A Single Universal Scale of Radical Stabilization Energies Does Not Exist: Global Bond Dissociation Energies and Radical Thermochemistries Are Described by Combining Two Universal Scales

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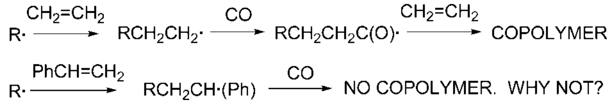

Results from any single scale of radical stabilization energies are dependent on the species chosen for setting its zero. A scale of radical destabilization energies with a universal zero reference point is shown to exist, but it must be used in conjunction with a universal scale capable of describing the polarities of bonds broken and formed. The use of the two scales is demonstrated for calculating bond dissociation enthalpies, enthalpies of reactions, enthalpies of formation, and the magnitude of steric effects, resonance, and conjugation stabilization. Examples of applications include explanations of some observed effects in autoxidations and polymerizations.

Introduction

A universal scale of radical stabilization energies has been the subject of extensive research, with mixed results. Pauling seems to have adopted the strengths of R−H bonds relative to H−H as a standard for a rough measure.[1] The weaker the R−H bond relative to H−H, the more stable the radical, presumably because it is easier to form the particular R•, with H• being the common other product. The CH_3−H bond is currently the most commonly used reference. The bond strength decreases in the series CH_3−H > CH_3CH_2−H > $(CH_3)_2CH$−H > $(CH_3)_3C$−H, and the radical stabilization energies (SE) increase in the reverse order $(CH_3)_3C\bullet$ > $(CH_3)_2CH\bullet$ > $CH_3CH_2\bullet$ > $CH_3\bullet$. The problem is that, when CH_3−F is taken as the reference compound, the order of the bond strengths is $(CH_3)_3C$−F ≈ $(CH_3)_2CH$−F > CH_3CH_2−F > CH_3−F. With F• as the common product, the bond easiest to cleave is that of CH_3−F. Therefore, the methyl radical now appears as the most stable. Another way used is to compare enthalpies of reactions. The more endothermic hydrogen abstraction presumably involves the more stable abstracting radical: for $CH_3\bullet + H{-}CH_3 \rightarrow CH_3{-}H + CH_3\bullet$, $\Delta H_{rxn} = 0$ kcal mol^{-1} and for $(CH_3)_3Si\bullet + H{-}CH_3 \rightarrow (CH_3)_3Si{-}H + CH_3\bullet$, $\Delta H_{rxn} \approx 11$, indicating that trimethylsilyl is more stable than the methyl radical. When the reactions involve abstraction of a chlorine atom instead, $CH_3\bullet + Cl{-}CH_3 \rightarrow CH_3{-}Cl + CH_3\bullet$, $\Delta H_{rxn} = 0$ kcal mol^{-1} and for $(CH_3)_3Si\bullet + Cl\text{-}CH_3 \rightarrow (CH_3)_3Si{-}Cl + CH_3\bullet$, $\Delta H_{rxn} \approx -28$, indicating that the methyl radical is more stable than trimethylsilyl. Such reversals, depending on the standard reference bond chosen, have been a perennial problem. Confusion also arises when a correlation is sought between radical stabilization energies and radical reactivity or persistence.

Definitions of stabilization energies (SE) that do not also account for the dipole of the bonds being broken or made will always fail, when the reference bond is changed. Bond dipoles affect bond strengths, often in major ways. We have proposed[2] a set of stabilization energies defined by eq 1 in terms of bond dissociation energies (BDE), an approach also used by Pauling.

$$\mathrm{SE[A\bullet]} = \frac{1}{2}(\mathrm{BDE[CH_3\text{-}CH_3]} - \mathrm{BDE[A{-}A]}) \qquad (1)$$

Taking account of bond dipoles is most simply done via Pauling-type electronegativities. SE values obtained by eq 1 were relative to SE[$CH_3\bullet$] = 0.0. Some zero reference must be set for any scale. This definition apparently has left the erroneous impression that comparisons can be made only to CH_3−CH_3,

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[1] (a) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570–3582. (b) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. BDE[A−B] = $^1/_2$(BDE[A−A] + BDE[B−B]) + 23(χ[A]−χ[B])^2.

[2] Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158–3172, Electronegativities were not obtained from global fits, but from only two typical molecules in each case.

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TABLE 1. Radical Destabilization Energies (DE) and Electronegativities (ε)

radical	DE[a]	ε
$HC\equiv C\cdot$	78.5	13.376
$N\equiv C\cdot$	69.6	13.908
$C_6H_5\cdot$	58.0	12.220
$CH_2{=}CH\cdot$	56.5[b]	12.220
$\cdot CH_2\cdot$	53.6	12.109
$BH_2\cdot$	52.5	8.968
$CH_3\cdot$	44.9	12.109
$CH_3CH_2\cdot$	44.2	11.807
$(CH_3)_2CH\cdot$	43.5	11.563
$(CH_3)_3C\cdot$	41.2[c]	11.404
$(CH_3)_3Si\cdot$	39.0	8.815
$SiH_3\cdot$	38.0	9.011
$CH_3C(O)\cdot$	37.0	10.719
$NH_2\cdot$	33.6	14.728
$C_6H_5CH_2\cdot$	33.3	12.018
$CH_3NH\cdot$	31.4	14.474
$H_2C{=}CHCH_2\cdot$	30.7	11.938
$CH_3S\cdot$	30.5	12.469
$Cl\cdot$	29.0	15.222
$PH_2\cdot$	27.7	10.901
$HO\cdot$	25.6	16.785
$C_6H_5NH\cdot$	22.0	14.632
$F\cdot$	19.0	18.886
$CH_3O\cdot$	19.0	16.493
$(CH_3)_3CO\cdot$	19.0	16.272
$O_2NO\cdot$	12.3	16.992
$NF_2\cdot$	11.0	15.471
$HOO\cdot$	7.5	16.258
$O_2N\cdot$	6.8	15.236
$C_6H_5O\cdot$	1.8	16.191
$ON\cdot$	−5.5	11.400
$ONO\cdot$	−5.7	16.478
$\cdot OO\cdot$	−23.3	15.174
$O\equiv C$	−33.6	11.903

[a] In kcal mol^{-1} at 298 K. [b] Resonance-free value. [c] Strain-free value.

rather than between any A$\cdot$ and B$\cdot$. In this work, a global scale is presented to be used with electronegativity values, ε. The validity of the approach is demonstrated even with negative bond dissociation energies, an unusual concept, but a valid one, as will be demonstrated.

Results and Discussion

Rather than defining radical stabilizations, we define radical destabilizations, DE. We set the zero of a scale of destabilization energy of radical A$\cdot$ at the zero of $^1/_2$(BDE[A−A]). Values so obtained are given in Table 1. With zero of the DE scale set at BDE[A−A] = 0, no confusion is introduced as to what compound sets the zero. All symmetrical A−A compounds do. Hence, this is a global scale of DE. For example, DE[$CH_3\cdot$] = $^1/_2$(BDE[CH_3-CH_3]) = $^1/_2$(89.8) = 44.9 kcal mol^{-1}, DE[Cl$\cdot$] = $^1/_2$(BDE[Cl−Cl] = $^1/_2$(58.0) = 29.0, etc. The last four entries of Table 1 require some comment, as they indicate negative BDE, and will be discussed below.

With such a DE scale, BDE of combinations of any A$\cdot$ and B$\cdot$ can be calculated with high accuracy by eq 2, using the global DE values and accounting for dipoles via ε.

$$\mathrm{BDE[A{-}B]} = \mathrm{DE[A\bullet]} + \mathrm{DE[B\bullet]} + (\varepsilon[\mathrm{A\bullet}] - \varepsilon[\mathrm{B\bullet}])^2 \quad (2)$$

Equation 2 is a restatement of Pauling's electronegativity equation,[1,2] in a somewhat more simplified form. There does not appear to have been a connection previously made between eq 2 and radical destabilization energies with a scale having a global zero. A self-consistent set for atoms and groups obtained previously[2] and enlarged in this work is also given in Table 1. The previously obtained values of χ are multiplied by $23^{1/2}$ to yield ε for eq 2. The group value χ[HO$\cdot$] was previously assigned as 3.500, equal to Pauling's value for the O in order not to proliferate scales, and now becomes ε[HO$\cdot$] = 16.785. The squared term in eq 2 can be viewed as accounting for the attractive force between charges of an electrostatic dipole in $^{\delta+}A-B^{\delta-}$, consistent with Coulomb's Law that requires the force to be proportional to the square of the charge. This explains the peculiar units of ε in kcal$^{1/2}$ mol$^{-1/2}$ and of $(\Delta\varepsilon)^2$ in kcal mol^{-1}. The electronegativity, ε[$CH_2{=}CH$], and the resonance-free value of DE[$CH_2{=}CH\cdot$] in Table 1 are obtained from the known BDE values of $CH_2{=}CH{-}CH_3$ and of $CH_2{=}CH{-}Cl$ and the established values of DE[$CH_3\cdot$] = 44.9, DE[Cl$\cdot$] = 29.0, ε[$H_3C\cdot$] = 12.109, and ε[Cl$\cdot$] = 15.222.[3]

Some examples of the application of eq 2 are provided below vs literature values, which are from the NIST database No. 69,[4] unless specified otherwise. A wide variety of common organic molecules are shown, as well as common radicals. Most of the bonds shown below were not treated in our previous work.[2] These typical examples provide an indication of the level of accuracy obtained. BDE values are for the gas phase in kcal mol^{-1}at 298 K.

BDE[$(CH_3)_3CO{-}Cl$] = 19.0 + 29.0 + (16.272 − 15.222)^2 = 49.1 vs 47.7 ± 2.[5]

BDE[$(CH_3)_3CO{-}CH_3$] = 19.0 + 44.9 + (16.272 − 12.109)^2 = 81.2 vs 81.2.

BDE[$(CH_3)_2CH{-}CH_2\cdot$] = 43.3 + 53.6 + (11.563 − 12.109)^2 = 97.2 vs 97.4.

BDE[F−OH] = 19.0 + 25.6 + (18.886 − 16.785)^2 = 49.0 vs 51.8 and 48.9.[6]

BDE[$C_6H_5{-}CO\cdot$] = 58.0 + (−33.6) + (12.220 − 11.903)^2 = 24.5 vs 26.4.[7]

BDE[F−CN] = 19.0 + 69.6 + (18.886 − 13.908)^2 = 113.4 vs 114.4.

BDE[$CH_3{-}ONO$] = 44.9 + (−5.7) + (12.109 − 16.478)^2 = 58.3 vs 58.4.

BDE[Cl−ONO] = 29.0 + (−5.7) + (15.222 − 16.478)^2 = 24.9 vs 23.6[8] and 24.6.[9]

BDE[HO−ONO] = 25.6 + (−5.7) + (16.785 − 16.478)^2 = 20.0 vs 19.7 ± 2[10] and 20.4.[11]

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(3) The are no resonance effects in BDE[$CH_2{=}CH{-}CH_3$] = 101.4 and BDE[$CH_2{=}CH{-}Cl$] = 94.5 kcal mol^{-1}. Using eq 2, we obtain two equalities with two unknown values: BDE[$CH_2{=}CH{-}CH_3$] = DE[$CH_2{=}CH\cdot$] + DE[$CH_3\cdot$] + (ε[$CH_2{=}CH\cdot$]−ε[$H_3C\cdot$])^2 and BDE[$CH_2{=}CH{-}Cl$] = DE[$CH_2{=}CH\cdot$] + DE[Cl$\cdot$] + (ε[$CH_2{=}CH\cdot$]−ε[Cl$\cdot$])^2. The unknowns are DE[$CH_2{=}CH\cdot$] and ε[$CH_2{=}CH\cdot$]. Substituting the known values and solving yields ε[$CH_2{=}CH\cdot$] = 12.220 and DE[$CH_2{=}CH\cdot$] = 56.5 kcal mol^{-1}. The strain-free value of DE[$(CH_3)_3C\cdot$] and ε[$(CH_3)_3C\cdot$] are similarly obtained by assuming no significant steric strain in $(CH_3)_3C{-}CH_3$ and in $(CH_3)_3C{-}Cl$.

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BDE[HOO−NO] = 7.5 + (−5.5) + $(16.258 - 11.400)^2$ = 25.6 vs 26.0.[12]

BDE[CH_3O−NO] = 19.0 + (−5.5) + $(16.493 - 11.400)^2$ = 39.4 vs 41.8.[13]

BDE[$C_6H_5CH_2$−NF_2] = 33.3 + 11.0 + $(12.018 - 15.471)^2$ = 56.2 vs 57.8.

BDE[$(CH_3)_3C$−NF_2] = 41.2 + 11.0 + $(11.404 - 15.471)^2$ = 68.7 vs 67.7.

BDE[CH_3−OO•] = 44.9 + (−23.3) + $(12.109 - 15.174)^2$ = 31.0 vs 32.4.[13]

BDE[$C_6H_5CH_2$−OO•] = 33.3 + (−23.3) + $(12.018 - 15.174)^2$ = 20.0 vs 20 ± 1.[14]

BDE[HC≡C−C≡CH] = 78.5 + 78.5 = 157.0 vs 157.0.[15]

BDE[HC≡C−C≡N] = 78.5 + 69.6 + $(13.376 - 13.908)^2$ = 148.4 vs 152.4 and 143.9.[13]

BDE[H_2B−F] = 52.5 + 19.0 + $(8.968 - 18.886)^2$ = 170.0 vs 172.4.[16]

BDE[CH_3CH_2−C(O)•] = 44.2 + (−33.6) + $(11.807 - 11.903)^2$ = 10.6 vs 10.2.[17]

BDE[$(CH_3)_3CO$−$Si(CH_3)_3$] = 19.0 + 39.0 + $(16.272 - 8.815)^2$ = 113.6 vs no experimental value.

BDE[CH_2=$CHCH_2$−OOH] = 30.7 + 7.5 + $(11.932 - 16.258)^2$ = 56.9 vs no experimental value.

BDE[C_6H_5O−OC_6H_5] = 1.6 + 1.6 = 3.6 vs no experimental value, but C_6H_5O• does not couple.

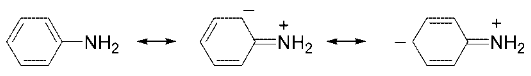
BDE[$C_6H_5CH_2$−C(O)•] = 33.3 + (−33.6) + $(12.018 - 11.903)^2$ = −0.3 vs no experimental value, but known rapid decarbonylation.

Agreement is good with covalent bonds, including highly polar ones and those of negative BDE, when reliable experimental values are available. Deviations between calculated and well-established experimental values are seldom larger than 2 kcal mol^{-1}. Eq 2 and the values of Table 1 provide BDE for combinations of the species listed therein (see Supporting Information). Many of these are not currently known from experiment, and four such examples are given at the end of the above list.

Notable by its absence from Table 1 is hydrogen. Hydrogen is unique in that, unlike any other atom or group, its electronegativity is variable and eq 2 would yield approximate values only, using DE[H•] = 52.1 and ε[H•] = 10.551. In Pauling's words, "hydrogen misbehaves".

When "special effects" are present, the difference between the calculated and actual value is a quantitative measure of the effect. A special effect is one that exists in the molecule, but not in the individual fragments. The calculated BDE[$(CH_3)_3C$−$C(CH_3)_3$] is greater than the experimental value by 6.4 kcal mol^{-1}, the known steric strain of the species. The calculated BDE[CH_2=CH−CH=CH_2] is 3.6 kcal mol^{-1} weaker than the experimental value, consistent with the extent of the known conjugation stabilization of 1,3-butadiene. Such an effect is not present in BDE[CH_2=CH−CH_3], for example. With the values of Table 1 and eq 2, BDE[C_6H_5−CH_2•] = 111.6 kcal mol^{-1} is obtained versus the experimental value of 123.9. The difference, 12.3 kcal mol^{-1}, is the usually quoted resonance stabilization energy of the benzyl radical. Also, BDE[•CH_2−CH_2•] = 107.2 kcal mol^{-1} is obtained by eq 2, compared to experimental BDE[CH_2=CH_2] = 172.3. The difference of 65.1 kcal mol^{-1} is the usually quoted value of the strength of the π bond of ethylene.

Aniline is extremely reactive in electrophilic aromatic substitutions. The calculated BDE[C_6H_5−NH_2] is 7.8 ± 2 kcal mol^{-1} weaker than the experimental value, because of resonance structures that impart strong negative charge at the ortho and para positions of the ring and induce partial double bond character to the C−N bond. This resonance effect is substantially greater than the conjugation stabilization of 1,3-butadiene.



Such differences between calculated and experimental values are not failures of eq 2, but provide a good measure of the magnitude of the special effect, as established by other approaches. Resonance effects, similar to those in aniline, are present in bonds of sp^2- and sp-hybridized atoms to oxygen, amine nitrogen, and •CH_2•. Examples of such sp^2- and sp-hybridized atoms are H_2B•, RCH_2=CH•, RC≡C•, O_2N•, C_6H_5•, etc.

The electronegativities listed in Table 1 pertain to neutral species in their normal valence state, as explicitly specified by Pauling.[1] Equation 2 should not be applied to species such as C−H, Al−Cl, HB-CH_3, etc., because the atoms involved in the bond are not in their normal valence state. Inappropriate application of Pauling's equation to such species and to bonds to H have led to the misconception that the electronegativity equation is not accurate in general.

The successful use of negative bond dissociation energies with eq 2 in the examples provided above can be understood in terms of the species involved. Two molecules of carbon monoxide do not couple (O≡C−C≡O does not exist). A good estimate of the repulsion between two CO molecules at covalent bond distances is obtained by using eq 2. With the known value of BDE[CH_3−C(O)• = 11.3 kcal mol^{-1} and the established ε[H_3C•] = 12.109 and ε[CO] = 11.903, eq 2 yields:

$$\mathrm{BDE[CH_3{-}C(O)\bullet] = DE[CH_3\bullet] + DE[C{\equiv}O]} + (\varepsilon[\mathrm{H_3C\bullet}] - \varepsilon[\mathrm{CO}])^2$$

$$11.3 = 44.9 + \mathrm{DE[C{\equiv}O]} + (12.109 - 11.903)^2$$

Solving for DE[C≡O] gives −33.6 kcal mol^{-1}, or a repulsion of 67.2 kcal mol^{-1} between the carbons of two CO molecules at covalent bond distances. Using this negative DE for CO in eq 2 yields BDE[F−C(O)•] = 34.1 versus the experimental value[4] of 33.6 kcal mol^{-1} and reasonably accurate values for BDE[C_6H_5−C(O)•] (see above) and BDE[Cl−C(O)•] = 6.4 kcal mol^{-1} versus a literature value of 6.6.[13]

Among the negative DE values of Table 1 is that of ONO−ONO, from BDE[ONO−ONO] = −11.3 kcal mol^{-1}, due to a spin-forbidden barrier to dissociation into ground-state NO_2.

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This interesting molecule exists, but its energy lies above the energy of two ground-state NO_2, which is the definition of BDE. This peroxide dissociates to yield NO_2 in the excited $^2B_2$ state that relaxes into the $^2A_1$ ground state, releasing energy. Hence, bond cleavage of ONO−ONO is exothermic. A CBS-QB3 calculation, including zero point energy correction, gave BDE = −11.2 kcal mol^{-1} for the most stable cis−cis conformer.[18] The value of −11.3 used in this work was obtained from eq 3, which is a mathematical corollary of eq 2, to be used when BDE[X−X] is not known.[2]

$$\mathrm{BDE[A-X]-BDE[B-X]} = a + b(\varepsilon[\mathrm{X}\bullet]) \qquad (3)$$

The constants a and b are: $a = {}^1/_2(\mathrm{BDE[A-A]} - \mathrm{BDE[B-B]}) + \{(\varepsilon[\mathrm{A}\bullet])^2 - (\varepsilon[\mathrm{B}\bullet])^2\}$ and $b = 2(\varepsilon[\mathrm{B}\bullet] - \varepsilon[\mathrm{A}\bullet])$. Denote A−X = CH_3−ONO and B−X = Cl−ONO. BDE[CH_3−ONO] = 58.37, BDE[Cl−ONO] = 25.0, BDE[CH_3−CH_3] = 89.8, and BDE[Cl−Cl] = 58 kcal mol^{-1} are known.[4] The values of $\varepsilon[H_3C\bullet]$ and $\varepsilon[Cl\bullet]$ have been established (Table 1). Substituting the known values, we obtain $a = {}^1/_2(89.8 - 58.0) + (12.109^2 - 15.222^2) = -69.17$ and $b = 2(15.222 - 12.109) = 6.226$. Substitution into eq 3 gives $58.4 - 25.0 = -69.17 + 6.226(\varepsilon[\mathrm{ONO}\bullet])$. Solving for $\varepsilon[\mathrm{ONO}\bullet]$ yields 16.478. With $\varepsilon[\mathrm{ONO}\bullet]$ established, substitution into eq 2 yields BDE[CH_3−ONO] = DE[$CH_3\bullet$] + DE[ONO•] + $(\varepsilon[H_3C\bullet] - \varepsilon[\mathrm{ONO}\bullet])^2$. Inserting the known values leads to 58.37 = 44.9 + DE[ONO−ONO] + $(12.109 - 16.478)^2$. Solving yields DE[ONO−ONO] = −5.65 and BDE[ONO−ONO] = 2 × DE = 2 × (−5.65) = −11.3, in remarkable agreement with the theoretical result of −11.2 kcal mol^{-1}. The other negative DE values of Table 1 were obtained in the same fashion. Although the negative BDE for O≡C−C≡O and •OO−OO• may be fictitious, the negative BDE of ONO−ONO is real. All treated negative BDE values perform successfully with eq 2 and its corollaries.

Enthalpies of formation ($\Delta_f H^o$) can also be obtained by eq 2 and values from Table 1, as shown in the following examples. For $CH_3CH_2\bullet + \bullet CH_2\bullet \rightarrow CH_3CH_2CH_2\bullet$, eq 2 gives BDE[$CH_3CH_2$−$CH_2\bullet$] = 97.9 kcal mol^{-1}. From the thermodynamic relation BDE[CH_3CH_2−$CH_2\bullet$] = $\Delta_f H^o$[$CH_3CH_2\bullet$] + $\Delta_f H^o$[$\bullet CH_2\bullet$] − $\Delta_f H^o$[$CH_3CH_2CH_2\bullet$], and the known[4] $\Delta_f H^o$[$CH_3CH_2\bullet$] = 28.7 and $\Delta_f H^o$[$\bullet CH_2\bullet$] = 92.35, $\Delta_f H^o$[$CH_3CH_2CH_2\bullet$] = 23.2 is obtained versus a literature value of 23.9 ± 0.5 kcal mol^{-1}.[4] Similarly by eq 2, BDE[CH_2=$CHCH_2$−OO•] = 17.9, from which $\Delta_f H^o$[CH_2=$CHCH_2OO\bullet$] = 23.0 kcal mol^{-1} is obtained versus the experimental value of 21.0 ± 1.3.[13] $\Delta_f H^o$[$FCH_2\bullet$] = −7.2 is similarly obtained versus a literature value[13] of −7.6 kcal mol^{-1}. $\Delta_f H^o$[ClC(O)•] = −3.8 kcal mol^{-1} is also obtained versus disparate literature values of −15.0,[4] −5.2,[13] and −4.0.[7]

Equation 2 and the values of Table 1 yield BDE[CH_3S-OO•] = 30.5 + (−23.3) + $(12.469 - 15.174)^2$ = 14.5 kcal mol^{-1} for a reaction that leads to autoxidation of RSH groups in proteins, via $RS\bullet + O_2 \rightarrow RSOO\bullet$. The thiylperoxy radical rearranges to a sulfonyl radical $RSO_2\bullet$, which reacts with O_2 to give $RSO_2OO\bullet$ and leads to H abstraction from another R′SH to form R′S• and to continue the autoxidation. Theoretical calculations[2] give BDE[CH_3S−SCH_3] = 61 kcal mol^{-1} and, from the known $\Delta_f H^o$[CH_3S-SCH_3] = −5.8,[4] we obtain $\Delta_f H^o$[$CH_3S\bullet$] = 27.6 kcal mol^{-1}. An experimental study of $CH_3S\bullet + O_2 \leftrightarrows CH_3SOO\bullet$ gave BDE[CH_3S-OO•] = 11.7 ± 0.9 kcal mol^{-1} by using an older value of $\Delta_f H^o$[$CH_3S\bullet$] = 29.8,[19] or 2.2 kcal mol^{-1} greater than the theoretical 27.6 adopted here. When the reported BDE is corrected by 2.2, BDE[CH_3S–OO•] = 13.9 ± 0.9 is obtained, compared to 14.5 kcal mol^{-1} by the present calculation, in excellent agreement. This low value of BDE explains the fact that the reaction of $CH_3S\bullet$ with O_2 has been reported to be reversible, even though it is diffusion-controlled.[20]

Another example of the use of eq 2 pertains to the radical chain copolymerization of alkenes with CO under pressure. Ethylene copolymerizes, but styrene has not been reported to do so in such reactions. Copolymerization of ethylene with CO results in forming a bond of BDE[RCH_2CH_2−C(O)•] = 10.6 kcal mol^{-1} by eq 2 (see above), whereas styrene would have to form a bond of BDE[$C_6H_5CH(R)$−C(O)•] < −0.3, which does not occur. Decarbonylation of $C_6H_5CH_2$−C(O)• is reported to be slightly exothermic,[21] consistent with BDE = −0.3 kcal mol^{-1} by eq 2. The value of BDE[CH_3CH_2−C(O)•] = 10.6 kcal mol^{-1} by eq 2 is in excellent agreement with a reported value of 10.2.[17]

The DE value of each radical cannot be a measure of its rate of reaction with various species or sites of a particular species. DE is a thermodynamic quantity and, as such, is not necessarily related to kinetics. Time is not a thermodynamic quantity. The reaction $C + O_2 \rightarrow CO_2$ is very exothermic and thermodynamically spontaneous, but its rate of reaction at room temperature is nil. The approach provided here is useful in calculating relative exothermicities of radical reactions so that, in closely related reactions, the faster one can be ascertained.

The phenoxyl radical is the one nearest to zero on the DE scale. It does not couple head to head with itself at room temperature, because BDE[C_6H_5O−OC_6CH_5] is less than 4 kcal mol^{-1}. This is not sufficient to overcome the unfavorable entropy change. However, this does not mean that phenoxyl radicals are unreactive. Two phenoxyl radicals do react head to tail to give $C_6H_5OC_6CH_5$=O, because the new C−O bond formed is stronger than 40 kcal mol^{-1} due to the electronegativity difference between carbon and oxygen. Phenoxyl radicals can be surprisingly reactive.[22] Phenolic antioxidants, for example, vitamin E, are good radical traps when the ring positions are blocked. Although antioxidant properties are often ascribed to the weak C_6H_5O−H bond of 87 kcal mol^{-1}, making it a good hydrogen donor to autoxidation chain propagating ROO• radicals, this is not the only, or even the major, factor. Toluene has an equally weak benzyl−H bond and is not an antioxidant. Benzyl radicals couple with oxygen to yield $C_6H_5CH_2OO\bullet$ that propagates the chain of autoxidation. Phenoxyl radicals cannot be chain carriers, because the values of Table 1 and eq 2 yield BDE[C_6H_5O–OO•] = −20.5 kcal mol^{-1}, a repulsion, and the species is not formed. By comparison, BDE[$C_6H_5CH_2$−OO•] = 20 kcal mol^{-1}, and its formation propagates autoxidation.

Additional comparisons between literature values and those calculated in this work are provided in Table 2 for some species produced in the atmosphere by radical reactions. The literature values are from a compilation by the Jet Propulsion Laboratory-National Aeronautics and Space Administration (JPL-NASA)[23]

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TABLE 2. Bond Dissociation Energies and Enthalpies of Formation of Species of Interest in Atmospheric Studies[a]

species	BDE JPL-NASA	BDE calcd	$\Delta_f H^o$ JPL-NASA	$\Delta_f H^o$ calcd
$\mathrm{CH_3O{-}Cl}$[b]	48.5 ± 1.5	49.6	−15.5 ± 1.5	−16.4
$\mathrm{CH_3{-}OO\cdot}$	32.9 ± 1.2	31.0	2.2 ± 1.2	3.8
$\mathrm{CH_3{-}OOH}$	71.5 ± 2.0	69.6	−33.3 ± 1.9	−31.3
$\mathrm{CH_3{-}C(O)\cdot}$	11.1 ± 0.3	11.3	−2.4 ± 0.3	−2.9
$\mathrm{CH_3{-}ONO}$	58.5 ± 0.1	58.3	−15.3	−15.6
$\mathrm{CH_3{-}ONO_2}$	81.9 ± 1.3	81.0	−29.2 ± 1.1	−29.2
$\mathrm{CH_3CH_2{-}OO\cdot}$	35.5 ± 2.4	32.2	−6.6 ± 2.4	−3.8
$\mathrm{CH_3CH_2{-}OOH}$	74.0 ± 3.3	71.5	−41.9 ± 3.3	−39.6
$\mathrm{(CH_3)_2CH{-}OO\cdot}$	36.3 ± 2.8	32.2	−15.6 ± 2.7	−10.2
$\mathrm{HO{-}F}$	51.4 ± 1.1	49.0	−23.5 ± 1.0	−20.7
$\mathrm{HO{-}Cl}$	55.8 ± 0.3	57.0	−17.9 ± 0.3	−18.7
$\mathrm{HO{-}NH_2}$	63.4 ± 2.2	63.4	−9.6 ± 2.2	−8.6
$\mathrm{HO{-}NO}$[b]	49.5 ± 0.3	49.1	−18.8 ± 0.2	−18.2
$\mathrm{HO{-}ONO}$[b]	22.8	20.0	−5.7	−2.8
$\mathrm{HO{-}ONO_2}$	39.6 ± 1.0	37.9	−12.7 ± 0.6	−11.6
$\mathrm{F{-}C(O)\cdot}$	31.1 ± 2.0	34.2	−38.5 ± 2.0	−41.6
$\mathrm{F{-}OO\cdot}$[c]	12.9 ± 0.5	9.5	6.1 ± 0.5	10.0
$\mathrm{F{-}ONO}$[c]	11.1	19.1	16.0	7.9
$\mathrm{F{-}ONO_2}$	34.0 ± 0.8	34.9	2.5 ± 0.5	1.1
$\mathrm{F{-}Cl}$	61.3 ± 0.2	61.4	−13.3 ± 0.1	−13.4
$\mathrm{Cl{-}CH_2\cdot}$	94.3 ± 0.9	92.3	28.0 ± 0.7	29.1
$\mathrm{Cl{-}OO\cdot}$	5.6 ± 1.0	5.6	23.4 ± 1.0	23.4
$\mathrm{Cl{-}OOH}$[b]	32.0 ± 1.0	37.6	0.2 ± 0.1	−5.1
$\mathrm{Cl{-}NO}$	38.2 ± 0.1	38.1	12.6 ± 0.1	12.5
$\mathrm{Cl{-}ONO}$[b]	21.8 ± 2.0	24.9	15.4 ± 1.5	12.0
$\mathrm{Cl{-}NO_2}$	34.2 ± 0.5	35.8	3.0 ± 0.3	1.1
$\mathrm{Cl{-}ONO_2}$	41.1 ± 0.6	44.4	5.5 ± 0.5	1.4

[a] In kcal mol^{-1}. Literature[23] values and calculated in this work. [b] Calculated JPL-NASA values. [c] Estimated JPL-NASA values.

for all values in common with this work. Agreement is generally good with the experimental values reported. The greatest discrepancies of 8.0 and 5.6 kcal mol^{-1} for F−ONO and Cl−OOH, respectively, are not with experimental values; the former is described as "estimated" and the latter as "calculated" in the JPL-NASA compilation.

The group electronegativities of Table 1 are somewhat different from Pauling-type group elctronegativities reported by others, especially those resulting from global fits that include many bonds to H. For example, values of $\varepsilon/(23^{1/2})$ of this work can be compared to χ_G values of Datta and Singh obtained from BDEs of bonds to H,[24] as follows (D and S values in parentheses, with χ_G[H] fixed at 2.1): $\mathrm{CH_3}$, 2.525 (2.68); $\mathrm{CH_3CH_2}$, 2.462 (2.59); HO, 3.500 (3.46); $\mathrm{H_2N}$, 3.071 (3.10); $\mathrm{O_2N}$, 3.177 (3.38); F, 3.938 (4.00); Cl, 3.174 (3.00); $\mathrm{F_2N}$, 3.226 (3.18); $\mathrm{H_3Si}$, 1.879 (1.76); and $\mathrm{(CH_3)_3CO}$, 3.393 (3.41). Differences are due to the known variable electronegativity of H.[1,2]

The SE values reported previously[2] can be obtained by SE = 44.9 − DE, for species in common with the previous work.[2] In this work, the zero has been shifted in the DE scale, many additional compounds are treated, and negative BDE values are used successfully. The overall accuracy of the method can be evaluated further by comparing values reported in the Tables of the Supporting Information to well-established BDE values.

High level ab initio calculations are now feasible for reasonably sized molecules, but the method presented here has its advantages: it is much simpler and not less accurate, when applicable; it provides conceptual insights into the effects of radical destabilization energies and the effect of bond dipoles; and it allows quantitative evaluation of the magnitude of special effects.

Conclusions

Corollaries of Pauling's electronegativity equation provide a "universal" scale of radical destabilization energies for use with electronegativity differences. A scale with a common zero for all species is conceptually advantageous. Eq 2 is useful in calculating enthalpies of reactions, enthalpies of formation, experimentally unavailable BDE and $\Delta_f H^o$ values, and the magnitude of effects of resonance, conjugation stabilization, and steric hindrance, as well as aspects of behaviors of antioxidants and of copolymerizations. The successful use of negative BDE values with eq 2 is demonstrated.

Supporting Information Available: Five Tables of all calculated BDE values. This material is available free of charge via the Internet at http://pubs.acs.org.

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