Pauling's Electronegativity Equation and a New Corollary Accurately Predict Bond Dissociation Enthalpies and Enhance Current Understanding of the Nature of the Chemical Bond

Nikita Matsunaga, Donald W. Rogers, and Andreas A. Zavitsas*

Department of Chemistry and Biochemistry, Long Island University, University Plaza, Brooklyn, New York 11201

zavitsas@liu.edu

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Contrary to other recent reports, Pauling's original electronegativity equation, applied as Pauling specified, describes quite accurately homolytic bond dissociation enthalpies of common covalent bonds, including highly polar ones, with an average deviation of ±1.5 kcal mol^{-1} from literature values for 117 such bonds. Dissociation enthalpies are presented for more than 250 bonds, including 79 for which experimental values are not available. Some previous evaluations of accuracy gave misleadingly poor results by applying the equation to cases for which it was not derived and for which it should not reproduce experimental values. Properly interpreted, the results of the equation provide new and quantitative insights into many facets of chemistry such as radical stabilities, factors influencing reactivity in electrophilic aromatic substitutions, the magnitude of steric effects, conjugative stabilization in unsaturated systems, rotational barriers, molecular and electronic structure, and aspects of autoxidation. A new corollary of the original equation expands its applicability and provides a rationale for previously observed empirical correlations. The equation raises doubts about a new bonding theory. Hydrogen is unique in that its electronegativity is not constant.

Introduction

During 2001, the centennial year of Linus Pauling's birth, we reexamined his equation[1] relating electronegativity to homolytic bond dissociation enthalpy:

$$D[\text{A-B}] = \frac{1}{2}\,(D[\text{A-A}] + D[\text{B-B}]) + 23(\Delta\chi)^2 \quad (1)$$

The bond dissociation enthalpy (D) of A-B is given by two terms. The first is the covalent term and involves what may be called the inherent bonding ability of A and B atoms or groups, expressed by $D[\text{A-A}]$ and $D[\text{B-B}]$. The second is the polar term, takes account of the relative tendency of A and B to distort the equal sharing of bonding electrons, generating a dipole between A and B, and is given by the square of the difference in their electronegativity $(\Delta\chi)^2 = (\chi[\text{A}] - \chi[\text{B}])^2$. The factor 23 is a proportionality constant for units of kcal mol^{-1}. Pauling defined electronegativity as representing "the attraction of a neutral atom in a stable molecule for electrons," with the atom being in its "normal oxidation state." This excludes salts. An arbitrary χ scale was established for

the elements, fluorine being assigned a value of 4.0, oxygen 3.5, carbon 2.5, etc.

Much has been written about eq 1, some complimentary and some critical, especially in recent years, and we do not attempt to provide a complete list of works on the topic. Efforts have been made to improve the accuracy of eq 1 by adding other factors to it. Typical examples are works adding polarizability terms[2] or devising new electronegativity scales and taking account of various other molecular properties.[3] A recent work includes a good description of such approaches.[3d] One recent reexamination concluded that eq 1 is valid for only a small number of bonds of low polarity, involving the halogens, O, S, N, P, C, and H,[4a] whereas another concluded that it fails with bonds to sulfur and iodine.[4b] An extensive investigation of 171 bonds of all hybridizations involving metals and nonmetals of the first three rows of the periodic table found a root-mean-square error of 7.3 kcal mol^{-1} when using eq 1.[2] This large an error not only would destroy any utility of eq 1 for predictive purposes but also undermines the whole idea of electronegativity as a quantitative concept. In addition to questionable accuracy, one of the criticisms is that Pauling's definition of electronegativity is not quantum mechanically viable, i.e., it is thermodynamically ad hoc and does not build

* To whom correspondence should be addressed. Fax: (718)488-1465.

(1) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570−3582. Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Pauling also considered a "geometric mean" alternative equation, because of the alkali metal hydrides, but concluded that "We shall accordingly use the arithmetic mean...", i.e., eq 1; his widely quoted electronegativity values are based on eq 1.

(2) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299−11308.

(3) (a) Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983. (b) Yuan, H. *Acta Chim. Sin.* **1964**, *30*, 341. (c) Luo, Y.-R.; Benson, S. W. *Acc. Chem. Res.* **1992**, *25*, 375−381 and references therein. (d) Suresh, C. H.; Koga, N. *J. Am. Chem. Soc.* **2002**, *124*, 1790−1797.

(4) (a) Murphy, L. R.; Meek, T. L.; Allred, A. L.; Allen, L. C. *J. Phys. Chem. A* **2000**, *104*, 5867−5871. (b) Perks, H. M.; Liebman, J. F. *Struct. Chem.* **2000**, *11*, 375−378 and references therein.

on any of the electronic properties of atoms that result from Schrödinger's equation.[4a]

In terms of accuracy, relation to physical and quantum mechanical properties, and most importantly, current relevance and usefulness, the results of our examination of eq 1 are quite different. We demonstrate that the equation is much more accurate than any recent works indicate, provided that (a) some aspects that are clearly inferred from the original formulation of the equation are taken into consideration, so that the equation is not applied to cases for which it was not derived; and (b) accuracy is tested using reliable *D* values.

With these two provisos, eq 1 performs well with a large variety of covalent bonds, including highly polar ones. Among other aspects, it improves our understanding of the factors influencing reactivity in electrophilic aromatic substitution; it sheds light on a proposed new bonding theory; it correctly predicts molecular structure from effects of conjugation; it enhances our understanding of antioxidants; and it is useful for obtaining reliable estimates of *D* for many bonds, for which values are not available or are widely inconsistent. We find that a weakness of Pauling's equation is that the electronegativity of the hydrogen atom is unique in not being constant but depends substantially on the atom or group connected to it.

One important application of eq 1 involves stabilization energies of carbon radicals relative to $H_3C\cdot$, which are often equated to differences in *D*[R-H]. By this definition, radical stabilization energies are in the inverse order of the corresponding *D*[R-H] (R = Me > Et > *i*Pr > *t*Bu) and are given by *D*[Me-H] − *D*[R-H]. This is fairly common practice in the recent literature,[5] although not universal.[6] Generally the argument is that because H· is a common product, the difference in energy required to break each C-H bond reflects the relative stability of the R· formed. Expressed in another common way, the most stable radical is the easiest to form. The argument appears reasonable, but it is flawed. If this were true, differences in *D*[R-OH] also should reflect the relative stabilities of R·, since ·OH is now a common product. However, the order is quite different in the alcohol series, with *D*[R-OH]: *i*Pr > *t*Bu > Et > Me. Application of the same argument now results in the conclusion that the methyl radical is the most stable, being the easiest to form! The same conundrum results when the argument is applied to alkyl chlorides, fluorides, amines, and ethers. Thermodynamic quantities, such as radical stabilization energies, cannot depend on the precursor. Equation 1 resolves this difficulty.

Results and Discussion

The original form of Pauling's equation is used in this work. However, eq 1 can be recast in terms of the

(5) Some recent examples of this widespread practice include: Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Inorganic Chemistry*; Wiley: Chichester, UK, 1995; p 33. Mayer, P. M.; Glukhovtsev, M. N.; Gauld, J. W.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 12889−12895. Wayner, D. D.; Clark, K. B.; Rauk, A.; Yu, D.; Armstrong, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 8925−8932. Carey, F. A. *Organic Chemistry*, 5th ed.; McGraw-Hill: Boston, 2002; p 171. Solomons, T. W. G.; Fryhle, G. B. *Organic Chemistry*, 7th ed.; John Wiley & Sons: New York, 2000; p 436.
(6) Leffler, J. E. *An Introduction to Free Radicals*; Wiley: New York, 1993.

enthalpies of formation of the stable molecules involved.[4b] From the thermodynamic relationship $D[\text{A-B}] = \Delta H_f°[\text{A}\cdot] + \Delta H_f°[\text{B}\cdot] − \Delta H_f°[\text{AB}]$, eq 1 is equivalent to $\Delta H_f°[\text{AB}] = \frac{1}{2}(\Delta H_f°[\text{AA}] + \Delta H_f°[\text{BB}]) − 23(\Delta \chi)^2$. Another mathematically equivalent form of eq 1 involves Hess's law for the enthalpy of the reaction[4b] A-A + B-B → 2A-B, where $\Delta H_{rxn} = 2(−D[\text{A-B}]) + D[\text{A-A}] + D[\text{B-B}] = −23(\chi[\text{A}] − \chi[\text{B}])^2$. There must be conservation of the number of formal bonds.

Several electronegativity scales similar or related to Pauling's have been proposed, but we attempt to adhere to the original scale by assigning $\chi[\text{OH}] = 3.500$, equal to Pauling's value for oxygen, in order not to proliferate such scales. Pauling's χ values were assigned to elements, but the concept has been extended subsequently to encompass groups (alkyl, alcoxyl, etc.).

C(sp³) and Si(sp³) Bonds to Alkyls. Alcohols and Silanols. The electronegativity of methyl was established as follows: With the known values of *D*[Me-Me], *D*[HO-OH], *D*[Me-OH], and $\chi[\text{OH}] = 3.500$ shown in boldface in Table 1, solving eq 1 yields $\Delta \chi = 0.974$ and $\chi[\text{Me}] = 3.500 − 0.975 = 2.525$. This is identical, to two significant figures, to the value of 2.5 given to carbon by Pauling. The electronegativity of ethyl, allyl, benzyl, and silyl is similarly established with the known values of *D*[Et-Et], *D*[Allyl-Allyl], *D*[Bz-Bz], and *D*[H_3Si-SiH_3], and the corresponding *D*[R-OH] (all in boldface, Table 1). The results are $\chi[\text{Et}] = 2.462$, $\chi[\text{Allyl}] = 2.488$, $\chi[\text{Bz}] = 2.506$, and $\chi[H_3\text{Si}] = 1.879$. $\chi[\text{OH}]$ was chosen to anchor the χ scale because *D*[R-OH] values are generally known accurately. Pauling's use of only one decimal figure for electronegativity values 70 years ago was necessitated by the poor knowledge of bond dissociation enthalpies at the time. With current more accurate values, use of two decimals is needed for stringent tests of accuracy, and precision of 1 kcal mol^{-1} requires a third when $\Delta \chi \geq 2$.

The above straightforward procedure for obtaining $\chi[\text{R}]$ should not be applied in the same way to the isopropyl and *tert*-butyl groups because of proviso (a) above. It is clear that Pauling's equation does not take into account "special effects": steric crowding, conjugation, or resonance, i.e., *effects present in A-A or B-B but not in A-B, or vice versa*. The experimental *D*[*t*Bu-*t*Bu] does not provide a measure of the inherent bonding ability of the *tert*-butyl group because of the well-known steric hindrance in di-*tert*-butyl (2,2,3,3-tetramethylbutane), which has been estimated at 6.9 kcal mol^{-1} by one molecular mechanics calculation.[7] Solution of this problem is straightforward. The fair assumption is made that steric hindrance is negligible in *D*[*t*Bu-Me] and *D*[*t*Bu-OH]. Then, eq 1 can be expressed as eqs 2 and 3 and solved simultaneously for the two unknowns, $\chi[\text{*t*Bu}]$ and strain-free *D*[*t*Bu-*t*Bu]:

$$D[t\text{Bu-Me}] = \frac{1}{2}(D[t\text{Bu}−t\text{Bu}] + D[\text{Me}−\text{Me}]) +$$
$$23(\chi[t\text{Bu}] − \chi[\text{Me}])^2 \quad (2)$$

$$D[t\text{Bu-OH}] = \frac{1}{2}(D[t\text{Bu}-t\text{Bu}] + D[\text{HO-HO}]) +$$
$$23(\chi[t\text{Bu}] − \chi[\text{OH}])^2 \quad (3)$$

The result is $\chi[t\text{Bu}] = 2.378$ and $D[t\text{Bu}-t\text{Bu}] = 82.4$; the latter value reflects the inherent bonding ability of

TABLE 1. Calculated Bond Dissociation Enthalpies (eq 1, in Parentheses), Literature Values, and Enthalpies of Formation of Radicals Adopted for This Work (in Brackets) in kcal mol^{-1} at 298 K[a]

A→ χ→ B↓	Me 2.525	Et 2.462	iPr 2.411	tBu 2.378	Allyl 2.488	Bz 2.506	SiH$_3$ 1.879	SiMe$_3$ 1.838	OH **3.500**
Me ΔH$_f$° = [34.82] 34.82^b 34.99^c	**89.8** 89.7^b 89.9^c	(88.8) 88.3^b 88.9^c	**88.7** 88.9^b 88.7^c 88.7^d	86.6 86.0^b 87.2^c	(75.6) 75.9^b 75.9^c	(78.2) 77.2^b 79.3^c 76.7^d	(92.5) 89.6 ±1.2^e	**94.8** 94.2 ±1.9^e	92.3 92.1^b 92.5^c
Et [28.7] 28.4^b 28.9^c		**87.7** 87.2^b 88.2^c	(87.4) 87.1^b 87.1^c	(85.2) 83.8^b 84.7^d	(74.5) 74.7^f	(77.1) 76.0^b 75.8^d	(89.7) 87.8^e	(91.8)	94.2 94.0^b 94.4^c
iPr [21.8] 2 2.0^b 21.51^c			(87.0)^g 86.6^b 86.1^d	(84.7)^g 82.0^b 81.8^d	(74.3) 74.7^b 74.5^d	(77.0) 76.7^b 76.0^d	(88.0) 87.2^f	(90.1)	96.3 96.5^b 96.1^c
tBu [11.6] 11.0^b 12.31^c				(82.4)^g 76.0^b 77.2^d	(72.1) 72.5^f	(74.8) 73.6^f	(85.0)	(86.9)^g	95.7 95.0^b 96.3^c
Allyl [40.9] 40.9^b 40.8^c				**61.3** 61.4^b 61.3^c		(63.9) 62.9^f	(77.2)	(79.4)	79.8 79.8^b 79.8^d
Bz [49.5] 49.5^b 48.4 ±1.5^c						**66.5** 66.6 ±1.4^b 64.4 ±2.1^c 65.6^d	(80.3)	(82.5)	81.5 81.4^b 81.3^c 80.9^d
H$_3$Si [47.7] 47.9^c 47.9^e							**76.0** 74.1^c 76.7 ±1.0^e 76.2^h	(77.0)	124.0 124.0^i 124.4^h
Me$_3$Si [3.4] -0.8^c 3.6 ±1.7^e								(78.0) 80.5^c 79.3 ±2.5^e	128.1 128.1^c 132.6 ±1.9^e
HO [9.3] 9.32^b 9.39^c									**51.1** 51.2^b 50.9^c

[a] Boldface lettering denotes the two values in each row used to obtain χ and D by eq 1 (in parentheses). [b] From ΔH$_f$° values in ref 8. [c] Reference 9. [d] From ΔH$_f$° of ref 8 for the compound and ΔH$_f$° of the radicals adopted for this work. [e] From ref 21, with uncertainties shown when they exceed 1.0 kcal/mol. [f] From ΔH$_f$° values of the compound in ref 10 and ΔH$_f$° of the radicals adopted for this work. [g] Strain-free energy. [h] Ab initio value of ref 2 at 0 K, increased by 1.5 to estimate 298 K. [i] Reference 59.

tBu, free from steric strain. An error of 1 kcal mol^{-1} in D[tBu-Me] or in D[tBu-OH] causes a change of 0.022 in the calculated χ[tBu]. The accuracy of this approach, with eqs 2 and 3, improves as $23(χ[R] - χ[X])^2$ increases. In the same way we obtain χ[iPr] = 2.411 and D[iPr-iPr] = 87.0, the latter reflecting the strain-free inherent bonding ability of isopropyl. Comparison of the strain-free values to the actual D[tBu-tBu] = 76.6 ± 0.6 and D[iPr-iPr] = 86.4 ± 0.3 (Table 1) gives a strain of 5.8 ± 0.6 in di-*tert*-butyl and 0.7 ± 0.3 in di-isopropyl.

Similarly, it is not known whether the experimental D[Me$_3$Si-SiMe$_3$] is affected by steric crowding, as is the case with di-*tert*-butyl. Therefore, D[Me$_3$Si-SiMe$_3$] and χ[Me$_3$Si] were obtained by the same procedure as used

(7) Winiker, R.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1980**, *113*, 3456–3476.

for *tert*-butyl, from D[Me$_3$Si-Me] and D[Me$_3$Si-OH]. The resulting strain-free D[Me$_3$Si-SiMe$_3$] = 78.0 is consistent with the experimental value of 79.3 ± 2.5 and demonstrates that there is no significant steric crowding affecting the Si−Si bond in hexamethyldisilane, evidently because of the larger covalent radius of Si compared to that of C. The value of χ[Me$_3$Si] = 1.838 is near the value of 1.8 assigned by Pauling to silicon. The χ values in Table 1 follow the trends one would reasonably expect. Increasing alkylation lowers the electronegativity of carbon and of silicon. Electron affinity and ionization energy, which are other properties relevant to attraction of a species for electrons, are also lowered.

Bond dissociation enthalpies for any combination of the above groups can now be calculated by use of eq 1, and the results are shown in Table 1 in parentheses. The data used as anchor points to obtain all other calculated values in the table are shown in boldface. Only χ[OH] was set arbitrarily. The calculated D values are in agreement with literature values, within the expected accuracy of the latter. When stated experimental uncertainties exceed 1 kcal mol^{-1}, they are listed in this and subsequent tables. The calculated strain-free value obtained for D[iPr-tBu] (2,2,3-trimethylbutane) is greater than the average of the two literature values in Table 1 by 2.8 ± 0.2 kcal mol^{-1}, indicating this much strain enthalpy, intermediate between that of di-*tert*-butyl and di-isopropyl. The use of the calculated strain-free values for D[tBu-tBu] and D[iPr-iPr] to calculate bonding of these groups to ethyl, allyl, and benzyl leads to values in good agreement with experiment (Table 1).

Gas phase literature values of D at 298 K used in this work were obtained mostly from two widely available sources, primarily the NIST database 69[8] for enthalpies of formation of compounds and radicals to obtain D[A-B] and the compilation of Kerr[9] for D values, ΔH$_f$° of radicals, and ΔH$_f$° of molecules derivable therefrom. We adopted values of ΔH$_f$° of radicals for this work, specified in the tables in brackets, exercising some subjective judgment from among available data or taking their average, as detailed in the tables. Other sources included the NIST database 25,[10] when a value is not available in NIST 69,[8] and values from the primary literature, experimental or theoretical, as specified in the Tables for each case.

C(sp^3) and Si(sp^3) Bonds to OR, NH$_2$, Cl, F, NO$_2$, NHR, and ONO$_2$. Pauling's equation has been described as performing poorly with polar bonds. The calculations for each species of Table 1 involve polar bonds to OH but may not fully address the issue, as most of the bonds of

(8) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; July 2001, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov). IE and AE data compiled by Lias, G. S., Rosenstock, H. M., Draxl, K., Steiner, B. W., Herron, J. T., Holmes, J. L., Levin, R. D., Liebman, J. F., Kafafi, S. A.
(9) Kerr, J. A. In *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1996−1997. There is a misprint in D values given for bonds to CH$_3$C(O). All values must be increased by 3.4, except for the value to hydrogen. While the latter was updated to reflect a change in Δ$_f$H° of the acetyl radical from previous editions, all other values were not.
(10) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database 25*; Stein, S. E., Ed.; 1994. Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. Version 2.0.

this table are relatively nonpolar. We applied eq 1 to the compounds of Table 2, where highly polar bonds are involved, e.g., H_3Si-F. The electronegativities of A = OMe, NH_2, Cl, F, NO_2, NHMe, and NHPh were obtained by solving eq 1 with the known D[Me-A] and D[A-A] (in boldface in Table 2) and χ[Me]. For example, D[Me-OMe] = 83.1 = $^1/_2$(89.8 + 37.9) + 23$(\Delta\chi)^2$. Solving gives $\Delta\chi$ = 0.914 and χ[OMe] = 2.525 + 0.914 = 3.439. D[O_2NO-ONO_2] and D[PhO-OPh] are not known, but D[O_2NO-Me], D[O_2NO-OH], D[PhO-Me], and D[PhO-CH_2CHCH_2] are known. This allows the calculation of D[O_2NO-ONO_2] and χ[ONO_2], as well as D[PhO-OPh] and χ[OPh], as was done with tBu (eq 1 being formulated as two simultaneous equations with two unknowns in each case). Again, the χ values obtained (Table 2) follow reasonably expected trends. Relative to χ[OH], χ[OMe] is lower because of the greater electron donating ability of methyl and χ[ONO_2] is higher because of the electron withdrawing ability of NO_2. Similarly, χ[NHMe] < χ[NH_2] and the most electronegative nitrogen species is NO_2, where the formal positive charge on nitrogen enhances its electron attracting ability.

Table 2 demonstrates very good agreement between literature values and those calculated by eq 1, especially in cases where the experimental values are well established. In the preponderance of such cases, the D values calculated by eq 1 differ from literature values by about as much as the latter differ among themselves. Values of calculated D are also given for bonds for which experimental measurements do not appear to exist. Three apparent failures are present in Table 2 involving HO-NO_2, CH_3O-NO_2, and F-NO_2, where calculated values differ from experimental by 14 kcal mol^{-1}. These three and additional apparent failures to be presented will be considered in detail later. There is a difference of about 8 kcal mol^{-1} between the calculated and the literature value for D[Me_3Si-Cl]; the literature value is an estimate and may be too high because our calculated values for other D[H_3Si-X] and D[Me_3Si-X], including D[H_3Si-Cl], are generally consistent with available data. There are disparities in literature values for alkyl fluorides and the question as to what the correct D[R-F] values are[11] has been addressed by the measurements of Rüchardt et al.[12] in favor of those proposed by Benson.[11b] The values from eq 1 in Table 2 are also in agreement with Rüchardt's findings.

Pauling based χ values on a global fit to "all available" D values.[1] We set each χ in Tables 1 and 2 by only two molecules and attain good accuracy. The ability of eq 1 to treat highly polar covalent bonds accurately is demonstrated by examining D[Me_3Si-F], where $\Delta\chi$ = 2.100. Equation 1 predicts D = $^1/_2$(78.0 + 38.0) + 23(2.100)^2 = 58.0 + 101.4 = 159.4, in excellent agreement with the experimental value of 158.2 ± 2.6 kcal mol^{-1}. The $\Delta\chi$ term contributes 65% of the Si-F bond dissociation enthalpy and only 35% is due to inherent covalent bonding ability.

D[A-X] − D[B-X]. An interesting and useful corollary of Pauling's equation is eq 4, derivable from eq 1; we are

(11) (a) Liebman, J. F.; Martinho Simões, J. A.; Slayden, S. W. *Struct. Chem.* **1995**, *6*, 263. (b) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1997**, *101*, 3042−3044.
(12) Schaffer. F.; Verevkin, S. P.; Rieger, H.-J.; Beckhaus, H.-D.; Rüchardt, C. *Liebigs Ann./Recueil* **1997**, 1333−1344.

TABLE 2. Calculated Bond Dissociation Enthalpies (eq 1, in parentheses), Literature Values, and Enthalpies of Formation of Radicals Adopted for This Work (in brackets) in kcal mol^{-1} at 298 K[a]

A→ χ→ ΔHf°→ B↓	-OMe 3.439 [4.2] 4.1^b 4.2^c	-NH2 3.071 [45.1] 45.5^b 44.2^c	-Cl 3.174 [29.0] 28.99^b	-F 3.938 [19.0] 18.97^b	-NO2 3.177 [7.9] 7.91^b	-OPh 3.376 [13.0] 13±1^b 11.4^c	-NHMe 3.018 [42.4] 42.4±3^c 38±2^d	-NHPh 3.051 [58.5] 56.7±2^c	-ONO2 3.543 [17.0] 17.0^b 17.6^c
Me	**83.1** 82.9^b 83.2^c	**85.3** 84.6^b 85.3^c	**83.6** 83.8^b 83.4^c	109.8 109.8^b 112.8^c 109.7^f	61.5 62.0^b 60.8^c 61.6^g	64.1 64.06^b 62.5^c	81.9 81.9 ±2.1^c	**73.2** 71.4±2^c7 3.2±2^e	81.0 81.0^b 81.8^c
Et	(84.8) 84.2^b 84.8^c	(85.9) 84.6^c 85.1^h	(84.5) 84.2^b 84.4^c	(113.0) 110.7^c 113.4^i	(62.4) 61.0^h	(64.9) 65.7^b	(82.4)	(73.8) 73.8 ±1.4^e	(83.0) 82.4^b
iPr	(86.7) 86.3 ±2^b 86.0^c	(87.4) 87.7^b 85.8^c	(85.9) 85.0^b 85.1^c	(116.1) 110.7^c 116.2^i 117.0^f	(63.8) 63.1^b 59.1^c	(67.9) 67.8^h	(83.4)	(74.8)	(85.2)
tBu	(86.0) 82.6^b 84.4^c	(85.8) 85.3^b 85.6^c	(84.7) 83.0^b 84.8^c	(116.2) 117.0^i 117.5^f	(62.7) 58.5^c 61.8^e	(66.0)	(82.0)	(73.5)	(84.7)
Allyl	(70.4) 70.0^h	(72.0) 75.0^h 73.3^j	(70.5) 71.2^b	(98.0) 96.9^h 97.4 ±2^k 96.8±2^l	(48.4)	**50.6** 50.6^m 49.8 ±2^c	(68.5)	(59.9)	(68.5)
Bz	(72.2) 71.7 ±2^h	(74.1) 74.0^b 71.1^c	(72.5) 74.0^b 72.4^c	(99.4) 98.7^b,i 98.6 ±2^k 97.2^n	(50.4) 50.1^b 46.1 ±2.3^g	(52.5) 53.1^o	(70.7)	(62.0)	(70.2)
H3Si	(112.9)	(104.2) 103.7^p 104.9^q	(106.1) 110.6^e 105.6^r 109.5^t 108.4^t	(154.5) 156.7^c 152.5 ±1.2^s	(83.6)	(91.3)	(99.2)	(91.6)	(113.9)
Me3Si	(116.9) 119.6 ±2^h 122.6 ±2.6^s	(107.7)	(109.1) 117.1 ±1.9^s	(159.4) 158.2 ±2.6^r	(87.1)	(95.2)	(102.4) 100.1 ±2^s	(94.8)	(118.1)
HO	(44.6) 44.7^b	(63.3) 64.4^h	(57.0) 56.1^b 60.0 ±3.1^c	(49.0) 51.8^b 48.9^u	(34.8) 49.3^b	(27.7) 28.4^v	(62.3) 63.7^h	(52.1)	**38.4** 37.8 ±2^c 39.0^h
MeO	(37.9) 38.2^b 37.6^c	(55.6) 55.3 ±2^h	(49.6) 47.2^h 48.6 ±1.5^w	(43.7) ≤47.4^x	(27.4) 41.2^b	(20.8)	(54.4) 55.6^h	(44.4)	(31.4)
H2N	(55.6) 55.3 ±2^h	(67.1) 68.2^b 65.8^c	(62.8) 61.1^h	(69.8) 69.1±2^h	(40.6)	(37.5)	(65.0) 64.1 ±2^c 64.9^h	(55.5) 52.3^c 55.0^h	(50.9)
Cl	(49.6) 47.2^h 48.6 ±1.5^w	(62.8) 61.1^h	(58.0) 58.0^b	(61.4) 60.0^b	(35.8) 34.0^c	(31.7)	(60.9) 53.4^h	(51.3)	(44.4) 39.6^h 41.8^x 42.6^x
F	(43.7) ≤47.4^y	(69.8) 69.1 ±2^h	(61.4) 60.0^b	(38.0) 38.0^b	(39.1) 52.9^b	(28.1)	(69.9)	(59.0)	(34.8) 33.5^b
A	**37.9** 38.2^b 37.6^c	**67.1** 68.2^b 65.8^c	**58.0** 57.98^b	**38.0** 37.94^b	**13.65** 13.65^b 13.6^c	(3.6)	**62.8** 62.8 ±2.8^c	**43.9** 43.9 ±1.8^z	(24.5)

[a] Boldface lettering denotes the two values in each column used to obtain χ and D by eq 1 (in parentheses). [b] Values of $\Delta H_f°$ from ref 8. [c] Reference 9. [d] Reference 10. [e] $\Delta H_f°$ of the compound from ref 8, with $\Delta H_f°$ of the radicals adopted for this work. [f] $\Delta H_f°$ of the compound estimated in ref 11b, with $\Delta H_f°$ of the radicals adopted for this work. [g] Reference 63. [h] $\Delta H_f°$ of the compound from ref 10, with $\Delta H_f°$ of the radicals adopted for this work. [i] $\Delta H_f°$ of the compound from ref 12, with $\Delta H_f°$ of the radicals adopted for this work. [j] $\Delta H_f°$ of the compound from group additivity value in ref 10, with $\Delta H_f°$ of the radicals adopted for this work. [k] Reference 64 from the IR stretching frequency. [l] G3 calculation, this work. [m] Reference 39. [n] Reference 19f, theoretical value B3LYP. [o] Thermolysis at 548 K, ref 19i. [p] Reference 2, ab initio value at 0 K increased by 1.5 to adjust to 298 K. [q] Reference 65, ab initio value. [r] Reference 66, theoretical value, DFT. [s] Reference 21. [t] Reference 67, ab initio value. [u] Reference 68, ab initio value. [v] $\Delta H_f°$ of the compound estimated in reference 69 with $\Delta H_f°$ of the radicals adopted for this work. [w] Ab initio value, reference 70. [x] Ab initio values: Zou, P.; Derecskei-Kovacs, A.; North, S. W. *J. Phys. Chem. A* **2003**, *107*, 888−896. [y] Upper limit, reference 71. [z] Based on D[PhNH-H] = 89.8, reference 72.
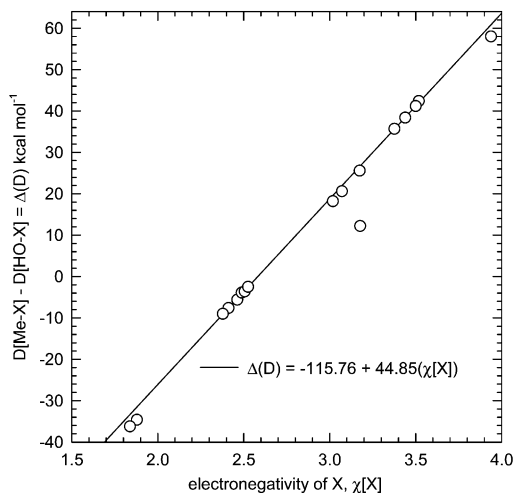
FIGURE 1. Difference $D[CH_3\text{-X}] - D[HO\text{-X}]$ of literature values vs electronegativity of X. The straight line is the "theoretical" required by eq 4. For the identity of each point, see text.

not aware of its having been used heretofore:

$$\Delta(D) = D[\text{A-X}] - D[\text{B-X}] = a + b(\chi[\text{X}]) \qquad (4)$$

The constant a is $^1\!/_2(D[\text{A-A}] - D[\text{B-B}]) + 23\{(\chi[\text{A}])^2 - (\chi[\text{B}])^2\}$ and the slope b is $46(\chi[\text{B}] - \chi[\text{A}])$. The difference in bond dissociation enthalpies of A and B with a common X should be linearly related to the electronegativity of X. Equation 4 should be valid for any combination of groups from Tables 1 and 2, subject to proviso (a) regarding special effects. For example, for $\Delta(D) = D[\text{Me-X}] - D[\text{HO-X}]$, the needed values from Tables 1 and 2 yield $a = -115.76$ and $b = 44.85$. We tested the validity of eq 4. Figure 1 shows the plot of $\Delta(D)$ of the average of literature values from Tables 1 and 2 vs electronegativities of 17 different X groups. From left to right in the figure, X = SiMe$_3$, SiH$_3$, tBu, iPr, Et, Allyl, Bz, Me, NHMe, NH$_2$, Cl, NO$_2$, OPh, OMe, OH, ONO$_2$, and F. The line is drawn with the slope and intercept required by eq 4. The agreement of the "theoretical" line with literature values is excellent, the only point deviating being the aforementioned NO$_2$. Linear regression through the literature $\Delta(D)$ values yields "experimental" $a = -116.3$ and $b = 44.5$ ($r = 0.9915$), in excellent agreement with the prediction of eq 4. Figure 1 covers the very wide range of 94 kcal mol^{-1}.

It has long been recognized that the difference between $D[\text{Me-X}]$ and $D[\text{R-X}]$ is not constant but depends on the nature of X.[13a,b] Equation 4 rationalizes, generalizes, and quantifies the effect. Accuracy improves with increasing $\Delta\chi$ between A and B or between X and A or B.

In this context, Luo and Holmes[14] made useful estimates for many experimentally unavailable bond dis-

sociation enthalpies of Allyl-X and Bz-X, after observing that for many known cases $D[\text{Et-X}] - D[\text{Allyl-X}]$ is fairly constant at 13.2 ± 1.0 and $D[\text{Et-X}] - D[\text{Bz-X}]$ at 11.9 ± 1.5 kcal mol^{-1}; therefore, they estimated $D[\text{Allyl-X}]$ and $D[\text{Bz-X}]$ from known or estimated $D[\text{Et-X}]$ by subtracting 13.2 or 11.9, respectively. Equation 4 yields $D[\text{Et-X}] - D[\text{Allyl-X}] = 10.2 + 1.20(\chi[\text{X}])$ and $D[\text{Et-X}] - D[\text{Bz-X}] = 5.57 + 2.02(\chi[\text{X}])$. For the benzyl case, eq 4 predicts $\Delta(D) = 9.2$ with $\chi[\text{X}] = 1.8$; 9.6 with 2.0; 10.6 with 2.5; 11.61 with 3.0; 12.7 with 3.5; and 13.7 with 4.0. The average is $\Delta(D) = 11.2 \pm 1.4$, consistent with the estimates made. However, there is a spread of 4.5 kcal mol^{-1} and this variation is predictable by eq 4. Similarly for the allyl case, eq 4 yields $\Delta(D) = 12.4$ with $\chi[\text{X}] = 1.8$, 12.6 with 2.0, 13.2 with 2.5, 13.8 with 3.0, 14.4 with 3.5, and 15.0 with 4.0; the average is $\Delta(D) = 13.6 \pm 0.9$, consistent with the estimates. Again, however, there is a predictable spread of 2.6 kcal mol^{-1}. The success of the previous estimates[14] is due to the fact that Et, Allyl, and Bz have similar electronegativities, leading to small values for the slope b in eq 4.

"Charge-Shift" Bonding. This type of bonding has been postulated recently to be a distinct class of bonding deriving "primarily if not only, from the fluctuation of charge inherent in the resonance between the two bonding forms" (ionic and covalent), on the basis of "breathing-orbital valence bond" calculations. This type of bonding was described as "a class by itself, not associated necessarily with bond polarity in the traditional sense of Pauling or Sanderson."[15] Further, it was pointed out that Pauling's approach "ignores completely the charge-shift nature of homonuclear bonds and would severely underestimate the effect in all polar bonds."[15]

Charge-shift bonding was ascribed to F-F, H$_3$C-F, H$_3$-Si-F, HO-OH, H$_3$C-OH, H$_2$N-NH$_2$, H$_3$C-NH$_2$, and H$_3$Si-Cl. Therefore, eq 1 must fail with such bonds, as with any other "special effect." Tables 1 and 2 include each of these eight bonds and the fact is that there are no failures involving any of them. The claim that the bond in H$_3$Si-Cl is neither ionic nor covalent but bonded almost exclusively by "charge-shift resonance," is refuted by the fact that eq 1 successfully predicts $D = 106.1$ kcal mol^{-1}, consistent with literature values; 39.1 kcal mol^{-1} is due to the $23(\Delta\chi)^2$ term and 67.0 to the covalent term. Equation 1 is successful with each of the specified bonds, *in the traditional sense of Pauling and ignoring "charge shift" completely.* Equation 1 does not severely underestimate any of the specified polar bonds and shows that there is nothing distinguishing these bonds, as a class by themselves, from any of the other bonds in Tables 1 and 2. One proponent of charge shift bonding suggested that the reason eq 1 is successful with these bonds is because it overestimates the covalent term and underestimates the polar term, in mutual compensation. Such a fortuitous, but perfectly exact, cancellation of errors in all eight cases may be a possibility, but its probability cannot be very high.

Radical Stabilities. We return to the conundrum that results by equating $D[\text{Me-H}] - D[\text{R-H}]$ to carbon radical stabilization energies. Stabilization energy defined in this way[16] is Me$\cdot$ = 0.0, Et$\cdot$ = 4.0, iPr$\cdot$ = 5.9, tBu$\cdot$ = 9.0, Allyl$\cdot$

(13) (a) Benson, S. W.; Shaw, R. *Adv. Chem. Ser.* **1968**, *75*, 287. (b) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. (c) Winiker, R.; Beckhaus, H.-D.; Rüchardt. C. *Chem. Ber.* **1980**, *113*, 3456−3476. Kratt, G.; Beckhaus, H.-D.; Bernlöhr, W.; Rüchardt, C. *Thermochim. Acta* **1983**, *62*, 279−294. Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 529−538. Rüchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem.* **1986**, *130*, 1−22. Welle, F. M.; Beckhaus, H.-D.; Rüchardt, C. *J. Org. Chem.* **1997**, *62*, 552−558. Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935−1943 and references therein.

(14) Luo, Y.-R.; Holmes, J. L. *J. Phys. Chem.* **1994**, *98*, 303−312.

(15) Shurki, A.; Hiberty, P. C.; Shaik, S. *J. Am. Chem. Soc.* **1999**, *121*, 822−834.

= 16.7, and Bz· = 15.2 kcal mol^{-1}. Potential problems with this approach were noted by Walling in 1957, who pointed out that ascribing differences in D[R-H] solely to radical stabilization enthalpies is a rather superficial treatment,[17] and were revisited by Rüchardt[13b] and by Nicholas and Arnold.[18] The problem here is that D[R-H] is not affected only by the stability of the radicals formed upon homolysis. The ground or starting state of the various C-H bonds is also affected by the $\Delta\chi$ term, but to different extents. Keeping in mind that bond dissociation enthalpy is the difference between the starting and the final states, one may not disregard the $\Delta\chi$ effect on the starting state, the molecule. The $\Delta\chi$ term stabilizes the R-H bond by D[R-H] $- \frac{1}{2}D$[H-H] $- \frac{1}{2}D$[R-R], where D[R-R] is the strain-free value from Table 1. This stabilization in methane is 7.8 kcal mol^{-1}, in ethane 4.9, in the 2° C-H bond of propane 3.3, and in the 3° C-H bond of isobutane 2.5. These components of D[Me-H] $- D$[R-H] have no relation to the stabilization energy (SE) of the carbon radicals. There is no $\Delta\chi$ effect with the separated fragment radical products. In the series of alkyl fluorides (Table 2), the $\Delta\chi$ term stabilizes the C-F bond by 45.9 kcal mol^{-1} in Me-F, by 50.1 in Et-F, by 53.6 in iPr-F, and by 56.0 in tBu-F. The C-F bond in methyl fluoride is weaker than C-F of ethyl, isopropyl, and *tert*-butyl fluorides not because the methyl radical is more stable, but because the enthalpy of the ground state of the other C-F bonds is lowered more by the $\Delta\chi$ effect. Again, the polar component of D[Me-F] $- D$[R-F] is not related to stabilities of the carbon radicals. In pointing to the importance of differences in the starting states, our focus is similar to that of Rüchardt et al.[13b] However, they ascribed bond enthalpy differences in the alkyl R-X series primarily to strain effects on the molecule (and factors affecting them, primarily the size of X). Rüchardt, Beckhaus et al. properly excluded $\Delta\chi$ effects from their extensive subsequent studies of highly strained C-C bonds by focusing mostly on symmetrical R-R.[13c] Here we focus quantitatively on electronegativity effects.

The proper definition of carbon radical stability is SE-[R·] $= \frac{1}{2}(D$[Me-Me] $- D$[R-R]), where D[R-R] is the strain-free value of the C-C bond in the hydrocarbons (Table 1). This is the definition of SE given by Pauling and, by this definition, SE[Me·] = 0.0, SE[Et·] = 1.1, SE-[iPr·] = 1.4, SE[tBu·] = 3.7, SE[Allyl·] = 14.3, and SE-[Bz·] = 11.7 kcal mol^{-1}. Stabilization energies obtained by differences in D[R-H] are overestimated significantly. The properly defined SE values are transferable, as shown in the following examples: D[Et-Allyl] = D[Me-Me] $-$ SE[Et·] $-$ SE[Allyl·] = 89.8 $-$ 1.1 $-$ 14.3 = 74.4, compared to the literature value of 74.7 (Table 1). Using the values derived from differences in D[R-H] yields D[Et-Allyl] = 69.1. $\Delta\chi$ effects are minor for C-C bonds among the carbon species treated so far, which is the reason for the successful transferability of our SE values with these hydrocarbons. For all carbon radicals in Table 1, SE can be conveniently approximated by SE[R·] = D[Me-Me] $-$ D[Me-R], with an error of less than 0.5 kcal mol^{-1}.

(16) For D[R-H] we used the $\Delta H_f°$ values of the hydrocarbons from NIST 69[8] and the $\Delta H_f°$ adopted for the radicals in this work, Table 1.

(17) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 51–52.

(18) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1850–1859.

Equation 1 leads to a general definition of radical stability applicable to all radicals, not only those that are carbon-centered. For any atom or group B, stabilization relative to methyl is given by SE[B·] $= \frac{1}{2}(D$[Me-Me] $-$ D[B-B]), an identity of eq 1 applicable when there is no reason to expect special effects. For example, this yields SE[HO·] $= \frac{1}{2}(89.8 - 51.1)$ = 19.35, SE[F·] $= \frac{1}{2}(89.8 - 38)$ = 25.90 and, therefore, D[HO-F] = SE[Me-Me] $-$ SE[HO·] $-$ SE[F·] $+ 23(\chi$[HO] $- \chi$[F])^2 = 89.8 $-$ 19.35 $-$ 25.90 + 23(3.500 $-$ 3.938)^2 = 49.0 vs literature values of 51.8 and 48.9 (Table 2). Values of such radical stabilities, SE, of the other species treated are ·SiH$_3$, 6.9; ·SiMe$_3$, 5.9; ·OMe, 26.0; ·ONO$_2$, 32.7; ·OPh, 43.1; Cl·, 15.9; ·NH$_2$, 11.4; ·NHMe, 13.5; ·NHPh, 23.0; and ·NO$_2$, 38.1 kcal mol^{-1}. When $\Delta\chi$ is considered along with the proper definition of radical stability, the same SE value is obtained whether one examines alkanes, silanes, halides, amines, alcohols, ethers, etc., as befits a thermodynamic function.

There is continuing interest and debate[19] directed toward establishing the extent to which benzylic and quasi benzylic bond dissociation enthalpies (with various ring substituents on ArCH$_2$-X, ArO-X, ArNH-X, ArS-X, etc.) are influenced by the stabilities of the radicals formed or by ground-state effects, i.e., stabilization of the molecule by bond dipoles, as rationalized by Pauling's electronegativity concept.[19b–d] There is now general agreement that ground-state effects must be taken into account, but their importance relative to radical stability has been the subject of continued debate over the last 30 years.[20]

Bonds to Phenyl, Vinyl, Ethynyl, Acetyl and BH$_2$. Bonds involving sp^2 and sp hybridization are examined next in Table 3. Bond dissociation enthalpies for such species generally are not known as accurately as those for bonds to sp^3 carbon, and larger deviations between calculated and literature values are to be expected, by proviso (b) above. Keeping in mind proviso (a), the experimental value of the C-C bond in 1,3-butadiene should not be used to establish the inherent bonding ability of vinyl, because of the known conjugative stabilization in this case, a "special effect" that would be absent, for example, in H$_3$C-CHCH$_2$. The same could be true for biphenyl, diacetylene (1,3-butadiyne), etc. Therefore, the approach here must be identical to that followed for tBu, i.e., using eq 1 to form two equations with two unknowns. For bonds to sp^2 and sp hybridized species, the combination of D[R-Me] and D[R-Cl] was used as anchor points, with the values shown in boldface in Table 3. We avoid using D[R-OH] as an anchor point in Table 3 because the very high reactivity of phenol in electrophilic aromatic substitution may be rationalized in terms of resonance structures such as **I** and **II**. The orientation of substitution can also be rationalized in terms of the same structures, even though many rationalize both reactivity and orientation by resonance structures of the intermediate adduct of the electrophile. Similarly, both reactivity and orientation with an electron withdrawing substituent, like the acetyl group of acetophenone, can be rationalized by resonance structures such as **III** and **IV**.

Were such structures to reflect reality, the Ph-OH bond would involve a "special effect," not present in Ph-Me or in HO-OH, would have partial double bond character,

TABLE 3. Calculated Bond Dissociation Enthalpies (eq 1, in Parentheses), Literature Values, and Enthalpies of Formation of Radicals Adopted for This Work (in Brackets) in kcal mol^{-1} at 298 K[a]

A→ χ→ ΔHf°→ B↓	−Ph 2.548 [79.75] 81±2[b] 78.9±0.8[c]	−CH=CH2 2.548 [71.35] 71±1[b] 71.7±0.8[c]	−C≡CH 2.789 [133.0] 133±2[b] 135.3[c]	−C(O)Me 2.235 [-2.6] -2.9±0.7[b] -2.4±0.3[c]	−BH2 1.87
Me	**102.9** 103.9[b] 101.6[c]	**101.4** 100.9[b] 101.8[c]	**123.5** 123.5±2[b]	**83.8** 84.1[b] 84.4[c]	(107.2) 106.6[d] 106.1[e]
Et	(102.0) 101.5[f] 102.3±2[b]	(100.5) 100.2[f] 99.6±1[b]	(123.3) 122.0[f] 121.9±2.1[b]	(82.0) 83.1[f] 82.5[b] 84.2[c]	(104.4)
iPr	(101.9) 100.6[f] 102.1±2.1[b]	(100.4) 99.7[g]	(123.8) 123.6[f] 122.0±2.1[b]	(81.2) 82.0[f] 81.9[b] 81.8[c]	(102.7)
tBu	(99.9) 96.8[f] 97.4±2.1[b]	(98.4) 97.5[g]	(122.1) 119.2[f] 119.8±2.2[b]	(78.7) 78.5[f] 79.1[c]	(99.6)
Allyl	(88.7) 83.7[g] 88.6[h]	(87.2) 86.9[f]	(109.7)	(69.1)	(91.9)
Bz	(91.3) 89.9[f] 91.1±2.1[b]	(89.7) 83.9[g] 88.3[h]	(112.1)	(71.9) 69.5[f] 69.2±1.1[b]	(95.0)
H3Si	(106.3)	(104.8) 100.2[i] 101-107[j]	(134.0) 123.8[i] 129.4[d]	(77.9) 72.0[d]	(90.5) 87.4[k]
Me3Si	(108.6)	(107.1) 104.7±1.5[i]	(136.8)	(79.6)	(91.5)
Ph	(116.0)[m] 116.0[f] 118.5±2.8[b] 114.3±1.1[c]	(114.5)[m] 116.0[f] 115.4[l]	(136.3)[m] 139.5[f] 140.7±2.8[b]	(97.3)[m] 97.2[c] 97.8[g]	(121.0)[m]
H2C=CH	(114.5)[m] 116.0[f] 116.9±2.2[b]	(113.0)[m] 116.7[f] 116.0±1.4[b]	(134.8)[m] 134.0[f] 133.6±2.1[b] 135.8[l]	(95.8)[m] 96.2[f] 95.5±2.8[b] 96.8±2.8[c]	(119.5)[m] 118.6[d]

A→ χ→ ΔHf°→ B↓	−Ph 2.548 [79.75] 81±2[b] 78.9±0.8[c]	−CH=CH2 2.548 [71.35] 71±1[b] 71.7±0.8[c]	−C≡CH 2.789 [133.0] 133±2[b] 135.3[c]	−C(O)Me 2.235 [-2.6] -2.9±0.7[b] -2.4±0.3[c]	−BH2 1.87
HC≡C	(136.3)[m] 139.5[f] 140.7±2.8[b]	(134.8)[m] 134.0[f] 133.6±2.1[b] 135.8[l]	(154.0)[m] 155.0[b] 160.0[l]	(121.1)[m]	(148.9)[m] 149.0[d]
MeC(O)	(97.3)[m] 97.2[c] 97.8[g]	(95.8)[m] 96.2[f] 95.5±2.8[b] 96.8±2.8[c]	(121.1)[m]	(74.0)[m] 72.9[b] 74.2[c]	(92.5)[m] 92.8[d]
F	(121.4) 125.2[f] 126.5[g]	(119.9) 122.0[f] 122.4±1[b]	(126.4) 122.0[f] 132.5[d] 129.2[n] 126.9[o]	(122.6) 122.8[f] 122.5[b] 122.6[c]	(169.8) 172.4[e]
Cl	**96.0** 96.9[b] 95.4[c]	**94.5** 94.0±1[b] 95.1[p]	**109.4** 110.9±2[b] 112.7[d] 107.2[o] 107.9[p]	**86.3** 86.2[b] 84.7[c]	(120.6) 124.9[k]
O2N	(73.4) 71.3[f] 72.8[b] 71.3[c]	(72.4)	(87.3)	(63.5)	(98.6)
HO	(104.4)[m] 112.1[f] 113.3±2[b] 111.1[c]	(102.9)[m] 111.3[f] 110.9±2[b]	(114.2)[m] 132.4[f] 132.4±2[b] 125.5[d]	(99.4)[m] 110.2[c] 110.0[g]	(139.1)[m] 152.7[d]
H2N	(97.8)[m] 104.1[f] 105.7±2[b] 102.1[c]	(96.3)[m] 103.7[d] 102.8[g]	(112.4)[m] 123.1[d]	(86.6)[m] 99.5[f] 99.6[b] 99.7[c]	(119.2)[m] 142.5[q]

[a] Boldface lettering denotes the two values in each column used to obtain χ and D by eq 1 (in parentheses). [b] From ΔHf° values in ref 8. [c] Reference 9. [d] Reference 2, their Table 1. [e] Reference 73, G2 calculations. [f] ΔHf° of the compound from ref 8, with ΔHf° of the radicals adopted in this work. [g] ΔHf° of the compound,[10] with ΔHf° of the radicals adopted in this work. [h] Reference 74. [i] From D and ΔHf° values given in the review of ref 21. [j] Range of ab initio values in ref 21. [k] Reference 65. [l] With ΔHf° of 1,3-butadiyne estimated by group additivity, reference 75. [m] Resonance-free or conjugation-free energy. [n] ΔHf° of the compound from G3 calculations of ref 76a. [o] ΔHf° of the compound from high-level theoretical value of ref 73b. [p] Recommended in ref 76c. [q] Reference 2; bond dissociation enthalpy at 0 K, their Table 7, increased by 1.5 kcal mol^{-1} to approximate 298 K.

and the experimental D[Ph-OH] would be higher than the resonance-free value needed for use with eq 1, and similarly for Ph-COCH3. Reactivity in electrophilic aromatic substitutions on toluene is weakly enhanced, relative to benzene, and on chlorobenzene weakly diminished, both primarily by the inductive effect. Equation 1 should describe this accurately, hence our selection of D[R-Me] and D[R-Cl] as "anchor points" in Table 3. Equations 5 and 6 show the procedure for phenyl. The
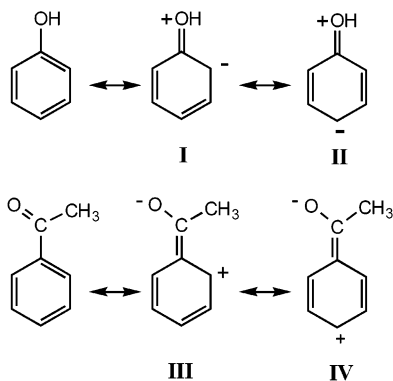
same approach was used for CH2=CH-, HC≡C- and CH3C(O)-:

$$D[\text{Ph}-\text{Me}] = \frac{1}{2}(D[\text{Ph}-\text{Ph}] + D[\text{Me}-\text{Me}]) +$$
$$23(\chi[\text{Ph}] - \chi[\text{Me}])^2 \quad (5)$$

$$D[\text{Ph}-\text{Cl}] = \frac{1}{2}(D[\text{Ph-Ph}] + D[\text{Cl-Cl}]) +$$
$$23(\chi[\text{Ph}] - \chi[\text{Cl}])^2 \quad (6)$$

With the known values of D[Ph-Me] and D[Ph-Cl] and D[Me-Me], D[Cl-Cl], χ[Me] and χ[Cl] from Tables 1 and

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2, we solve for the two unknown values and obtain $\chi[Ph]$ = 2.548 and $D[Ph\text{-}Ph]$ = 116.0, the latter being the conjugation-free value for biphenyl. The calculated $\chi[R]$ and $D[R\text{-}R]$ values in Table 3 were similarly obtained from the experimental $D[R\text{-}Me]$ and $D[R\text{-}Cl]$ shown in boldface for R = vinyl, ethynyl and acetyl.

H$_2$B, which is in the sp^2 group, is included in Table 3. There are no reliable experimental values available for the boranes, but high-level ab initio calculations exist. We adopted the value $D[H_2B\text{-}BH_2]$ = 104.9 kcal mol^{-1} at 298 K from a G3 calculation we performed for the "perpendicular" conformation, evocative of the staggered conformation of ethane and consistent with another ab initio value of 104.1 at 0 K.[2]

Both phenyl and vinyl have χ = 2.548, greater than the value of 2.525 of methyl, as would reasonably be expected on the basis of higher percent s character. Appropriately, $\chi[HC\equiv C]$ is the highest of the carbon species at 2.789, as a result of the highest percent s character.

There is good agreement between D values calculated by eq 1 and literature values for the first six rows of Table 3, involving bonds to sp^3 carbon. The calculated strain-free value for $D[t\text{Bu-Ph}]$ is 2.8 kcal mol^{-1} greater than experiment, about the same steric strain as $D[t\text{Bu-}i\text{Pr}]$. Literature values are less certain with silanes and $D[H_3\text{-}Si\text{-}CHCH_2]$ and $D[H_3Si\text{-}CCH]$ given by eq 1 are in better agreement with ab initio values, rather than those based on group additivity.[21]

The conjugation-free value calculated by eq 1 for $D[Ph\text{-}Ph]$ is 116.0 kcal mol^{-1}, compared to experimental 116.4 ± 2. This indicates little or no conjugation between the two rings in biphenyl. In effect, eq 1 infers that the two rings in biphenyl are not coplanar. Experimental determinations of the structure of biphenyl and *para*-substituted biphenyls in the gas and liquid phase (electron diffraction, Raman, NMR) have shown that the two rings are not coplanar. Dihedral angles of 30−45° have been reported.[22] There is consistency between conclusions drawn from eq 1 and experimental determinations of molecular structure.

For styrene, the experimental $D[Ph\text{-}CHCH_2]$ is 116.0 kcal mol^{-1}. Measurements of the enthalpy of hydrogenation of styrene to ethylbenzene[23] show that the exothermicity is smaller than that of terminal alkenes by 2.0 kcal mol^{-1}, slightly more than half the conjugative stabilization of 1,3-butadiene. This result leads to an "experimental" conjugation-free value of $D[Ph\text{-}CHCH_2]$ = 116.0−2.0 = 114.0. The vinyl group is not coplanar with the benzene ring from gas-phase electron diffrac-

tion[24] and NMR[25] measurements, showing dihedral angles of 27° and 17°, respectively. An older Raman study[26] indicated a planar structure with a rotational barrier of 1.8 kcal mol^{-1}, leading to a conjugation-free value of 116.0−1.8 = 114.2. The conjugation-free value given by eq 1 is 114.5 kcal mol^{-1}, indicating a conjugative stabilization of 1.5, in agreement with the experimental results within their uncertainty.

Measurements of the enthalpy of hydrogenation of phenylacetylene to ethylbenzene indicate 3.4 kcal mol^{-1} of conjugative stabilization relative to unconjugated terminal alkynes.[27] Those of 1-propynylbenzene to propylbenzene, relative to 2-butyne, give a conjugative stabilization of 2.9.[27] The conjugation-free $D[Ph\text{-}CCH]$ given by eq 1 is 3.2 kcal mol^{-1} smaller than the experimental value, in good agreement with the hydrogenation data.

The conjugation-free bond dissociation enthalpy of the C-C bond in 1,3-butadiene is calculated by eq 1 to be 113.0 kcal mol^{-1}, compared to experimental 116.7. Equation 1 indicates conjugative stabilization of 3.7 kcal mol^{-1}, in agreement with the usually quoted value of 3.6 ± 0.3 in 1,3-butadiene from enthalpies of hydrogenation.

For vinylacetylene (1-buten-3-yne), the conjugation-free $D[CH_2CH\text{-}CCH]$ is 134.8 kcal mol^{-1} by eq 1 and is within the error limit of the literature values. This indicates little, if any, conjugative stabilization. The difference between the enthalpy of hydrogenation of the compound ($-100.8 ± 0.5$)[28] and the sum of those for terminal alkenes ($-30.2 ± 0.3$) and terminal alkynes ($-69.5 ± 0.4$)[29] is only 1.1 ± 0.7.

The conjugation-free $D[HCC\text{-}CCH]$ = 154.0 given by eq 1 is only 1 kcal mol^{-1} lower than one literature value of 155.0 for the C-C single bond in diacetylene but considerably smaller than a value of 160.0 from a group additivity estimate. With this conflicting information at this time, it cannot be determined whether there is significant conjugative stabilization.

There is no evidence of conjugative stabilization between the carbonyl of CH$_3$C(O) and phenyl because the calculated conjugation-free $D[Ph\text{-}COCH_3]$ is in agreement with the available literature values in Table 3. Space-filling models show that, for coplanarity to be attained in acetophenone, two of the methyl hydrogens and the *ortho* hydrogen have to be at a precise conformation, forming a tight gear-tooth arrangement. This is avoided by a ca. 30° rotation of C=O from coplanarity with the ring. The absence of strong double bond character in Ph-COCH$_3$ indicates that resonance structures **III** and **IV** are not the major factor in the deactivating effect of the acetyl substituent in electrophilic aromatic substitutions. The effect on reactivity appears to be primarily inductive in nature, as is the case with halogen substituents. Similarly, the calculated conjugation-free value for $D[Ph\text{-}$

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NO$_2$] is nearly the same as experiment, again showing the absence of significant double bond character in C-N and indicating that the deactivating effect of the nitro group is due primarily to an electron withdrawing inductive effect and not a resonance effect. These conclusions for the acetyl and nitro groups are supported by the quite similar values of their σ_m and σ_p Hammett substituent constants.

For methyl vinyl ketone, the conjugation-free value of D[CH$_2$CH-COCH$_3$] = 95.8 kcal mol^{-1} given by eq 1 is near experimental values of 96.2, 95.5 ± 2.8 and 96.8 ± 2.8 (Table 3), but the sizable experimental uncertainties make difficult the assignment of an exact conjugation energy for α,β unsaturated carbonyl systems.

D[CH$_3$C(O)-COCH$_3$] = 74.0 kcal mol^{-1} given by eq 1 is consistent with literature values of 72.9 and 74.2, indicating little or no conjugation between the two carbonyls of 2,3-butanedione.

Experimental values for bonds to fluorine are matched by eq 1. This includes the strongest single bond in this work, D[H$_2$B-F] = 170 kcal mol^{-1}. This agreement again confirms the ability of eq 1 to treat polar bonds successfully. There is some disagreement between calculated D[Ph-F] and literature values, but acceptable agreement for D[CH$_2$CH-F] and D[MeC(O)-F]. D[HCC-F] calculated by eq 1 is in better agreement with recent ab initio values for fluoroacetylene than with the value of the NIST database 69; the G3 calculation was reported to have corrected much of the error associated with fluorinated compounds in G2.[30]

The last two rows in Table 3 involve the hydroxyl and amino groups. Here, the resonance-free values given by eq 1 are lower than experimental by substantial amounts, of the order of 10 kcal mol^{-1}, indicating extensive resonance effects in their C-O and C-N bonds. This is evidence that resonance structures **I** and **II** are responsible for the enhanced reactivity of phenols and anilines in electrophilic aromatic substitutions and is supported by their quite different σ_m and σ_p Hammett substituent constants. The situation is similar for bonds to phenyl of the other -OR and -NHR groups of Table 2 but not included in Table 3. Strong special effects are also demonstrated as influencing the D values of HO- and H$_2$N- bonds to vinyl, ethynyl, acetyl, and BH$_2$. Evidently, the same type of effect is operative in HO-NO$_2$, CH$_3$O-NO$_2$, and F-NO$_2$ (Table 2) and must also be present in the calculated value for H$_2$N-NO$_2$ (Table 3). Nitric acid is a planar molecule,[31] the typical sp^2 geometry.

The strong barrier to rotation of the C-N bond in amides has been studied extensively,[32] and eq 1 gives a D[MeC(O)-NH$_2$] value that is 12.9 kcal mol^{-1} smaller than experimental. This difference should be the rotational barrier of the C-N bond in gas-phase acetamide. It can be compared to the experimental value of 16.4 ± 0.3 determined recently for formamide by gas-phase NMR.[33] C-N bonds of acetamides have lower barriers than those of formamides, e.g., by 3.7 kcal mol^{-1} in *N,N*-dimethylacetamide compared to *N,N*-dimethylformamide,[32b] because of the lower positive charge of the acetamide carbonyl carbon.[32a] A corresponding decrease for the rotational barrier of acetamide, relative to formamide, would lead to a gas-phase rotational barrier of 12.7 kcal mol^{-1} for acetamide, consistent with theoretical calculations of 12.45−13.98,[32c] in good agreement with 12.9 from eq 1. Formal Lewis resonance structures can be written for amides, placing a negative charge on the carbonyl oxygen and a double bond between nitrogen and the adjacent carbon, but better explanations have been proposed[32a] in terms of charge transfer. All other -OR and -NHR groups included in Table 2 but not in Table 3 show similar effects toward vinyl, ethynyl, acetyl, and BH$_2$. The significantly lower than experimental values calculated by eq 1 for HO- and H$_2$N- bonding to sp^2 and sp hybridized groups are not failures of eq 1. Consistent with proviso (a) above, the values given by eq 1 should not match experiment and the difference provides a simple and direct way of quantifying any "special effect." By itself, the experimental value provides no clue.

The available ab initio values for H$_2$B bonded to CH$_3$, SiH$_3$, vinyl, ethynyl, acetyl, fluorine, and chlorine are matched satisfactorily by eq 1 with χ[BH$_2$] = 1.87, within expected uncertainties. There is no evidence of any strong "special effect" in these cases, even though significant hyperconjugation effects, B-H → B(p), have been proposed for the "perpendicular" conformation of H$_2$BBH$_2$ (a dihedral angle of 90° between the planes defined by each BH$_2$).[34] Our G3 calculations of BH$_3$ and H$_2$BBH$_2$ geometries (MP2/6-31G(d) method) show B-H bond lengths of 1.191 and 1.197 Å, respectively, a change equivalent to that of the elongation of the C-H bond in ethane compared to methane. Significant hyperconjugation effects in H$_2$BBH$_2$ would be expected to produce more drastic changes; in addition, the angle ∠BBH is 121.9°, whereas a value smaller than 120° would be expected from this type of bonding. The planar structure is not a conformer but a transition state (we find one imaginary frequency of 492 cm^{-1} with the HF method) lying 10.4 kcal mol^{-1} higher than the perpendicular structure. HF methods, however, are often inaccurate in calculating TS energies, but it is clear that the planar structure is not relevant to this work. Delocalization effects into the empty p orbital of boron in X$_2$BBX$_2$ have also been postulated to be of comparable magnitude for X = CH$_3$, F, OH, and NH$_2$.[34] Any "special effect" present in H$_2$BBH$_2$ but absent in H$_2$B-X should produce failure of eq 1. Its success shows that BH$_2$ behaves similarly in bonds with all groups for which values are available, except for the usual additional stabilization of OH and NH$_2$ bonded to any sp^2 center.

Table 3 allows the calculation of stabilization energies (SE, relative to methyl) for phenyl, vinyl, ethynyl, acetyl, and BH$_2$ radicals, from their conjugation-free D[R-R]. The SE values are −13.1, −11.6, −32.1, 7.9, and −7.6 kcal mol^{-1}, respectively, where the negative sign indicates destabilization.

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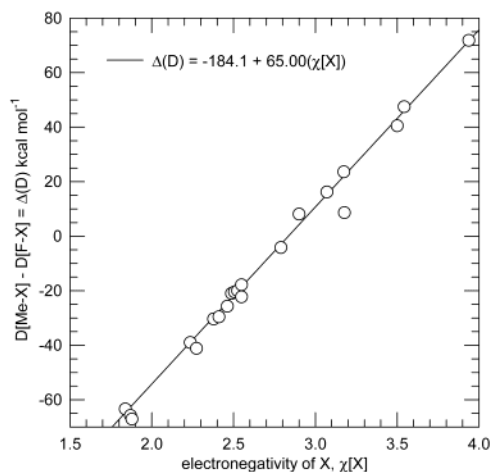
FIGURE 2. Difference $D[CH_3-X] - D[F-X]$ of literature values vs electronegativity of X. The straight line is the "theoretical" required by eq 4. For the identity of each point, see text.

The results of Tables 1–3 allow a more general test of eq 4, over a wider range. The difference $\Delta(D) = D[Me-X] - D[F-X]$ of literature values is plotted vs $\chi[X]$ for 21 different X in Figure 2, where the points are, from left to right: SiMe$_3$, BH$_2$, SiH$_3$, COCH$_3$, PH$_2$ (see below), tBu, iPr, Et, Allyl, Bz, Me, Ph, CH=CH$_2$, C≡CH, C≡N (see below), NH$_2$, Cl, NO$_2$, OH, ONO$_2$, and F. The point deviating significantly from all others in Figure 2 is the nitro group. The line in Figure 2 is drawn with the "theoretical" intercept and slope required by eq 4: $a = -184.1$ and $b = 65.00$. A linear regression through the literature points gives an "experimental" $a = -186.3$ and $b = 65.3$ ($r = 0.9953$), in agreement with the prediction of eq 4. The variety of groups and extremely wide range of 135 kcal mol^{-1} in $\Delta(D)$ in Figure 2 again attests to the validity and generality of eq 4, in the absence of significant special effects.

The single case of significant deviation in Figure 2 (NO$_2$) is probably due to charge transfer from the lone pairs of fluorine to the nitrogen, which carries a full positive formal charge unlike any other sp^2 group treated. For the chloride, eq 1 yields $D[Cl-NO_2] = 35.8$, in fair agreement with a literature value of 34.0.[8] This difference in behavior for the two halogens is likely due to the shorter bond in F-NO$_2$ (1.47 Å) compared to Cl-NO$_2$ (1.84 Å).

Bonds to H, SH, SR, PH$_2$, and CN. Hydrogen is conspicuous by its absence from Tables 1–3. With the known values[8] of $D[H-H]$ and $D[H-A]$, along with $\chi[A]$ from the tables, $\chi[H]$ can be calculated vs each A. A rather wide range of values is obtained, without a pattern apparent to us: $\chi[H] = 1.95$ vs Me, 2.01 vs acetyl, 2.03 vs allyl, 2.06 vs Et, 2.07 vs Bz and NH$_2$, 2.13 vs iPr, 2.16 vs OH, 2.17 vs SiH$_3$ and OPh, 2.18 vs tBu, 2.20 vs Cl, 2.22 vs NHPh, 2.23 vs vinyl, 2.24 vs SiMe$_3$ and OMe, 2.26 vs F and Ph, 2.27 vs ONO$_2$, and 2.50 vs C≡CH. Unique behavior by hydrogen is not uncommon in chemistry and Pauling[1] noted that hydrogen's electronegativity "misbehaves." Using an average value of $\chi[H] = 2.2$, as recommended by Pauling, gives generally the correct trends in $D[H-A]$, but the overall accuracy is much lower than that obtained with all other bonds treated here. Previous evaluations of eq 1 were weighted heavily with

H-A bonds and this is one reason for pessimistic conclusions regarding its accuracy. Nevertheless, even with bonds to hydrogen, eq 1 is useful for understanding some facts that appear surprising at first.

$D[Me-H] = 104.8 > D[Me_3C-H] = 95.8$ kcal mol^{-1}, but the reverse is seen with silicon, $D[H_3Si-H] = 91.8 < D[Me_3Si-H] = 94.4$.[21] Hydrogen's electronegativity is intermediate between that of C and Si. Increasing alkyl substitution on C or Si decreases the electronegativity of both. Increasing alkyl substitution on C decreases $\Delta\chi$ with H and decreases the strength of the C-H bond; increasing alkyl substitution on Si increases $\Delta\chi$ with H and increases the strength of the Si-H bond, contributing to the drastic reversal in behavior. Similarly, $D[Me-H] = 104.8$ is considerably stronger than $D[Me-Me] = 89.8$. However, $D[Me_3Si-H] = 94.4$ is about the same as $D[Me_3Si-Me] = 94.2$.[21] Equation 1 predicts that $D[H-A]$ is likely to be significantly greater than $D[Me-A]$ for all A more electronegative than carbon because of the greater $\Delta\chi$ in H−A compared to Me-A. However, this is not necessarily true for A less electronegative than H, as with Si. Consequently, from G2 calculations at 0 K,[2] $D[H_2B-H] = 105.2$ and $D[H_2B-Me] = 104.1$; and $D[HBe-H] = 93.3$ and $D[HBe-Me] = 93.1$ kcal mol^{-1}.

The unique variability of $\chi[H]$ does not allow use of eq 1 or eq 4 for bonds to hydrogen. While functions similar to, but considerably more complex than, eq 4 have been used,[3c,35a] one such involving bonds to hydrogen has been questioned as demonstrating one of the hazards of electronegativity correlations.[35b] Questioning the validity of linear correlations between $\Delta(D)$ and $\chi[X]$ in general is not justified in view of Figures 1 and 2. No variability in χ is seen with any other of the atoms and groups in Tables 1–4.

Equation 1 has been reported to fail with bonds to sulfur.[4b] It is a requirement of eq 1 that $D[A-B] \geq \frac{1}{2}(D[A-A] + D[B-B])$. Using the commonly quoted value[9] of $D[HS−SH] = 66.0 \pm 2.0$ kcal mol^{-1}, eq 1 gives $D[Me-SH] = \frac{1}{2}(89.8 + 66.0) + 23(\Delta\chi)^2 = 77.9 + 23(\Delta\chi)^2$, compared to literature values of 73.6[8] and 74.7 $\pm$ 1.[9] Pauling assigned equal electronegativities to S and C, but even with $\Delta\chi = 0$, eq 1 appears to fail by implying negative $23(\Delta\chi)^2$. This led us to question the value of $D[HS-SH] = 66.0$. We performed a G3 calculation and obtained $D[HS-SH] = 61.6$ at 298 K, with the usual uncertainty of $\pm$ 2 kcal mol^{-1}. With the G3 value and $\Delta\chi = 0$, eq 1 gives $D[Me-SH] = 75.7 \pm 2$, in acceptable agreement with literature values. Similarly, eq 1 gives $D[Ph-SH] = 88.8 \pm 2$, within combined uncertainties of literature values of 85.5 $\pm$ 2[8] and 86.5 $\pm$ 2;[9] also, $D[Et-SH] = 74.6 \pm 2$ vs 72.7[8] and $D[Bz-SH] = 63.6 \pm 2$ vs 60.6 $\pm$ 1.3.[8]

Equation 1 also appears to fail with bonds to SMe, when the usually quoted[9] value of $D[MeS-SMe] = 65.2 \pm 0.9$ kcal mol^{-1} is used with $23(\Delta\chi)^2 = 0$, yielding $D[Me-SMe] = 77.5$ vs experimental 73.6 $\pm$ 0.8.[9] All reactions A-A + B-B → 2 A-B are required by eq 1 to be exothermic or thermoneutral in the rare case of $\chi[A] = \chi[B]$.[4b] The bonds of both reactants have a zero $\Delta\chi$ term, while those of the products would have nonzero $\Delta\chi$. Using enthalpies of formation[8] for the reaction Me-Me + MeS-SMe → 2

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TABLE 4. Calculated Bond Dissociation Enthalpies (eq 1, in Parentheses), Literature Values, and Enthalpies of Formation of Radicals Adopted for This Work (in Brackets) in kcal mol⁻¹ at 298 K[a]

A→ χ→ $\Delta H_f°$→ B↓	−OH **3.500** [9.3]	−OOH 3.334 [3.5] 3.5[b]	−OMe 3.439 [4.2]	−OOMe 3.292 [2.2] 2.2±1.2[c]	−OPh 3.376 [13.0]
Me	**92.3**[d]	**69.6** 69.6[e] 69.1[f] 71.5±1.9[c]	**83.1**[d]	**67.0** 67.0[e] 66.0[f]	**64.1**[d]
Et	(94.2)[d]	(71.0) 74.1±3.2[c] 71.5[b]	(84.8)[d]	(68.2)	(64.9)[d]
Allyl	(79.8)[d]	(56.8)	(70.4)[d]	(54.1)	**50.6**[d]
HO	**51.1**[d]	(35.8) 35.8[g] 33.9[h]	(44.6)[d] 44.1[e] 45.3[g] 44.3[f]	(35.1) 34.2[g] 34.2[i]	(27.7)[d]
HOO	**19.3** 17.8[h] 19.1[j]		(28.8) 29.6[h]	(18.1)	(11.5)
MeO			37.9[d]	**28.0** 28.0[g]	(20.8)
MeOO				(17.1)	(10.7)
PhO					(3.6)[d]

[a] Boldface lettering denotes the two values in each column used to obtain χ and calculated D (in parentheses). [b] Reference 69. [c] Reference 40d; equilibrium study. [d] From Tables 1 and 2. [e] $\Delta H_f°$ of the compound from ref 8, with $\Delta H_f°$ of the radicals adopted for this work. [f] $\Delta H_f°$ of the compound from ref 77 with $\Delta H_f°$ of the radicals adopted for this work. [g] Reference 78, ab initio calculation, G2. [h] Reference 44, ab initio calculation, G2 at 0 K. [i] Theoretical value, G2(MP2) calculated in this work. [j] Reference 79, ab initio calculation, G2M at 0 K.

Me-SMe, $\Delta H_{rxn} = 2(\Delta H_f°[MeSMe]) - \Delta H_f°[Me-Me] - \Delta H_f°[MeS-SMe] = 2(-8.96) - (-20.04) - (-5.76) = 7.9$. This result violates the exothermicity or thermoneutrality requirement. However, recent theoretical calculations have indicated $D[MeS-SMe] = 61.0^{36a}$ and $60.0,^{36b}$ substantially lower than 65.2. With $D[MeS-SMe] = 60.5 \pm 2$, and $\Delta\chi = 0$, eq 1 gives $D[Me-SMe] = 75.2 \pm 2$, in reasonable agreement with the literature value, and $D[Ph-SMe] = 88.2 \pm 2$ vs $86.5 \pm 2.0.^9$ With $\Delta\chi = 0$, using Hess's law for the above reaction yields $\Delta H_{rxn} = -2D[Me-SMe] + D[Me-Me] + D[MeS-SMe] = -2(75.2) + 89.8 + 60.5 = -0.1 \pm 2$, just exothermic and consistent with the requirement of eq 1. Any nonzero $\Delta\chi$ would make this value more negative. The simple equation of Pauling, in tandem with current high-level quantum mechanical calculations, suggests the need for an experimental reexamination of the strengths of S-S bonds. The fact that eq 1 gives values consistent with experiment for bonds of HS and MeS to phenyl indicates that conjugation effects with the ring are minor or nonexistent, unlike those in Ph-OH and Ph-OR.

There are few reliable experimental values for bonds to phosphorus, but there are theoretical calculations for

some bonds to PH₂.[2,37] We find that eq 1 gives values in fair agreement with theoretical values, using $D[H_2P-PH_2] = 55.4 \pm 2$ kcal mol⁻¹ (our G3 calculation at 298 K) and $\chi[PH_2] = 2.273$. For comparison with other theoretical calculations reported at 0 K, such values were increased by $(5/2)RT = 1.5$ to estimate 298 K, a good approximation for molecules of four or more atoms and within the uncertainty of ab initio values. The results are (bond, D calculated by eq 1, theoretical values): H_3Si-PH_2, 69.2, 71.4,[2] and 71.6;[37a] H_3C-PH_2, 74.1, 71.5,[2] 72.2,[37b] and 70.0 (our G3 calculation); $CH_3C(O)-PH_2$, 64.7, 62.6;[2] $H_2CCH-PH_2$, 85.9, 81.9,[2] and 84.8;[37b] $HCC-PH_2$ 110.8, 109.3,[2] and 116.9;[37b] H_2N-PH_2, 75.9, 77.3;[2] $Cl-PH_2$, 75.4, 79.6;[2] $HO-PH_2$, 87.9, 90.0,[2] and 87.9 (our G3 calculation); $F-PH_2$, 110.5, 111.8.[2] Normal behavior, without special effects, is seen with PH₂ bonds to sp² and sp centers, unlike NH₂.

Bond dissociation enthalpies involving the nitrile group are not known very accurately, as evidenced by reports of $D[NC-CN] = 134.1^8$ and 128.1 ± 1^9 kcal mol⁻¹; $D[HCC-CN] = 152.4^8$ and $143.9;^9$ $\Delta H_f°[CN] = 104.0^8$ and $105.5 \pm 1.1.^9$ A self-consistent set of D values in fair agreement with available data is obtained by eq 1 with $\Delta H_f°[CN] = 106.5$, adopted for this work and consistent with the G3 value of $106.7,^{38}$ and $\chi[-CN] = 2.90$, as follows (bond, D by eq 1, literature values): $D[F-CN] = 113.3, 114.4^8$ and $112.3 \pm 1.2;^9$ $D[Cl-CN] = 100.3, 100.0^8$ and $100.7 \pm 1.2;^9$ $D[Me-CN] = 117.7, 121.1^8$ and $121.8;^9$ $D[Et-CN] = 117.8, 120.1;^8$ $D[iPr-CN] = 118.5, 120.6;^8$ $D[tBu-CN] = 117.0, 115.8;^8$ $D[CH_2CHCH_2-CN] = 104.1, 107.2;^8$ $D[Ph-CN] = 130.4, 132.7;^8$ $D[CH_2CH-CN] = 128.9, 132.1;^8$ $D[HCC-CN] = 146.8, 152.4^8$ and $143.9 \pm 1,^9$ and $D[NC-CN] = 139.1, 134.1.^8$

Peroxides, Trioxides, Tetroxides and Bonds to O₂, NO, ·CH₂·, and CO. Bond dissociation enthalpies of weak bonds involving an O-O linkage are of importance in studies of combustion, autoxidation, phenolic antioxidants, radical initiators, etc., and we applied eq 1 to a typical group of such bonds. Table 4 shows some results given by eq 1 (in parentheses) from the two known values in each column (boldface). Overall agreement with available experimental and theoretical data is satisfactory. Nine new values are calculated, and others for similar bonds to iPr, tBu, and Bz can be obtained in the same way. For self-consistency it is reassuring that, from the measured $D[PhO-Me]^{8,19i}$ and $D[PhO-CH_2CHCH_2],^{39}$ the calculated $D[C_6H_5O-OH] = 27.7$ kcal mol⁻¹ is in good agreement with 28.4 obtained from the group additivity estimate of $\Delta H_f°[PhOOH] = -6.1$ (Tables 3 and 4). The failure of phenoxy radicals to couple, head to head, with each other or with alkylperoxy radicals is known, and the calculated very weak bonds for such compounds in Table 4 are consistent with this, considering the entropic cost of coupling. Other weak bonds to phenoxy can be calculated by eq 1 or from the established electronegativities and radical stabilization energies. For example, $D[PhO-NHPh] = D[Me-Me] - SE[PhO·] - SE[·NHPh] + 23(\chi[PhO] - \chi[NHPh])^2 = 89.8 - 43.1 - 23.0 + 23-$

(36) (a) Carles, S.; Lecompte, F.; Schermann, J. P.; Defrançois, C.; Xu, S.; Nilles, J. M.; Bowen, K. H.; Bergès, J.; Houée-Levin, C. *J. Phys. Chem. A* **2001**, *105*, 5622−5626. MP2/6-311+G(2d,2p) calculations giving $D_e = 61.8$ kcal mol⁻¹, which includes ZPE; $1/2 h\nu$ of the S-S stretching frequency is 0.76. (b) Mousavipour, S. H.; Emad, L.; Fakhraee, S. *J. Phys. Chem. A* **2002**, *106*, 2489−2496; MP4SDTQ/6-311G(d,p). Their $D[Me-SMe] = 70.9$ implies $\Delta H_f°[MeS·] = 27.1$ and, from $\Delta H_f°[MeSSMe] = -5.8,^8$ $D[MeS-SMe] = 60.0$.

(37) (a) Baboul, A. G.; Schlegel, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 8444−8451. (b) Boyd, S. R.; Boyd, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 4214−4219; quoted at 298 K.

(38) Montgomery, J. A. Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532−6542.

(39) Colussi, A. J.; Zabel, F.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 161−178. Very low-pressure pyrolysis.

$(3.376 - 3.051)^2 = 26.2$. This approach should not be used for bonds of RO- or RNH- to sp^2 or sp hybridized centers, because of expected resonance or charge-transfer effects as demonstrated above.

Properties of alkylperoxy radicals are of interest because they are chain-propagating species in combustion and autoxidations. Equation 1 is not applicable to radical species such as ROO·. $D[Me-O_2·]$ cannot be described in terms of $D[Me-Me]$ and $D[·OO-OO·]$ because the latter would denote the interaction energy between two oxygen molecules at covalent bond distances. This would be a repulsion (O_4 is not stable), not a binding energy. However, eq 4 should be applicable if $\chi[·O_2·]$ were known, because it does not involve a $D[X-X]$ term. Equation 4 was used to obtain $\chi[·O_2·]$. From $D[Me-O_2·] = 31.0$[40] kcal mol^{-1} and $D[Allyl-O_2·] = 18.4 \pm 1.2$,[40a,41] $\Delta(D) = 12.6 = a + b(\chi[·O_2·])$, where $a = 18.516$ and $b = -1.702$. Solving for $\chi[·O_2·]$ yields 3.476. This allows the use of eq 4 to calculate $D[Bz-O_2·]$ from $\Delta(D) = D[Me-O_2·] - D[Bz-O_2·] = 13.85 - 0.874(3.476) = 10.8$. Hence, $D[Bz-O_2·] = 31.0 - 10.8 = 20.2$, in agreement with the reported experimental value of 20 ± 1.[42] The properties of PhO-O$_2$· are of interest because it would propagate autoxidation reactions even in the presence of phenols. Specific attempts to find this species, or any other oxygen/phenoxy radical adduct, have failed.[43] Equation 4 gives $D[HO-O_2·] - D[PhO-O_2·] = 42.66 - 5.704(\chi[·O_2·]) = 22.8$. From $D[HO-O_2·] = 3.45$,[44] $D[PhO-O_2·] \approx -19$, a repulsion, hence the failure to detect the species. Other values for alkyl groups can be calculated similarly by eq 4: $D[Et-O_2·] = 32.8$, $D[iPr-O_2·] = 34.9$, $D[tBu-O_2·] = 34.2$, $D[H_3Si-O_2·] = 60.7$ and $D[Me_3Si-O_2·] = 66.0$. The values for the alkylperoxy radicals fall between the different values recommended by Benson[40a] and by Knyazev and Slagle[40d] and are about at the limits of their respective reported uncertainties. This procedure does not reproduce reported[9] values for $D[F-O_2·]$ or $D[Cl-O_2·]$. Equation 4 should not be used to estimate D of bonds of ·O$_2$· to sp^2 or sp hybridized centers because of expected resonance or charge-transfer effects, as seen with Ph-OH, H$_2$B-OH, etc.

Application of eq 4 to bonds with nitric oxide leads to the following results for nitroso compounds. From the known values of $D[Me-NO] = 39.9$[9] and $D[Cl-NO] = 38.22$[8] kcal mol^{-1} $\Delta(D) = 1.79 = -69.17 + 29.85(\chi[-NO])$. Solving for $\chi[-NO]$ gives 2.377. This appears too low a χ value for nitrogen. However, using this value with eq 4, $\Delta(D) = D[HO-NO] - D[Me-NO] = 115.76 - 44.85(2.377)$, gives $\Delta(D) = 9.2$, or $D[HO-NO] = 39.9 + 9.2 = 49.1$, vs the literature value of 49.22,[8] confirming the χ value. Also, eq 4 with $\chi[-NO] = 2.377$ gives reasonable values for $D[iPr-NO] = 38.1$ (vs 36.5 ± 3.1[9]), $D[tBu-NO] = 35.8$

(40) Literature values: (a) 30.0 ± 1.1 from group additivity: Benson, S. W. *J. Phys. Chem.* **1996**, *100*, 13544−13547. (b) 30.9 ± 0.8: Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342. (c) 32.2: ref 9. (d) 32.7 ± 0.9: Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem. A* **1998**, *102*, 1770−1778.

(41) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem. A* **1998**, *102*, 8932−8940.

(42) Elmaimouni, L.; Minetti, R.; Sawyersin, J. P.; Devolder, P. *Int. J. Chem. Kinet.* **1993**, *25*, 399−414.

(43) (a) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095. (b) Platz, J.; Nielsen, O. J.; Wallington, T. J.; Ball, J. C.; Hurley, M. D.; Straccia, A. M.; Schneider, W. F.; Sehested, J. *J. Phys. Chem A* **1998**, *102*, 7964−7974.

(44) Mckay, D. J.; Wright, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 1003−1013; G2(MP2) at 0 K.

(vs 39.5 ± 1.5[9]), $D[H_3Si-NO] = 38.2$ (vs 38.0 ± 1.4[45]), and $D[CH_3O-NO] = 39.4$ (vs 41.3 ± 1.0[8]). Similarly, [Ph-NO] $= 53.3$ (vs 54.5 ± 2[8] and 50.8 ± 1[9]), indicating no particular resonance effect with the ring in nitrosobenzene, like nitrobenzene and unlike aniline. The low χ value of -NO indicates that there is some negative charge on nitrogen, evidently with contribution by the Lewis dot structure **VI**, despite the counterintuitive placement of the charges. We performed a theoretical calculation at the level of full valence CASSCF/TZP, which confirmed that 30% of the odd spin is on the oxygen, according to Mulliken population analysis.

$$·\ddot{N}::\ddot{O}: \longleftrightarrow {}^{-}:\ddot{N}::\ddot{O}·^{+}$$

$$\textbf{V} \qquad\qquad \textbf{VI}$$
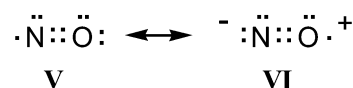
The importance of NO as a biological signaling agent has been demonstrated, and the possible role of S-nitrosothiols in its transport and release has led to measurements of $D[RS-NO]$.[46] Available values are matched by eq 4, using $\chi[MeS] = 2.59$, a reasonable value for sulfur and near Pauling's value of 2.5. With the theoretical value of $D[MeS-SMe] = 60.5 \pm 2$ kcal mol^{-1} and $\chi[-NO] = 2.373$, $\Delta(D) = D[Me-NO] - D[MeS-NO] = 10.0$, or $D[MeS-NO] = 39.9 - 10.0 = 29.9$ kcal mol^{-1}, compared to $D[CH_3(CH_2)_5S-NO] = 28.1$ determined experimentally and $D[MeS-NO] = 32.4 \pm 2$ from ab initio calculations.[46]

Peroxynitrites (ROONO) are involved in tropospheric processes leading to terrestrial ozone formation and NO$_x$ removal. $D[ROO-NO]$ was the subject of recent theoretical calculations,[47] which gave values of 20−22 kcal mol^{-1}. Equation 4, with needed data from Tables 1−4, yields $D[Me-NO] - D[ROO-NO] = -66.27 + 35.28(2.377) = 17.6$ and $D[MeOO-NO] = 22.3$, in good agreement. However, eq 4 yields $D[F-NO] = 69.5$, or 13 kcal mol^{-1} greater than a literature value of 56.3,[8] although there is good agreement above with $D[Cl-NO]$.

Equation 4 was also applied to bonds with triplet methylene, ·CH$_2$·. From $\Delta H_f°[·CH_2·] = 92.35$[8] kcal mol^{-1}, $\Delta H_f°[ClCH_2·] = 29.1 \pm 1$[9] and $\Delta H_f°$ of Me·, Et·, and Cl· from Tables 1 and 2, we obtain $\Delta(D) = D[Me-CH_2·] - D[Cl-CH_2·] = 98.47 - 92.25 = 6.22 = a + b(\chi[·CH_2·])$; $a = -69.17$, $b = 29.854$ and, solving, $\chi[·CH_2·] = 2.525$. This value of χ used with eq 4 yields $D[Me-CH_2·] - D[F-CH_2·] = -19.33$, or $D[F-CH_2·] = 118.4$. The thermodynamic relationship $\Delta H_f°[FCH_2·] = \Delta H_f°[F·] + \Delta H_f°[·CH_2·] - D[F-CH_2·]$ yields $\Delta H_f°[FCH_2·] = -7.1$ compared to the literature value of -7.6 ± 2.[9] Similarly, eq 4 gives $D[Me-CH_2·] - D[tBu-CH_2·] = 2.90$, $D[tBu-CH_2·] = 95.63$ and $\Delta H_f°[tBuCH_2·] = 8.4$ vs literature values of 8.7 ± 2[9] and 8.0[10] for the neopentyl radical. Applied to $D[Ph-CH_2·] - D[Me-CH_2·]$, eq 4 yields a resonance-free value of $\Delta H_f°[Bz·] = 60.5$ vs literature values of 49.5[8] or 47.8,[9] indicating stabilization energies of 11.0[8] or 12.7,[9] vs SE[Bz·] = 11.7 obtained above from different data. A similar calculation yields SE[HC≡CHCH$_2$·] $= 12.2 \pm 1.0$ for the

(45) Krasnoperov, L. V.; Kalinovski, I. J.; Niiranen, J. T.; Gutman, D. *J. Phys. Chem. A* **1997**, *101*, 4929−4938.

(46) Bartberger, M. D.; Mannion, J. D.; Powel, S. C.; Stamler, J. S.; Houk, K. N.; Toone, E. J. *J. Am. Chem. Soc.* **2001**, *123*, 8868−8869.

(47) Zhang, D.; Zhang, R.; Park, J.; North, S. W. *J. Am. Chem. Soc.* **2002**, *124*, 9600−9605; B3LYP/6-31G(d,p) and CCSD(T)/6-31G(d).

propargyl radical. This procedure should not be used for estimating D values for bonds of methylene to -OR or -NHR groups, because of their expected special effect on interaction with sp^2 centers.

Equation 1 can be used to obtain $D[\cdot CH_2\text{-}CH_2\cdot]$ and the enthalpy of formation of this species. From $\Delta H_f°$ of $CH_3\cdot$, $\cdot CH_2\cdot$, and $CH_3CH_2\cdot$, $D[CH_3\text{-}CH_2\cdot] = 98.47$ kcal mol^{-1}. $D[CH_3\text{-}CH_2\cdot] = \frac{1}{2}(D[\text{Me-Me}] + D[\cdot CH_2\text{-}CH_2\cdot]) + 23(\Delta\chi)^2$, or $98.47 = \frac{1}{2}(89.8 - D[\cdot CH_2\text{-}CH_2\cdot]) + 0.0$. Solving yields $D[\cdot CH_2\text{-}CH_2\cdot] = 107.14$. Therefore $\Delta H_f°[\cdot CH_2\text{-}CH_2\cdot] = 2\Delta H_f°[\cdot CH_2\cdot] - D[\cdot CH_2\text{-}CH_2\cdot] = 77.56$. Since $\Delta H_f°[CH_2=CH_2] = 12.54$,[8] the difference in $\Delta H_f°$ between the two C_2H_4 species is the energy of the π bond, 65.0 kcal mol^{-1}. The activation energy for thermal *cis/trans* isomerization of simple alkenes (1,2-dideuterioethene) is usually quoted[48] as 65.0 kcal mol^{-1}.

Bonds to CO cannot be treated by eq 1 because $D[\text{OC-CO}]$ would be the interaction energy between two carbon monoxide molecules at covalent distances, a repulsion. However, eq 4 is applicable. From $D[\text{Me-C(O)}\cdot] = 11.3$[8] kcal mol^{-1} and $D[\text{F-C(O)}\cdot] = 34.1$,[8] $\Delta(D) = -22.8 = -184.1 + 65.00(\chi[\text{CO}])$; solving gives $\chi[\text{CO}] = 2.482$. Using this value of χ and eq 4, yields $\Delta(D) = D[\text{Me-C(O)}\cdot] - D[\text{Cl-C(O)}\cdot] = -69.17 + 29.85(2.482) = 4.9$, or $D[\text{Cl-C(O)}\cdot] = 11.3 - 4.9 = 6.4$ (vs literature values of 17.6,[8] 7.8[9] and 6.6[10]). Similarly, we obtain $D[t\text{Bu-C(O)}\cdot] = 7.8$ and $D[\text{Bz-C(O)}\cdot] = -0.3$, the last value being consistent with the known rapid decarbonylation of $C_6H_5CH_2C(O)\cdot$. Bonding of CO to other alkyl groups can be calculated similarly, but not for bonds to sp^2 or sp hybridized groups or to -OR or -NHR.

Ionic and Organometallic Bonds. Pauling defined electronegativity to be a measure of the attraction for electrons of "neutral atoms in a stable molecule." Equation 1 is not applicable to salts. $D[\text{Na-Na}]$ and $D[\text{Cl-Cl}]$ are irrelevant to the major attractive interactions in Na$^+$Cl$^-$ and the electronegativities of Na and Cl are not the same as those of Na$^+$ and Cl$^-$.

While eq 1 is successful with bonds to boron (Table 3), it does not duplicate bond enthalpies obtained by ab initio calculations for organometallic bonds,[2] e.g., for bonds between Li and C, N, O, etc. Evidently, such bonds belong in the ionic category. This is in agreement with recent findings that C-Li bonds are predominantly ionic: "the C-Li interactions for example in CH$_3$Li are rather characteristic of closed shell ionic species CH$_3^{-}\cdots$Li$^+$."[49] Comparing physical properties of lithium alkyls to alkyl fluorides, with about the same $\Delta\chi$, the former show peculiar aggregates in organic solutions and the latter do not. The nature of the ionic species formed in the aggregates has been known, and the theoretical reasons for them have been understood for some time.[50] Pauling noted that bonds of the alkali and alkaline earth metals with nonmetals are ionic.[1] Bonding between the alkali metals themselves is treated accurately. Known D values for KNa,[51] RbNa,[52] CsNa,[51] and KRb[53] are given correctly

by eq 1, to three significant figures, in terms of the homonuclear D[A-A] and D[B-B] and the χ values assigned by Pauling[1] to the elements involved. Some evaluations of eq 1 included many ionic (LiF, NaCl, RbF, etc.) and organometallic bonds[2,4a] and, therefore, are not valid tests of accuracy.

Sufficiently extensive and reliable BDE information for bonds of transition metals is not available for establishing the performance of eq 1 with such bonds, proviso (b).

Bonds to Br, I and to Multivalent Atoms. In progressing to higher atomic numbers, an effect appears that is not major with elements up to chlorine: relativistic spin−orbit splitting or coupling. This splitting between the $^2P_{3/2}$ (ground) and $^2P_{1/2}$ states of fluorine and chlorine atoms is small, 1.2 and 2.5 kcal mol^{-1} respectively, but it is 10.5 for Br$\cdot$ and 21.7 for I$\cdot$.[54a]

Many bonds between bromine and the various groups of Tables 1−3 are treated well by eq 1, with χ[Br] = 2.880 and D[Br-Br] = 46.09[8] kcal mol^{-1}. Agreement with literature values is to within their stated uncertainties for bonds to Me, Et, iPr, tBu, Ph, vinyl, ethynyl, acetyl, HO and Cl. For $D[C_6H_5CH_2\text{-Br}]$, experimental values differ, 56.2[8] and 59.3,[9] while eq 1 yields 59.5. However, eq 1 fails to agree with literature D values for Br-F, giving 67.8 instead of 59.7,[8] and for H$_3$Si-Br, giving 84.1 instead of 89.9.[21] Spectroscopic measurements have shown that BrF dissociates to F($^2P_{3/2}$) and Br($^2P_{1/2}$), the latter not being the ground state.[54b]

Application of eq 1 to bonds with iodine also presents a peculiar pattern. With D[I-I] = 36.1[8] kcal mol^{-1} and χ[I] = 2.80, there is agreement with a large variety of bonds as follows (bond, D by eq 1, and literature value[8]): I-F = 66.8, 67.1; I-Cl, 50.3, 50.3; I-Br, 41.2, 42.5; I-OH, 54.9, 55.9 ± 3.2;[9] H$_3$Si-I, 75.6, 73.7;[8] Me$_3$Si-I, 78.3, 82.2 ± 2;[21] and MeS-I, 49.3, 49.3 ± 1.7.[9] However, eq 1 invariably overestimates by 8−10 kcal mol^{-1} literature values for all carbon−iodine bonds. With iodine from the fifth row of the periodic Table, eq 1 again is inconsistent.

Failures of eq 1 with some bromides and iodides and successes with others appears to be indicating some "special effect" here, most likely the relativistic spin−orbit coupling. Ab initio calculations have shown[54c] that this effect can change D[Br-Br] by 6.9 and D[I-I] by 12.7 kcal mol^{-1}. For dissociation of bonds to Br and I, it then becomes important to establish what fraction dissociates into which state. The effect of the group bonded to iodine on the channels producing $\cdot$I($^2P_{3/2}$) and $\cdot$I($^2P_{1/2}$) is beyond the scope of this work and has been explored.[55]

In this context, it is appropriate to quote the title of the article announcing the G3 theoretical calculation:[30] "Gaussian-3 (G3) theory for molecules containing first-

(48) Vollhardt, K. P.; Schore, N. E. *Organic Chemistry, Structure and Function*, 4th ed.; W. H. Freeman and Co.: New York, 2002; p 436.

(49) Ponec, R.; Roithová, J.; Gironés, X.; Lain, L.; Torre, A.; Bochicchio, R. *J. Phys. Chem.* A **2002**, *106*, 1019−1025 and references therein.

(50) Epiotis, N. E. *Top. Curr. Chem.* **1989**, *130*, 47−166 and particularly p 126.

(51) Zavitsas, A. A. *J. Am. Chem. Soc.* **1991**, *113*, 4755−4767 and references therein. Values converted to 298 K.

(52) Wang, Y.-C.; Kajitani, M.; Kasahara, S.; Baba, M.; Ishikawa, K.; Katô, H. *J. Chem. Phys.* **1991**, *95*, 6229−6237. Value converted to 298 K.

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(54) (a) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement no. 1 (JANAF Thermochemical Tables). (b) Clyne, M. A. A.; McDermid, I. S. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 644 and 1644. (c) Visscher, L.; Dyall, K. G. *J. Chem. Phys.* **1996**, *104*, 9040−9046; CCSD(T) level.

(55) Griffiths, J. A.; Jung, K.-W.; El-Sayed, M. A. *J. Phys. Chem.* **1996**, *100*, 7989−7996.

and second-row atoms." There is yet a way to go before we fully understand chemical bonding, but Pauling's equation was a giant step forward and is still useful in many areas. Only a few have been presented here, but it is worth noting that the satisfactory conclusion of an 80-year quest for an accurate "universal" potential energy function for ground-state diatomics was achieved by including Pauling's electronegativity in the Morse equation.[51]

Equation 1 is not valid for bonds to *atoms* of multivalent elements. For example, for A = Me and B = N, eq 1 expressed in terms of Hess's law is Me-Me + N≡N → 2 Me-N, with $\Delta H_{rxn} = -23(\Delta\chi)^2$. This and similar reactions do not meet the requirement of conservation of the number of formal bonds. Tests of accuracy that include bonds to *atoms* of multivalent elements, as in Me-N, Me-C, Si-Cl, H-Si, etc.,[4a] are inappropriate. Pauling refers to electronegativity as pertaining to an atom in its "common oxidation state" and to bonds of "atoms in their normal covalencies (four for carbon, three for nitrogen, etc.)".[1]

Relationships with Physical Properties and Quantum Mechanics. There are relationships between eq 1 and physical properties.[56] For example, the sum of ionization energy (IE) plus electron affinity (EA) of radicals A· shows the same general trend as electronegativity, *within a homologous series of the same central atom and same hybridization*. IE and EA values are available[8,9] for the following five groups of carbon, oxygen, nitrogen and silicon radicals (A·, χ[A], Σ[IE + EA] of A·): (1) Me·, 2.525, 9.92 eV > Et·, 2.462, 8.12 eV> *i*Pr·, 2.411, 7.00 eV > *t*Bu·, 2.378, 6.54 eV. (2) O₂NO·, 3.543, 16.48 eV > HO·, 3.500, 14.85 eV > ·O₂·, 3.476, 12.52 eV> CH₃O·, 3.439, 12.29 eV > PhO·, 3.376, 10.81 eV. (3) O₂N·, 3.177, 12.29 eV > H₂N·, 3.071, 11.55 eV > PhNH·, 3.051, 10.00 eV > MeNH·, 3.018, 7.15 eV. (4) H₃Si·, 1.879, 9.54 eV > Me₃Si·, 1.838, 7.47 eV. (5) N≡C·, 2.90, 17.46 eV > HC≡C·, 2.789, 14.58 eV. This correspondence of trends between Pauling's electronegativity and measured physical properties within each group of radicals, shown graphically in Figure 3, should be sufficient to remove doubts about eq 1 being unrelated to physical properties. There are severe discontinuities in the (IE + EA) trends from group to group in Figure 3. Pauling noted that the good linear correlation that exists between (IE + EA) of a radical and the corresponding χ is valid only for univalent atoms (the halogens and alkali metals).[1] He also pointed out that hydrogen "misbehaves" in this correlation, which is the basis of the Mulliken scale of electronegativity.

As to the criticism that eq 1 does not appear to relate to other theories, there has been progress in this direction.[57] Recent theoretical calculations, B3LYP/6-31++G-(d,p), of molecular electrostatic potentials with the bond critical point approach[58] gave a set of electronegativity values[3d] that can be compared with those obtained by eq 1. The ab initio value of χ[OH] was reported as 3.542 in Pauling's scale. Shifting the ab initio values lower by
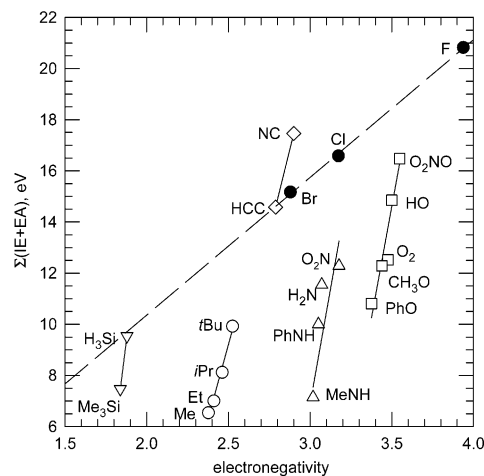

FIGURE 3. Sum of ionization energy plus electron affinity of radicals vs χ (open symbols). The dashed line shows the Mulliken-type correlation for monovalent species (solid symbols).

0.042 units, to bring the ab initio χ[OH] in line with χ[OH] = 3.500 assigned in this work, results in the following comparisons (group, this work, theoretical value[3d]): Me₃Si, 1.838, 1.877; PH₂, 2.273, 2.259; Me, 2.525, 2.513; Et, 2.462, 2.480; vinyl, 2.548, 2.799; MeNH, 3.018, 3.104; NH₂, 3.071, 3.075; Cl, 3.174, 2.918; NO₂, 3.177, 3.487; HO, 3.500, 3.500; F, 3.938, 3.896. Hydrogen was also found[3d] to exhibit unique behavior. These recent theoretical calculations result in electronegativities mostly quite similar to those obtained from Pauling's 70-year old equation. Used with eq 1, the ab initio electronegativities occasionally do not produce accurate *D*[A-B] values, unlike those obtained with the χ values of Tables 1−3. For example, with the ab initio χ values,[3d] *D*[Me-Cl] = 77.7 vs literature 83.8,[8] and *D*[Me₃Si-OH] = 125.1 vs 128.1.[59] There is a major discrepancy in one case: the reported ab initio χ[MeC(O)] = 2.881[3d] vs 2.235 from Table 3. The ab initio value produces grossly erroneous results when used with eq 1 to calculate *D* values. For example, *D*[MeC(O)-F] = 81.7 vs 122.5.[8] Similarly general agreement exists between our χ values and another bond critical point approach,[58] which yields, for example, χ[MeS] = 2.60 (adjusted to χ[HO] = 3.500), compared to 2.59 used in this work with the S-nitrosothiols and peroxynitrites, χ[NO₂] = 3.17, χ[CO] = 2.52, χ[-OO·] = 3.53, all in agreement with χ from eq 1. There is again a discrepancy in χ[CH₃C(O)], but it is smaller, the ab initio value[58] being 2.54.

There have been questions about the appropriateness of a $(\Delta\chi)^2$ term in eq 1,[4] because it gives χ the peculiar units of kcal$^{1/2}$ mol$^{-1/2}$. Suggestions have been made that better correlations are obtained with a k|$\Delta\chi$| term for the polar contribution.[4,60] However, if a linear dependence is postulated between |$\Delta\chi$| and fractional charges on A and B,[61] Coulomb's law requires a square term for this type of (attractive) interaction and the problem is addressed.[62]

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Conclusion

Pauling's electronegativity equation accurately describes homolytic bond dissociation enthalpies of common covalent bonds, including highly polar ones. Tables 1–4 presented bond dissociation enthalpies for 256 bonds, and additional values were presented in the text. Excluding anchor points, the average deviation between values calculated by eq 1 and literature values listed in the Tables is ± 1.5 kcal mol^{-1} for 117 bonds, for which there is no reason to expect special effects. When two or more literature values are given, their average was used for this calculation. For comparison, the average deviation between the literature values given in the tables is also ± 1.5; when more than two literature values are given, the greatest spread was used and when a single value is given, the stated uncertainty. Estimates were made for 79 bonds for which no experimental values are reported in standard databases and from which enthalpies of formation of the corresponding compounds can be obtained.

Some recent evaluations of the accuracy of eq 1 have resulted in misleadingly pessimistic conclusions by applying the equation to bonds not appropriate for it, e.g., ionic bonds, the C-C single bond in butadiene, C-N in acetamide, bonds to atomic multivalent species, etc.

Pauling's equation is also successful in *not* matching experimental values in all cases where special effects (steric, conjugation, resonance, charge transfer) were already known to exist and, in conjunction with the experimental value in each case, in quantifying the magnitude of the effect. Useful insights are thus obtained into the nature of the chemical bond and the structure and reactivity of molecules and reactive intermediates.

It is a valid question to ask why should one bother with eq 1 when, with automated programs available today (like Gaussian), other calculations can be performed that provide good agreement with experimental bond dissociation enthalpies. We believe that Pauling's equation has merit in providing an intuitive feeling about the nature of covalent bonding. It is simple. Also, it is at its most interesting and enlightening for the message it sends when it does *not* reproduce experimental values.

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