For 2° vs 1° radicals, $\Delta(SE_H) = 6.5 - 4.3 = 2.2$. For 3° vs 1°, $\Delta(SE_H) = 8.9 - 4.3 = 4.6$. The $\Delta(SE_H)$ values are in good agreement with the corresponding $\Delta(\Delta_fH)$ values of eqs 3−5. The corresponding $\Delta(SE_A)$ values are $1.4 - 1.1 = 0.3$ for 2° vs 1° and $3.7 - 1.1 = 2.6$ for 3° vs 1°. The agreement of $\Delta(SE_A)$ with $\Delta(\Delta_fH)$ is indeed poor as reported,[5] and SE_H values are clearly a better choice and more valid in this respect. Although the trend is the same, all reported SE_H values are quite different from their SE_A counterparts. In the present work we present many shortcomings of the widely used eq 1 for obtaining carbon radical stabilization energies.

Results and Discussion

The reason for the superior agreement between $\Delta(SE_H)$ and $\Delta(\Delta_fH)$ is that the two quantities are the same, *by definition*. Equation 6 is the thermodynamic definition of BDE[R−H].

$$\text{BDE}[\text{R}-\text{H}] = \Delta_fH[\text{R}^\bullet] + \Delta_fH[\text{H}^\bullet] - \Delta_fH[\text{RH}] \qquad (6)$$

Applying eq 6 to *n*-propyl and isopropyl, radicals of the same carbon skeleton, yields eqs 7 and 8.

$$\begin{aligned}\text{BDE}[\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}] &= \Delta_fH[\text{CH}_3\text{CH}_2\text{CH}_2^\bullet]\\ &\quad + \Delta_fH[\text{H}^\bullet] - \Delta_fH[\text{CH}_3\text{CH}_2\text{CH}_3] \qquad (7)\end{aligned}$$

$$\begin{aligned}\text{BDE}[(\text{CH}_3)_2\text{CH}-\text{H}] &= \Delta_fH[\text{CH}_3\text{CH}(^\bullet)\text{CH}_3]\\ &\quad + \Delta_fH[\text{H}^\bullet] - \Delta_fH[\text{CH}_3\text{CH}_2\text{CH}_3] \qquad (8)\end{aligned}$$

Subtraction of eq 8 from 7 yields eq 9, where the left-hand side is the definition of $\Delta(SE_H)$ and the right-hand side is $\Delta(\Delta_fH)$ of propyl and isopropyl by eq 3.

$$\begin{aligned}&\text{BDE}[\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}] - \text{BDE}[(\text{CH}_3)_2\text{CH}-\text{H}]\\ &\quad = \Delta_fH[\text{CH}_3\text{CH}_2\text{CH}_2^\bullet] - \Delta_fH[\text{CH}_3\text{CH}(^\bullet)\text{CH}_3] \qquad (9)\end{aligned}$$

Hence, $\Delta(\text{BDE}[\text{R}-\text{H}]) = \Delta(SE_H) = \Delta(\Delta_fH)$, by definition.

Inserting the BDE and Δ_fH values cited[5] into eq 9 results in the equalities of eq 10.

$$\begin{aligned}101.0 - 98.6 &= 23.9 - 21.5 = 2.4 = \Delta(SE_H)\\ &= \Delta(\Delta_fH) \qquad (10)\end{aligned}$$

Applying eq 6 to isobutyl and *tert*-butyl, also radicals of the same carbon skeleton, yields eqs 11 and 12.

$$\begin{aligned}\text{BDE}[(\text{CH}_3)_2\text{CHCH}_2-\text{H}] &- \Delta_fH[(\text{CH}_3)_2\text{CHCH}_2^\bullet]\\ &+ \Delta_fH[\text{H}^\bullet] - \Delta_fH[(\text{CH}_3)_3\text{CH}] \qquad (11)\end{aligned}$$

$$\begin{aligned}\text{BDE}[(\text{CH}_3)_3\text{C}-\text{H}] &= \Delta_fH[(\text{CH}_3)_3\text{C}^\bullet] + \Delta_fH[\text{H}^\bullet]\\ &\quad - \Delta_fH[(\text{CH}_3)_3\text{C}-\text{H}] \qquad (12)\end{aligned}$$

Subtraction of eq 12 from 11 yields eq 13, where the left-hand side is the definition of $\Delta(SE_H)$ and the right-hand side is $\Delta(\Delta_fH)$ of isobutyl and *tert*-butyl by eq 5.

$$\begin{aligned}&\text{BDE}[(\text{CH}_3)_2\text{CHCH}_2-\text{H}] - \text{BDE}[(\text{CH}_3)_3\text{C}-\text{H}]\\ &\quad = \Delta H_f[(\text{CH}_3)_2\text{CHCH}_2^\bullet] - \Delta H_f[(\text{CH}_3)_3\text{C}^\bullet] \qquad (13)\end{aligned}$$

Inserting the BDE and Δ_fH values cited[5] into eq 13 results in the equalities of eq 14, and again, by definition, $\Delta(SE_H) = \Delta(\Delta_fH)$.

$$\begin{aligned}101.0 - 96.2 &= 16.8 - 12.0 = 4.8 = \Delta(SE_H)\\ &= \Delta(\Delta_fH) \qquad (14)\end{aligned}$$

Thus, eqs 10 and 14 yield exactly the values of eqs 3 and 5, respectively, as they must by their definition.

We provide another example, not in ref 5, of this kind of tautology by considering the heats of reactions 15 and 16, with ΔH_{rxn} calculated from the heats of formation of the species involved.

$$\begin{aligned}(\text{CH}_3)_2\text{CHCH}_2^\bullet &\rightarrow (\text{CH}_3)_2\text{C}{=}\text{CH}_2 + \text{H}^\bullet\\ &\Delta H_{\text{rxn}} = 31.0 \pm 0.26 \qquad (15)\end{aligned}$$

$$\begin{aligned}(\text{CH}_3)_3\text{C}^\bullet &\rightarrow (\text{CH}_3)_2\text{C}{=}\text{CH}_2 + \text{H}^\bullet\\ &\Delta H_{\text{rxn}} = 35.8 \pm 0.26 \qquad (16)\end{aligned}$$

The difference of 4.8 ± 0.4 kcal mol^{-1} in reactions 15 and 16 is the same as $\Delta(\Delta_fH)$ of eq 5. Branching (or attractive "1−3 protobranching") effects of the carbon skeleton were proposed as affecting thermochemistries in general and "contaminating" SE_A values.[5] A simpler rationalization can be provided: A weaker 3° C−H bond is broken in reaction 15 compared to a stronger 1° C−H bond broken in reaction 16. Because the products are the same, the difference in ΔH_{rxn} merely reflects the difference of the strengths of the bonds being broken. Again, by definition, $\Delta(\text{BDE}[\text{R}-\text{H}]) = \Delta(SE_H) = \Delta(\Delta_fH)$.

Modern BDE values are generally based on heats of formation data so that their relation in Poutsma's paper are not simply equivalent, but literally so. Therefore, the excellent agreement between $\Delta(SE_H)$ and $\Delta(\Delta_fH)$ cited as proof for the preference of SE_H over SE_A can be dismissed. The only

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(7) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69 (http://webbook.nist.gov/).

TABLE 1. BDE Calculated by eq 17 Using SE_H and SE_A Carbon Radical Stabilization Energies and Corresponding Experimental Values (kcal mol^{-1})[a]

R−R′	BDE[R−R′][b] by SE_H	BDE[R−R′][c] expt	BDE[R−R′][d] by SE_A
$CH_3-CH_2CH_3$	85.9	88.2 ± 0.5	88.8
$CH_3CH_2-CH_2CH_3$	81.6	87.4 ± 0.7	87.4
$CH_3CH_2-CH(CH_3)_2$	79.4	87.1 ± 0.7	87.4
CH_3-Ph	98.1	103.8 ± 2.0	102.9
$(CH_3)_2CH-CH{=}CH_2$	89.6	99.9 ± 1.1	100.4
$PhCH_2-CH_2CH_3$	70.5	76.0 ± 1.1	77.1
$CH_3CH_2-CH_2CH{=}CH_2$	68.9	74.7 ± 0.9	74.5
$CH_2{=}CHCH_2-CH_2Ph$	57.8	62.9 ± 1.2	63.9
$(CH_3)_2CH-CH_2Ph$	68.3	76.7 ± 1.1	77.0
$CH_3CH_2-CH{=}CH_2$	91.8	100.2 ± 1.1	100.5
CH_3CH_2-Ph	93.9	101.5 ± 2.1	101.7
$(CH_3)_2CHCH_2-CH{=}CH_2$	91.8	99.8 ± 1.1	100.5
$CH_2{=}CHCH_2-CH_2CH{=}CH_2$	56.2	61.4 ± 0.8	61.3

[a] The same SE_H value is used for all primary alkyl radicals and similarly for all secondary and tertiary alkyl radicals, as done in refs 5 and 6. [b] Values in column 2 were calculated with BDE[CH_3-CH_3] = 90.12 and the SE_H values of ref 5. [c] Reference 7. [d] Reference 6.

question that remains is which measure of stabilization energy is more generally applicable and more accurate.

SE_H values, *by themselves*, do not provide a quantitative measure of radical stabilization energies. If they did, the energy for breaking the C−C bond of propane to form methyl and ethyl radicals would be smaller than the energy of breaking the C−C bond of ethane by the stabilization energies of ethyl and of methyl radicals, $SE_H[CH_3CH_2^\bullet]$ = 4.3 and $SE_H[CH_3^\bullet]$ = 0.0, respectively: BDE[$CH_3-CH_2CH_3$] = BDE[CH_3-CH_3] − $SE_H[CH_3CH_2^\bullet]$ − $SE_H[CH_3^\bullet]$ = 90.12 − 4.3 − 0.0 = 85.9 kcal mol^{-1}. There is poor agreement with the experimental value of 88.2 ± 0.5.

In the absence of steric or resonance effects, BDE of eq 17, must be valid for all R−R′ using stabilization energies (SE) that constitute an inherent property of the radical and are, therefore, directly transferable. Table 1 shows the results of applying eq 17 to some R−R and R−R′ using the reported SE_H and SE_A values.

$$\mathrm{BDE[R-R']} = \mathrm{BDE[CH_3-CH_3]} - \mathrm{SE[R^\bullet]} - \mathrm{SE[R'^\bullet]} \qquad (17)$$

All BDE values obtained with SE_H in Table 1 are low, one by as much as 10 kcal mol^{-1}. While various rationalizations may be offered for these failures, such as branching and/or protobranching,[5] the fact is that SE_H values, by themselves, fail the test of eq 17. SE_A values match not only the experimental BDE[C−C] of Table 1 but of hundreds of other BDE[A−A′].[6]

Because all 1° C−H bonds that are not resonance-stabilized have the same BDE, within experimental uncertainty, SE_H values only predict the BDE[R−H] from which they were derived. The 1° C−H BDEs are the same 100.9 ± 0.4 kcal mol^{-1} in ethane, propane, butane, isobutane, and neopentane. Therefore, all their values of SE_H = 4.3 are the same, and SE_H cannot be used to make any predictions of BDE[C−H]. The degree of branching or protobranching at carbons adjacent to the C−H bond in question does not affect such BDEs. The same is true for 2° and 3° C−H bonds.

It was argued[5] that C−H bonds are relatively nonpolar, and therefore, the dipole effect on BDE can be neglected in obtaining SE_H values. The dipole effect ($C^{\delta-}-H^{\delta+}$) is a relatively small contributor to BDE[R−H], but it is not small compared to the *difference* of, for example, BDE[CH_3-H] − BDE[$(CH_3)_2CH-H$] = 6.5 kcal mol^{-1}, which is the SE_H of 2° alkyl radicals. The dipole effect contributes to BDE an amount equal to $23(\Delta\chi)^2$.[6] The relevant electronegativities, χ, of the radicals are $\chi[CH_3^\bullet]$ = 2.525 and $\chi[(CH_3)_2CH^\bullet]$ = 2.411.[6] With the usually quoted average of $\chi[H^\bullet]$ = 2.1,[8] the contribution of the dipole effect to BDE[CH_3-H] is 4.15 kcal mol^{-1}, and to BDE[$(CH_3)_2CH-H$] it is 2.22. Their difference of 1.93 kcal mol^{-1} constitutes 30% of the SE_H value of 6.5 and cannot be neglected. Similar percentages are obtained with 1° and 3° $R^\bullet$.

TABLE 2. BDE[R−H] Calculated by eq 1, Corresponding Experimental Values and Calculated by eq 2 (kcal mol^{-1})

R−H	BDE[a] by SE_H	BDE[b] expt	BDE[c] by SE_A
$CH_2{=}CHCH_2-H$	88.1	88.1 ± 0.7	86.2
$C_6H_5CH_2-H$	89.7	89.7 ± 1.0	89.1
$(CH_3)_3C-H$	96.2	95.2 ± 0.7	95.1
$(CH_3)_2CH-H$	98.6	98.6 ± 0.5	97.8
$CH_3CH_2CH(CH_3)-H$	98.6	98.6 ± 0.5	97.8
CH_3CH_2-H	100.8	100.5 ± 0.5	99.0
$CH_3CH_2CH_2CH_2-H$	100.8	101.0 ± 0.6	99.0
CH_3-H	105.1	104.8 ± 0.2	101.2
$CH_2{=}CH-H$	111.0	110.6 ± 1.0	113.2
C_6H_5-H	113.1	113.2 ± 2.0	114.7

[a] Using BDE[CH_3-H] = 105.1, as cited in ref 5. [b] Values of the NIST database.[7] [c] From ref 6.

The SE_A approach takes account of the contribution to BDE by various bond dipoles and was demonstrated to obtain accurate BDE values for many different bonds between various A and A′ groups.[6] It does not obtain BDE[R−H] values as accurately as BDEs between all other common groups, and this is why BDE[R−H] values were not reported previously.[6] They are provided here in Table 2. The electronegativity of H is known to be somewhat variable, depending on the group to which H is attached. Pauling pointed out that hydrogen, uniquely, "misbehaves" but provided an average value of $\chi[H^\bullet]$ = 2.1,[8a] which is the value commonly used.[8b−d] Unique behavior by H is not uncommon in chemistry. Despite this known variability, Table 2 demonstrates that eq 2 with a literature value of $\chi[H^\bullet]$ = 2.1 yields results for BDE[R−H] much superior to those of the SE_H approach with BDE[R−R′] bonds in Table 1, in terms of deviation from experimental values.

Table 2 confirms that SE_H values "predict" experimental R−H values exactly, or to within experimental uncertainty, because they are derived from the values they predict. With the SE_A approach, three values in Table 2 are within the stated experimental uncertainty. The mean average deviation with SE_A in Table 2 is MAD = 1.5 kcal mol^{-1}. The largest deviation from an experimental value is 3.6 kcal mol^{-1} for BDE[CH_3-H]. Some of the values are high and others low. By comparison, the results of using SE_H in Table 1 have MAD = 6.6. All calculated values are low; the largest deviation is 10.3 kcal mol^{-1} and the smallest is 5.1. In the case of the worst possible performance test of eq 2, due to the known variability of χ[H], it is considerably more

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(8) (a) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. For the value of χ[H] = 2.1, see p 90 . (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A*, 3rd ed.; Plenum Press: New York, 1990; p 15. (c) Smith, M. B; March, J. *March's Advanced Organic Chemistry*, 5th ed.; Wiley-Interscience: New York, 2001; p 14. (d) Reference 1a, p 7.

accurate than eq 1 with a literature value of χ[H] = 2.1. Combining MAD values for the 23 entries of Tables 1 and 2 yields MAD = 3.84 kcal mol^{-1} for SE_H and MAD = 0.94 for SE_A. The combined MAD for SE_A values is smaller by a factor of 4, even though the SE_H values in Table 1 are exact within experimental error, by definition. SE_A values are more accurate, and eq 2 is indisputably more generally applicable to a large variety of radicals in conjunction with dipole contributions to BDE, which are also indisputable. Conversely, SE_H values are not defined for calculating BDE[Cl−OH], BDE-[H_3Si−F], etc. and are thus useless for such tasks.

To avoid the problem of dipole effects present in C−H bonds, Pauling used BDE[CH_2=$CHCH_2$−CH_2CH=CH_2] to obtain the stabilization of the allyl radical relative to that of methyl, as is done in Table 1. There is no dipole in symmetrical A−A species in eq 2. Rüchard, Beckwith, et al.[9a] also noted that radical stabilization energies (RSE) based on symmetrical R−R are preferable: "The advantages of the use of RSE's is that they avoid the problem that values of differences in BDE(C−H) clearly do not correspond accurately to the differences in stability between primary, secondary, and tertiary alkyl radicals." An extensive compilation of RSE values for the homolysis of C−C bonds is available.[9b]

An analogy was made between the SE_A and SE_H approaches to the effect that:[5] SE_A allows empirical predictions of BDE-[R−R] compared with BDE[CH_3−CH_3] just as SE_H allows empirical predictions of BDE[R−H] compared with BDE-[CH_3−H]. In restricting the comparison only to BDE[R−H] and BDE[R−R], the proffered analogy omits the fact that SE_A values were used not only to obtain accurate values of BDE-[R−R] *and* of BDE[R−R′], but also of many BDE[A−A′], such as Cl−OH, H_3Si−F, H_2N−NHPh, $PhCH_2$−NO_2, and over 100 other bonds.[6] This is not a minor omission for an unbiased comparison of either the accuracy or the generality of the two approaches. SE_A values are directly transferable to a large variety of bonds, despite their alleged "perturbation" or "contamination" by branching and/or protobranching.[5] SE_A[Cl$^•$] and SE_A[F$^•$] obtained by eq 2 were used to obtain the correct BDE[Cl−F],[6] and it is not clear how protobranching contaminates them or perturbs values of SE_A[HO$^•$], SE_A[$H_3Si^•$], etc. SE_H values are not directly transferable. They pertain only to carbon radicals and only to C−H bonds.

The best choice of a reference BDE may always be debated.[10,11] To avoid such debates and put an end to future ones, an alternative was proposed recently.[12] Radical *destabilization energies*, defined as DE[A$^•$] = 0.5 × BDE[A−A], do not depend on any one particular reference molecule or bond. For any bond free of steric strain or resonance effects, BDE[A−B] = DE[A$^•$] + DE[B$^•$] + $(\varepsilon_A - \varepsilon_B)^2$, where ε is the respective electronegativity index. Calculated BDEs for over 400 various bonds are in agreement with well established experimental values.[12]

Conclusions

Radical stabilization energies defined by eq 1 do not constitute an inherent property of R$^•$ because they are not directly transferable to any bonds except to those between carbon and hydrogen from which they are derived. Equation 1 is not generally applicable but is limited *only* to carbon-centered radicals. The most general, unambiguous, quantitative, and transferable measure for *all* radicals is their instability relative to no single reference molecule or BDE.

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