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Inherent and Transferable Stabilization Energies of Carbon- and Heteroatom-centred Radicals on the Same Relative Scale and Their Applications

Michelle L. Coote,[a]* Ching Yeh Lin,[a] and Andreas A. Zavitsas[b]*

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Accurate G3(MP2)-RAD calculations are used to predict 264 R–H, R–CH_3, R–Cl and R–R bond dissociation energies for a wide-ranging test set of carbon and non-carbon centred R• radicals. The data are used to calculate a set of inherent and transferrable radical stabilization energies, denoted RSE_{Et}, which ranks the inherent stability of the 66 radicals studied on the same relative scale, irrespective of the nature of the radical centre. The Pauling electronegativity parameter for each radical is also calculated from the same data, along with the radical's inherent bonding ability $D[R\text{-}R]_{calc}$. This latter quantity is defined as the R–R bond dissociation energy expected in the absence of direct steric or resonance interactions that are present in R–R but absent in R-CH_3 and R-Cl. We show that the differences between D[R-R] and $D[R\text{-}R]_{calc}$ are typically very small except when R is sterically bulky, or there is a chain of (hyper)conjugation across the R–R bond. In such cases the difference between D[R-R] and $D[R\text{-}R]_{calc}$ provides a convenient means of quantifying the stabilization or destabilization of R–R due to these interactions. The predictability of the scheme is demonstrated by using these radical stabilities to calculate R–R' bond dissociation energies for 273 combinations of the 66 radicals studied, chosen to exclude steric or resonance interactions in R–R' bond. The predicted bond energies lie within an average of 1.6 kcal mol^{-1} from directly measured or calculated literature values.

Introduction

Radicals are important intermediates in a wide variety of processes such as polymerization, combustion, organic syntheses, chain and non-chain processes in biological systems, enzyme function and disease, ageing, etc. They are present in interstellar clouds and were found as important intermediates in the Miller-Urey experiment regarding organic compound synthesis on the primitive earth.[1] Thermodynamic measures of radical stability simplify the analysis of structure-reactivity relations.[2,3] They allow the prediction of the strengths of chemical bonds broken and made in a reaction and are factors that have a critical influence in chemical reactivity.[4]

Currently it is understood that RSEs are relative quantities and that there is no unambiguous way to define the absolute stability of a radical.[2] Is a methyl radical more or less stable than a hydroxyl radical, by how much, and relative to what? There is no question that anything called a radical stabilization energy must be an inherent property of the radical, be independent of its provenance, and be transferable to a variety of bonds made by the radical. We will demonstrate that inherent and transferable RSEs can be obtained; that inherently HO•, as an example, is more stable than H_3C• by 20.2 kcal mol^{-1} in a scale common to carbon-centred and heteroatom-centred radicals, based on the inherent bonding ability of the radicals.

Definitions of Radical Stability

The radical stabilization energy of a radical R• is most commonly defined in terms of the enthalpy change in the reaction R• + CH_4 → R–H + H_3C• and is obtained by equation (1), in which the reference bond dissociation energy to which all other R–H bonds are compared is D[H_3C–H].[2]

$$RSE_H[R\bullet] = D[CH_3\text{–}H] - D[R\text{–}H] \qquad (1)$$

However, it also recognized, that this definition applies only to carbon-centred radicals, where any bond dipole effects must be considered to be negligibly small by assuming that all C–H bonds have similar intrinsic strengths due to their similar orbital overlap, dipoles and low steric bulk of H. Equation (1) is not applicable to radicals that are not carbon-centred because D[CH_3–H] cannot be used as the reference bond for D[HO–H], where the dipole effect is very different. For RO–H bonds one may use HO–H as the reference and so forth for other bonds such as R_2N–H bonds relative to H_2N–H, RS–H bonds relative to HS–H, etc., with each type of bond being on a different scale.[3f,5]

An alternative definition of radical stabilization energies takes as the reference bond D[CH_3–CH_3], rather than D[H_3C–H]. The radical stabilization energy, RSE_{Et}, is defined by equation (2), where R· denotes both carbon-centred and heteroatom-centred radicals.[6]

$$RSE_{Et}[R\bullet] = \tfrac{1}{2}(D[CH_3–CH_3] – D[R–R]) \qquad (2)$$

The rationale for this approach is that both $D[CH_3–CH_3]$ and D[R–R] are free of any bond dipole effects on the bond dissociation energies because of symmetry, as has also been suggested previously for carbon-centred radicals.[7] The D[R–R] values that are used with this definition are those that are not subject to effects present in R–R but absent in $CH_3–CH_3$. For example, the D[R–R] bond is subject to destabilizing steric strain in di-*tert*-butyl, $(CH_3)_3C–C(CH_3)_3$, and to resonance stabilization by conjugation in 1,3-butadiene. Thermodynamic stabilizations or destabilizations by such effects are not inherent properties of the radicals formed on homolytic cleavage of the R–R bond but of the specific molecule as a whole. For such R–R, RSE_{Et} can be approximated quite accurately by equation (3).

$$RSE_{Et} \approx RSE_{Me} = D[CH_3–CH_3] – D[CH_3–R] \qquad (3)$$

For carbon-centred radicals, the differences between equations (2) and (3) are generally smaller than 0.5 kcal mol^{-1}, depending on the uncertainty of the values used, when R–R is free of effects of strain, conjugation, resonance, etc. When D[R–R] is perturbed by effects not present in CH_3–R, stabilization energies obtained by equation (3) are free of such effects, while those by equation (2) are not. Hence, the radical stabilization energy of the *tert*-butyl radical should be obtained by $D[CH_3–CH_3] – D[CH_3–C(CH_3)_3]$ and that of the vinyl radical by $D[CH_3–CH_3] – D[CH_3–CH{=}CH_2]$ where there are no effects of strain or carbon-carbon double bond conjugation. Unfortunately, like equation (1), the radical stabilization energies obtained via equation (3) are potentially subject to any bond dipole effects that may be present in CH_3–R but absent in CH_3-CH_3. For carbon-centred radicals these may be assumed to be small or negligible, but for non-carbon-centred radicals they are often very significant.

Thus, on the one hand, equations (1) and (3) only produce relative radical stabilities if dipole effects in R–H (equation 1) or R–CH_3 (equation 3) are negligibly different from CH_3–H or $CH_3–CH_3$, respectively. This unfortunately rules out most non-carbon-centred radicals. In contrast, equation (2) is not subject to dipole effects and thus is much more general, but is not valid when R–R bond stabilities are influenced by steric interactions, resonance, or any other effects not present in CH_3–R. Two recent methods have attempted to address these issues, and obtain radical stabilization energies that should be inherent and transferable for both carbon and non-carbon-centred radicals, irrespective of their steric bulk and other properties.[6,8] Both make use of Pauling's electronegativity equation, either as originally described by Pauling[9] with equation (4),[6] or with some empirical corrections to it,[8] to account for other possible effects on bond energies.

$$D[A–B] = \tfrac{1}{2}(D[A–A] + D[B–B]) + 23(\chi[A] – \chi[B])^2 \qquad (4)$$

In this equation, D[A–A]/2 and D[B–B]/2 expressed in kcal mol^{-1} describe the inherent bonding ability of the atoms or groups A and B, while $\chi[A]$ and $\chi[B]$ are the electronegativities χ of A and B, respectively, and measure their ability to attract electrons in a stable molecule in their normal oxidation state. The factor of 23 is empirical in units of kcal mol^{-1}. The term involving the χ values thus measures the contribution made to strengthening D by the extent of ionic character, or polarity, of the A–B bond. While many scales of electronegativity have been proposed,[10] the original Pauling scale of the elements with the electronegativity of oxygen given as 3.5 has been shown to give results in agreement with a very large variety of available experimental values of D. The equation, with χ values in three significant figures, has been shown to match experimental D values with a MAD of ±1.5 kcal mol^{-1}, which is comparable to the accuracy of the theoretical calculations.[6] It must be noted that the electronegativity of the hydrogen atom is unique in being somewhat variable depending on the group connected to it, although it is usually near 2.1.[9] As a result, equation (4) is not as accurate with bonds to H. In this work, we set the electronegativity of R = HO• at 3.500 to match Pauling's electronegativity value for oxygen so as to avoid proliferation of different electronegativity scales.

By allowing the contribution of dipole effects to bond strength to be quantified, Pauling's equation makes it possible to use polar bonds such as A–R, where A and R are dissimilar to one another, to quantify the inherent stability of the radicals A• and R•. This additional flexibility makes it possible to study both carbon-centred and non-carbon centred radicals while at the same time choosing A and R to avoid other complicating steric, resonance, or other interactions that are properties of the molecule as a whole, rather than of the radicals themselves. The original inherent radical stability scheme,[6] utilizing Pauling's original equation,[9] is outlined here. To calculate the inherent stability of some radical R• (where R can be carbon-centred or non-carbon centred), Pauling's equation is first applied to a pair of known bond energies that R makes with atoms or groups A and B yielding equations (5) and (6).

$$D[A–R] = \tfrac{1}{2}(D[A–A] + D[R–R]) + 23(\chi[A] – \chi[R])^2 \qquad (5)$$

$$D[B–R] = \tfrac{1}{2}(D[B–B] + D[R–R]) + 23(\chi[B] – \chi[R])^2 \qquad (6)$$

Provided D[A–A], D[A–R], D[B–B], D[B–R], $\chi[A]$ and $\chi[B]$ are known, these two equations can be solved to obtain the two unknowns: the electronegativity of R, $\chi[R]$, and its "inherent bonding energy", D[R–R], to which we will refer as $D[R–R]_{calc}$ so as to distinguish it from the actual R–R bond dissociation energy D[R–R]. Thus, $D[R–R]_{calc}$ is the part of the actual D[R–R] that is due only to inherent radical stability of R and any difference from the actual D[R–R] measures the effect of strain, resonance, etc. on the R–R bond. Subtraction of equation (6) from equation (5) yields equation (7), where $a = \tfrac{1}{2}(D[A–A] – D[B–B]) + 23\{(\chi[A])^2 – (\chi[B])^2\}$ and $b = 46(\chi[B] – \chi[A])$.

$$\chi[R] = (D[A–R] – D[B–R] – a) / b \qquad (7)$$

The value of $\chi[R]$ thus obtained is inserted into equation (5) or (6) to solve for the only unknown, $D[R–R]_{calc}$. $D[R–R]_{calc}$ is used in place of D[R–R] in equation (2) to obtain the RSE_{Et} value, which is the inherent and transferable radical stabilization energy of R.

In applying the scheme, A and B can in principle be any groups or atoms for which the bond energies and electronegativities are known, provided D[A–R] and D[B–R] are free of resonance or steric interactions between R and A or B. To satisfy this requirement, we use A = CH_3 and B = Cl for which reference values of $\chi[\cdot CH_3] = 2.520$, $\chi[Cl\cdot] = 3.176$, $D[CH_3–CH_3] = 88.6$, $D[Cl–Cl] = 57.2$ and $D[CH_3–Cl] = 82.8$ kcal/mol can be obtained by theoretical calculations (see below for details).

To solve equations (5) and (6) known values of $\chi[\bullet CH_3]$, $\chi[Cl\bullet]$, $D[CH_3–CH_3]$ and D[Cl–Cl] are required, and these are obtained as follows. Our starting point is a reference value of $\chi[HO\bullet] = 3.500$, which is chosen to coincide with Pauling's reference value of 3.500 for oxygen.[9] Theoretical G3(MP2)-RAD calculations yield $D[CH_3–OH] = 90.5$, $D[HO–OH] = 48.2$, and $D[CH_3–CH_3] = 88.6$ kcal mol^{-1}. Insertion of these values and of $\chi[HO\cdot] = 3.500$ into equation (4) yields $\chi[\bullet CH_3] = 2.520$.[‡] Likewise, theoretical values of $D[CH_3–Cl] = 82.8$, $D[Cl–Cl] = 57.2$ kcal mol^{-1}, and of $\chi[\bullet CH_3] = 2.520$ into equation (4) yields $\chi[Cl\bullet] = 3.176$.[‡] The theoretical bond energies are used here and throughout this work for self-consistency and are in good agreement with the available experimental values of $D[CH_3–OH]_{exp} = 92.1$ kcal mol^{-1}, $D[CH_3–CH_3]_{exp} = 90.0$, $D[HO–OH]_{exp} = 50.5$, $D[CH_3–Cl]_{exp} = 83.8$, and $D[Cl–Cl]_{exp} = 58.0$.

In the absence of steric or resonance effects, $\chi[R]$ can be obtained in three ways when the above D values are available: by equation (7), by equation (5) only, or by equation (6) only. Ideally, all three methods should yield the same χ if there are no errors, or uncertainties, in the experimental or theoretical D values being used. In practice and the preponderant number of cases, the three χ values are very similar. However, both experimental and theoretical values have uncertainties, and in 7 of the 66 groups treated, the three χ values are significantly different because of the particular distribution of such uncertainties in the four D values used with equation (7). In these cases (identified in Table 1), using the average of the three χ values counterbalances the uncertainties in D and yields reliable values. With the average $\chi[R\bullet]$ and with RSE_{Et} from the theoretical values of $D[CH_3–CH_3]$ and D[R–R], acceptable results are obtained for all their D[R–R´] combinations.

In a previous study[3e] we examined a large and representative test set of π-type carbon-centred radicals (RR'R"C•) and showed that the relative radical stabilities obtained via this universal scheme[6] gave values that were correlated with those obtained via equation (1) and with the spin densities on the nominal radical centre (and hence the extent of delocalization of the radical), providing mutual confidence that all three approaches were providing good measures of relative radical stabilities. In this work, we focus on the more challenging problem of obtaining radical stabilities for other types of radical, including heteroatom centred and σ-type carbon-centred radicals (RR´C•), where neither equation (1) nor the spin densities can be expected to provide a universal scale. To test the validity of our scheme, we first use it to estimate the stabilities and electronegativities of a large test set of carbon and heteroatom centred radicals R• from their $R–CH_3$ and R–Cl bond energies, and then examine whether the resulting radical stabilities and electronegativities can be used to predict accurate R–R' bond energies for various combinations of R and R'.

Theoretical Procedures

In the present work, we have used ab initio molecular orbital theory to calculate theoretical values of bond dissociation energies $D[CH_3–R]$, D[Cl–R], D[R–R], and D[R–H] for a wide variety of carbon- and heteroatom-centred R groups. Values of $D[CH_3–R]$, D[Cl–R] are used to estimate universal radical stabilities (RSE_{Et}), while values of D[R–R] and D[R–H] are obtained to assist with the analysis and interpretation of the results. The theoretical calculations provide reliable and self-consistent bond dissociation energies for many bonds that are not available from experiment and thus provide a wide spectrum of bond types. As in our previous study of π-type carbon-centred radicals,[3e] calculations have been carried out at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory using Gaussian 03[11] and Molpro 2006.6.[12] Thermochemical corrections (to obtain enthalpies at 298.15 K) have been evaluated using the standard textbook formulae for an ideal gas under the harmonic oscillator and rigid rotor approximations. A full set of geometries, total energies and bond dissociation energies are provided in the ESI.[†] For a large subset of our test set, corresponding gas-phase bond dissociation energies are available in the literature,[13] and these are compared with the corresponding theoretical values in Figure 1. The mean absolute deviation of theory from experiment is 1.8 kcal mol^{-1}, which is not only relatively small in its own right but is comparable to the corresponding mean absolute deviation of the various available experimental values from each other (1.4 kcal mol^{-1}, or 1.6 kcal mol^{-1} if the experimental R–R' bond dissociation energies are included).

Results and Discussion

Values of the R–H, $R–CH_3$, R–Cl, and R–R bond dissociation enthalpies at 298.15 K, as obtained using high-level quantum chemical calculations, are provided in Table 1 for a large test set of R groups, chosen to cover a range of different radical centres and other stereoelectronic properties. The $D[R–CH_3]$ and D[R–Cl] values have been used to calculate the inherent bonding

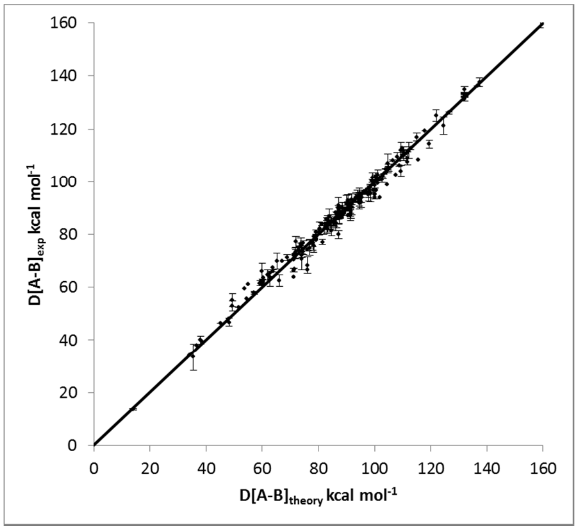

Figure 1. Comparison of the G3(MP2)-RAD theoretical bond dissociation energies in this study with corresponding experimental values from the literature.[13]

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Table 1 G3(MP2)-RAD bond dissociation enthalpies (gas-phase, kcal mol^{-1}, 298.15 K), and corresponding values of D[R–R]$_{calc}$, χ[R•], RSE$_{Et}$, and RSE$_{H}$^{a}

Group •R	D[R–H]	D[R–CH_3]	D[R–Cl]	D[R–R]	D[R–R]$_{calc}$	χ[R•]	RSE$_{Et}$[R•]	RSE$_{H}$[R•]
Deviations between D[R–R] and D[R–R]$_{calc}$ of less than 2.8 kcal mol^{-1}								
CH_3	104.0	88.6	82.8	88.6	88.6	2.520	0.0	0.0
CH_2CH_3	100.8	88.1	84.4	87.7	87.4	2.450	0.6	3.2
$CH(CH_3)_2$	98.5	87.9	85.7	85.4	86.5	2.401	1.0	5.5
cyclo-C_3H_5	108.8	98.2	92.0	107.6	107.8	2.533	-9.6	-4.8
$CH_2CH{=}CH_2$	86.8	73.8	68.9	59.2	59.0	2.490	14.8	17.2
$CH_2C{\equiv}CH$	91.4	78.1	69.6	67.3	67.2	2.609	10.7	12.6
$CH_2C{\equiv}N$	96.3	83.0	71.2	74.1	75.6	2.719	6.5	7.7
$C{\equiv}CH$	132.1	124.6	109.5	159.0	156.2	2.828	-33.8	-28.1
Ph	112.9	103.0	97.9	119.5	117.4	2.497	-14.4	-8.9
CH_2Ph	89.4	76.9	71.8	66.2	65.2	2.497	11.7	14.6
CH_2OH	96.3	86.7	83.2	83.4	84.5	2.444	2.0	7.7
CH_2Cl	99.2	88.6	79.2	87.4	87.9	2.639	0.3	4.8
CH_2SH	95.4	83.2	74.9	76.9	77.5	2.603	5.6	8.6
CH_2SCH_3	94.2	82.0	74.2	75.2	75.2	2.586	6.7	9.8
CH_2Br	100.4	89.2	79.5	89.3	89.0	2.649	-0.2	3.6
CH_2SiH_3	101.2	85.6	80.0	83.1	82.6	2.513	3.0	2.8
CH_2NH_2	93.3	82.3	82.0	76.1	74.5	2.338	7.1	10.7
$CH_2N(CH_3)_2$	93.0	79.8	82.1	69.6	67.7	2.251	10.5	11.0
$CH_2C(O)OH$	98.6	86.2	76.1	83.3	82.9	2.662	2.9	5.4
$CH_2C(O)CH_3$	96.3	83.9	75.2	79.6	78.8	2.616	4.9	7.7
$CH_2OC(O)H$	99.9	90.2	80.9	88.7	91.2	2.636	-1.3	4.1
$CH_2OC(O)CH_3$	99.6	89.9	81.4	88.7	90.8	2.609	-1.1	4.4
$CH_2C(O)NH_2$	98.4	85.9	80.2	84.2	83.2	2.517	2.7	5.6
CH_2-cyclo-C_3H_5	98.4	86.0	82.3	83.8	83.2	2.450	2.7	5.6
$CH_2S(O)CH_3$	102.0	84.8	77.8	82.3	80.9	2.560	3.8	2.0
$CH_2S(O_2)CH_3$	104.6	93.0	80.2	96.4	94.9	2.752	-3.2	-0.6
$C(O)NH_2$	94.6	87.5	84.7	87.7	85.9	2.421	1.3	9.4
$C(O)CH_3$	89.7	83.9	84.6	74.6	77.1	2.305	5.8	14.3
$C(O)N(CH_3)_2$	95.0	85.5	83.1	79.5	81.8	2.407	3.4	9.0
$C(O)N(CH_2CH_3)_2$	94.8	86.3	84.6	81.8	83.1	2.384	2.7	9.2
NH_2	106.5	82.9	60.3	63.9	62.9	3.077	12.8	-2.5
$NHCH_3$	99.3	80.4	59.2	60.0	60.2	3.030	14.2	4.7

NO_2	70.8	60.4	34.2	14.0	11.2	3.196	38.7	33.2
OH [b]	118.0	90.5	54.5	48.2	46.4	3.500	20.2	-14.0
OCH_3 [c]	104.8	83.0	48.0	38.1	38.1	3.410	25.3	-0.8
OCH_2CH_3	105.0	83.4	48.8	38.5	36.3	3.474	26.1	-1.0
OC(O)H [c]	112.3	90.1	49.0	39.0	39.0	3.550	24.8	-8.3
$OC(O)CH_3$ [c]	109.5	87.1	46.6	35.5	35.5	3.505	26.6	-5.5
F [c]	136.6	109.8	59.6	36.7	36.7	3.953	26.0	-32.6
Cl	103.4	82.8	57.2	57.2	57.2	3.176	15.7	0.6
Br	87.6	69.6	51.7	45.2	43.2	2.921	22.7	16.4
BH_2 [c]	104.7	104.0	125.1	104.8	104.8	1.874	-8.1	-0.7
SiH_3 [c]	91.2	87.1	108.1	74.7	74.7	1.829	7.0	12.8
PH_2 [c]	81.3	69.7	76.6	54.9	54.9	2.283	16.9	22.7

Deviations between D[R–R] and D[R–R]$_{calc}$ of more than 2.8 kcal mol^{-1}

$C(CH_3)_3$	97.2	87.9	86.5	81.5	86.2	2.374	1.2	6.8
$CH{=}CH_2$	110.4	100.3	94.6	115.0	112.0	2.517	-11.7	-6.4
(E)-$CH{=}CHCH_3$	111.7	101.2	95.7	117.6	113.8	2.510	-12.6	-7.7
$CH{=}C(CH_3)_2$	112.2	100.2	96.7	116.2	111.5	2.444	-11.5	-8.2
$C{\equiv}N$	126.5	121.9	102.7	137.4	146.1	2.964	-28.8	-22.5
CH_2F	101.0	91.9	84.5	91.7	95.1	2.573	-3.2	3.0
CH_2NO_2	101.1	90.6	78.2	87.2	90.4	2.739	-0.9	2.9
C(O)H	88.6	83.8	82.9	71.3	77.8	2.358	5.4	15.4
C(O)OH	100.6	95.2	86.3	87.2	101.3	2.623	-6.4	3.4
C(O)Ph	91.5	84.8	84.7	75.3	79.4	2.331	4.6	12.5
$C(O)OCH_3$	100.1	94.6	86.8	87.8	100.4	2.586	-5.9	3.9
$C(O)OCH_2CH_3$	99.7	94.1	86.7	87.5	99.5	2.573	-5.4	4.3
$C(O)OC(CH_3)_3$	98.1	92.4	86.1	85.2	96.2	2.536	-3.8	5.9
$C(O)NHCH_3$	94.9	87.9	85.6	90.3	86.6	2.404	1.0	9.1
NHC(O)H	115.6	97.7	66.9	88.4	75.2	3.348	6.7	-11.6
$NHC(O)CH_3$	111.8	93.9	63.8	83.7	69.4	3.325	9.6	-7.8
$S(O)CH_3$	54.3	49.6	51.2	14.4	7.3	2.268	40.7	49.7
$S(O_2)CH_3$	73.7	71.6	67.2	43.7	54.5	2.474	17.0	30.3
SH	90.6	73.1	63.2	62.0	56.8	2.656	15.9	13.4
SCH_3	86.3	72.0	65.2	62.8	55.3	2.553	16.6	17.7
SCH_2Ph	88.6	75.1	68.1	70.4	61.7	2.656	13.4	15.4
$N(CH_3)_2$	93.9	78.4	57.6	53.7	56.8	3.017	15.9	10.1

[a] D[R–R]$_{calc}$, obtained via Equation (7), χ[R•] obtained via equations (5) or (6), RSE$_{Et}$ obtained via equation (2) using D[R–R]$_{calc}$ rather than D[R–R], and RSE$_{H}$ obtained via equation (1). [b] Defined χ[HO•] = 3.500 and RSE$_{Et}$ = 20.2. [c] Obtained χ by averaging results from equations (5)–(7) (see text).

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ability of R, D[R-R]$_{calc}$, and its electronegativity, χ[R•], via equations (5)–(7), and the D[R-R]$_{calc}$ values have been used to obtain the radical stability, RSE$_{Et}$[R•] via equation (2). The values of RSE$_{H}$(R•), obtained from the D[R–H] via equation (1), have also been calculated and are included in Table 1 purposes of comparison.

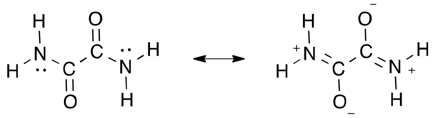
Inherent Bonding Ability Versus Actual R–R Bond Strength

As explained above, D[R-R]$_{calc}$ should in principle be in agreement with the corresponding actual D[R-R] values provided that the R–R bond is not subject to destabilization or stabilization by interactions (such as steric strain, resonance, or other effects) that are present in R–R but not R–CH_3 or R–Cl. We consider such agreement to be acceptable when D[R–R]$_{calc}$ differs from the theoretical D[R–R] by less than a reasonable estimate of the cumulative error in the bond dissociation energies. Assuming a 1.8 kcal mol^{-1} mean uncertainty (MAD ≈ 1.8) in each of the four D values used in equation (7) the cumulative uncertainty of D[R–R´]$_{calc}$ would be ±3.6 kcal mol^{-1}, though in the high-level ab initio values systematic error cancellation might be expected to reduce this value considerably. We thus suggest that agreement to within ±2.8 kcal mol^{-1} or less indicates that complicating interactions are absent or minor. Deviations of ±2.8 kcal mol^{-1} or greater indicate the existence of significant effects present in R–R´ but not in R–CH_3 or R–Cl. In Table 1 deviations of ±2.8 or less are listed first and those with greater deviations are listed below the horizontal line. For the 44 groups above the line in Table 1, the unsigned average deviation between D[R–R] and D[R–R']$_{calc}$ is 0.92 kcal mol^{-1}. The greatest deviations are 2.8 kcal mol^{-1} for R = -C≡CH and R = -NO_2. Deviations greater than ±2.8 kcal mol^{-1}, are discussed below.

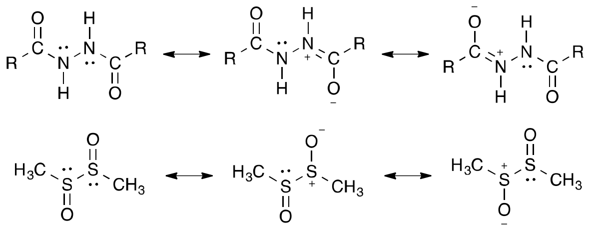
The first entry below the line is for $(CH_3)C$• for which D[R–R]$_{calc}$ exceeds D[R–R] by 4.7 kcal mol^{-1}. This is due to the effect of steric strain, which weakens the D[$(CH_3)C$–$C(CH_3)_3$] bond below that predicted by the inherent bonding ability of $(CH_3)C$•. The difference is reasonably consistent with other estimates of this destabilizing steric strain (ca. 6 kcal mol^{-1}).[14] The next three entries below the line are for radicals of the form •CH=CR'R" and these have D[R–R]$_{calc}$ weaker than D[R–R] by 3.0, 3.8 and 4.7, because R–R is now stabilized by resonance, over and above the inherent bonding ability of R•. The values are in line with the known thermodynamic stabilization of 3.8 kcal mol^{-1} for 1,3-butadiene due to stabilizing conjugation of the double bonds.

The 5th entry below the line is for cyanogen, N≡C–C≡N, which shows significant thermodynamic destabilization by 8.7 kcal mol^{-1} despite the presence of conjugated triple bonds. The present result is consistent with previously reported such effects in cyanogen,[15] and may be rationalized in terms of repulsion between the partial positive charges on the carbon atoms of the strongly electron-withdrawing cyano groups. The same type of destabilizing effect, though weaker, is found with the following two entries for CH_2F and CH_2NO_2 (3.4 and 3.2 kcal mol^{-1} respectively). Both have strongly electron-withdrawing groups attached to the carbon, inducing a significant partial positive charge on it.

In a similar manner, the subsequent molecules containing α-dicarbonyls have D[R–R]$_{calc}$ values that overestimate D[R–R] by 4.1 to a remarkable 14.1 kcal mol^{-1} for oxalic acid because of the destabilization of D[R–R] by repulsion between the partial positive charges on the two carbonyl carbons. This occurs despite the formally conjugated system of alternating double-single-double bonds, O=C–C=O, in such compounds. An exception to this trend is the diamide $CH_3NHC(O)$–$C(O)NHCH_3$ where the bond is stabilized by 3.7, as is ethanediamide, $H_2N(C(O)$–$C(O)NH_2$ by 1.8 in the upper part of Table 1. Evidently, resonance structures such as shown in Scheme 1 effectively delocalize the lone pair on nitrogen and significantly diminish the partial positive charges on the carbonyl carbons. The significant barrier to rotation of the C–N bond in amides is well known and is due to the partial double bond character of the C–N bond.


Scheme 1

The D[R–R] values for NHC(O)H and NHC(O)CH_3 are of interest because of the unusually strong N–N bonds, more than 24 kcal mol^{-1} stronger than D[CH_3NH–$NHCH_3$]. One possible rationalization for this result is that there is extensive resonance stabilization involved in such compounds, as shown in Scheme 2. In two of the resonance structures of RC(O)NH–NHC(O)R the positive charge on one nitrogen is adjacent to the lone pair of electrons of the other. This stabilizing interaction would strengthen the N–N bond. This type of effect is also present in $CH_3S(O)$–$S(O)CH_3$ where a stabilization of 7 kcal mol^{-1} is indicated. The resonance stabilization of the sulfoxide dimer is reversed in the sulfone dimer, $CH_3S(O_2)$–$S(O_2)CH_3$, where a destabilization of 11 kcal mol^{-1} is indicated. Evidently, the presence of two electron-withdrawing oxygens on the sulfone sulphurs induces a positive charge on both, thus causing repulsion as exhibited by the C–C bonds of other α-dicarbonyls. Sulfone groups are considerably more electron-withdrawing than sulfoxide groups.[16]


Scheme 2

Tetramethylhydrazine, the last entry in Table 1, shows some weakening of the $(CH_3)_2N–N(CH_3)_2$ bond, unlike hydrazine and 1,2-dimethylhydrazine. This is likely due to some steric strain as also occurs in the similarly shaped diisopropyl.[14]

In the entries for which there is acceptable agreement between $D[R–R]_{calc}$ and theoretical D[R–R] in the upper part of Table 1 the results show that D[R–R] of biphenyl is only 2.2 kcal mol^{-1} stronger than $D[R–R]_{calc}$, where the latter does not include effects of conjugation across R–R. The small stabilization by conjugation is because the rings of biphenyl are not coplanar. Unlike the conjugated dienes, the $D[R–R]_{calc}$ for the diyne HC≡C–C≡CH underestimates D[R–R] by only 2.8 kcal mol^{-1}, and this is consistent with previous reports that the enthalpy of hydrogenation of the first double bond of 1,3-butadiyne is essentially equal to that of the second for a thermodynamically measurable stabilization of near zero.[17]

Electronegativities and RSE_H Values

The application of Pauling's equation yields not only the inherent bonding ability of R• but also its electronegativity, χ. Figure 2 shows that the values of χ obtained are in good agreement with the electronegativity values proposed for the atoms by Pauling on the basis of their available dissociation energies: F = 4.0, O = 3.5, N = 3.0, Cl = 3.0, Br = 2.8, S = 2.5, C = 2.5, P = 2.1, B = 2.0, and Si = 1.8.[9] As Pauling specified, these values pertain to the normal oxidation states (carbon, tetravalent; nitrogen, trivalent; oxygen, divalent; etc.) for the groups in stable molecules.[9] It is clear from Figure 2, that the substitution pattern of the radical does affect the χ value obtained, though this effect is smaller than the differences between the atom types themselves.

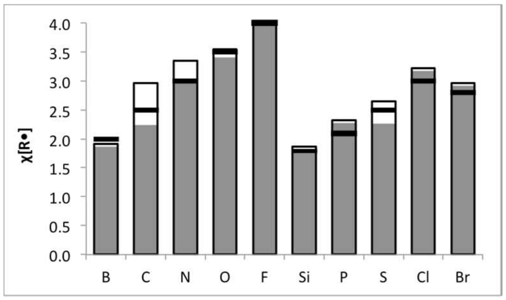


Figure 2. Range of χ values (the white section spans the minimum and maximum values) obtained for the species in Table 1. The solid line shows Pauling's original values[9] for the corresponding atoms.

The D[R–H] values in Table 1 were also used to calculate values of the traditional radical stabilization energy, RSE_H via equation (1). In applying $RSE_H[R•]$ values to non-carbon-centred radicals, the questionable assumption must be made that any bond dipole effect (or other effect, e.g. orbital overlap) on the strength of a C–H bond will be the same on the corresponding R–H bond. This weakness in obtaining inherent and transferable RSE_H values obtained by equation (1) has been known for a long time; its limitations were pointed out by Walling as early as 1957.[3j] On the other hand, more D[R–H] values have been determined experimentally than D[R–R′], $RSE_H[R•]$ values are easier to calculate, steric strain effects are negligible for bonds to the small hydrogen atom, and use of $RSE_H[R·]$ values gives the correct exothermicity or endothermicity of the many radical reactions proceeding through abstraction of a hydrogen atom. To assess their usefulness as descriptors of *relative* radical stability, we have thus compared corresponding $RSE_H[R•]$ and $RSE_{Et}[R•]$ values in Figure 3.

Consistent with our previous study of a wider test set of π-type carbon-centred radicals,[3e] there is generally good correlation between $RSE_H[R•]$ and $RSE_{Et}[R•]$ for the π-type carbon-centred radicals, though the former are offset to higher values on average. Somewhat surprisingly, many of the σ-type carbon centred radicals fall onto the same $RSE_H[R·]$ versus $RSE_{Et}[R·]$ correlation suggesting that the sp^2 C–H bonds show similar strengths to sp^3 ones. The correlation between $RSE_H[R•]$ and $RSE_{Et}[R•]$ breaks down altogether for the non-carbon centred radicals due to differences in R–H versus C–H bond strength. What is more important to note is that, in some cases, the correlations are poor even with a series of radicals of the same atom type, indicating that the RSE_H values are not predicting the correct relative radical stabilities within the series. Similar concerns have been raised previously for the use of P–H bond dissociation energies to assess trends in phosphoranyl radical stability.[18]

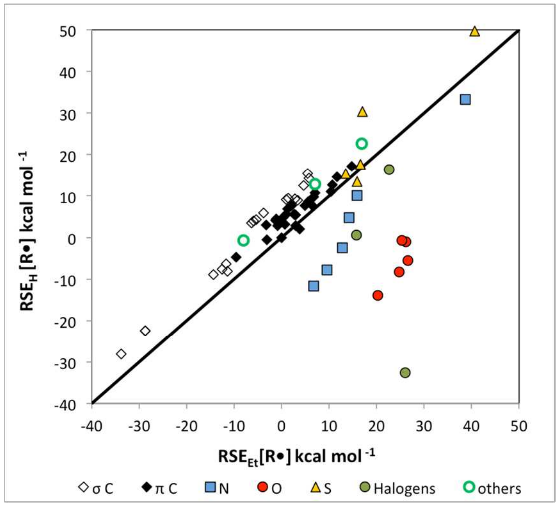


Figure 3. Comparison of RSE_H, as calculated via equation (1), and RSE_{Et}, as calculated via equations (5)-(7). Values above the line y = x indicate that the RSE_H values overestimate radical stability of R• by failing to account for the stronger R–H versus CH_3–H bond, while values below line are indicate a weaker R–H versus CH_3–H bond

The differences between corresponding $RSE_H[R•]$ and $RSE_{Et}[R•]$ values allow us to assess the contribution of R–H versus CH_3–H "inherent" bond strength differences to the $RSE_H[R·]$ values. For example, in Figure 2 it is seen that RSE_H values for sulphur-centred radicals tend to lie on or above the line y = x, indicating that RSE_H tends to overestimate radical stability because they fail to take into account the weaker S–H versus C–H bond strength. In contrast the nitrogen and oxygen centred radicals lie below the line indicating stronger O–H and N–H versus C–H bonds, with the O–H bonds stronger than the N–H ones. These trends are consistent with the electronegativity values in Table 1 and arise primarily in dipole effects. In a similar manner, the halogens make stronger bond with hydrogen than CH_3, with the strength increasing as expected Br < Cl < F.

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Table 2. Typical results compared to literature values of D[R–R'] (gas-phase, kcal mol^{-1}, 298.15 K).[a] D[R–R']$_{calc}$ by equation (8) with values of RSE$_{Et}$ and χ[R•] from Table 1, literature values D[R–R']$_{lit}$, D[R–R']$_{V}$ from Ref. 8, and for C–C bonds D[R–R']$_{H}$ by equation (9).

R–R'	D[R–R']$_{calc}$	D[R–R']$_{lit}$	D[R–R']$_{V}$	D[R–R']$_{H}$
CH_3CH_2–CH_2CH_3	87.4	87.9, 86.8		82.2
CH_3CH_2–$CH(CH_3)_2$	87.1	86.7, 87.1		79.9
CH_3CH_2–$C(CH_3)_3$	86.9	86.4, 88.3, 88.3		78.6
$PhCH_2$–CH_2Ph	65.2	62.6±2.2, 65.2, 66.9±1.4		59.4
$(CH_3)_2CH$–CH_2Ph	76.1	76.4, 75.8		68.5
$(CH_3)_3C$–$CH_2CH{=}CH_2$	72.9	73.2		64.6
cyclo-C_3H_5–Ph	112.6	112.4±1.5, 111.9±3		102.3
$H_2C{=}CH$–$CH{=}O$	95.5	97.7±1, 97.4±1.4		79.6
$HC{\equiv}C$–$CH{=}CH_2$	136.3	137.6, 133.6±2.4		123.1
Ph–$C{\equiv}CH$	139.3	141.2, 140.7±2.4		125.6
$N{\equiv}C$–$CH{=}CH_2$	133.7	133±1, 134.8, 133.8±1		117.5
CH_3–Ph	103.0	102.9±1, 103.8±2	101.0	97.5
CH_3–CH_2Ph	76.9	77.6, 77.2±1	75.0	74.0
CH_3–$CH{=}CH_2$	100.3	101.6, 101.0	98.7	95.0
CH_3–$CH_2C{\equiv}N$	83.0	84.3, 83.2±3	80.1	80.8
CH_3–$C{\equiv}N$	121.9	124.7±2.2, 121.1	123.1	111.1
CH_3–C(O)H	83.8	86.1, 86.0	84.1	73.2
CH_3–$C(O)CH_3$	83.9	84.8, 85.0	85.4	74.3
Ph–CH_2OH	101.1	98.3±1, 101.6±2.2	95.1	89.8
$H_2C{=}C$–CH_2OH	98.4	97.0, 98.6±1.4	92.5	87.3
CH_3–OH	90.5	92.2,[b] 92.1, 92.4	95.2	
CH_3CH_2–OH	93.2	94.2,[b] 94.0, 94.0	93.3	
$(CH_3)_2CH$–OH	95.2	95.5,[b] 95.5, 96.5	91.6	
$(CH_3)_3C$–OH	96.4	96.3,[b] 95.5, 95.0	90.0	
CH_3O–OH	43.3	43.8,[b] 45.4, 44.7	51.5	
CH_3CH_2O–OH	42.4	42.7±1.5	50.7	
HS–OH	68.9	70.1,[b] 70.1±1.4	73.2	
CH_3S–OH	72.4	72.5,[b] 72.6±2	71.4	
H_2N–OH	59.7	63.7,[b] 63.4±2.2	78.1	
F–OH	47.1	48.3,[b] 51.8	52.9	
Cl–OH	55.1	55.8,[b] 56.1	66.5	
Br–OH	53.4	55.7, 55.1	65.4	
CH_3–NH_2	82.9	84.8,[b] 85.2, 85.9	87.3	
CH_3O–NH_2	53.1	55.6,[b] 55.6±2.2	66.2	
HS–NH_2	64.0	66.8[b]	67.7	
F–NH_2	67.5	69.7,[b] 69.1±2, 68.5±2, 69.5±2	82.6	
F–F	36.6	39.6,[b] 38.0	23.3	
CH_3–F	109.8	110.6,[b] 110.0±2, 109.8	114.4	
CH_3CH_2–F	114.0	113.4,[b] 111.7±2	114.0	
$(CH_3)_2CH$–F	117.0	115.4,[b] 117.0, 116.0, 115.5±2	113.0	
$(CH_3)_3C$–F	118.7	116.9,[b] 117.0, 118.2±2	111.7	
$H_2C{=}CHCH_2$–F	97.0	96.9, 96.9	97.0	
$PhCH_2$–F	99.7	98.7, 98.9, 98.7	100.0	
$H_2C{=}CH$–F	121.7	123.3, 123.7±3, 122.4	123.5	
$N{\equiv}C$–F	113.9	115.4, 114.4	123.3	
Ph–F	125.8	127.1, 125.6±2, 127.7±2	124.7	
HC(O)–F	115.1	119.2, 119.4	109.6	
$CH_3C(O)$–F	119.3	122.2, 120.7	111.7	

$CH_3O–F$	44.1	44.7^b	43.2
HS–F	85.4	82.9,^{b} 83.8	86.4
Cl–F	60.8	60.9,^{b} 61.3, 60.0	59.7
$CH_3O–Cl$	48.9	48.5,^{b} 48.0, 47.1±1	56.6
HS–Cl	63.2	64.0^b	60.4
$CH_3–NO_2$	60.4	60.9, 62.2, 62.1	61.6
$CH_3–Br$	69.6	72.1, 69.9	75.1
$CH_3–SH$	73.1	74.5,^{b} 74.7, 73.8	72.3
$CH_3CH_2–SH$	73.1	73.8,^{b} 73.6, 73.0	70.5
$(CH_3)_2CH–SH$	72.7	73.6,^{b} 73.4, 73.7	68.8
$(CH_3)_3C–SH$	73.3	73.0,^{b} 72.0, 70.3	67.2
$H_2C{=}CHCH_2–SH$	58.6	59.2±2	55.0
$PhCH_2–SH$	62.6	61.3±1.5, 60.2±1	58.0
Ph–SH	87.7	86.9, 86.2±1.5, 87.4±2	83.6
$CH_3C(O)–SH$	69.6	73.7±2, 73.1±2	69.0
$CH_3O–SH$	60.5	61.2^b	62.0
$CH_3–SCH_3$	72.0	73.6,^{b} 73.9	69.2
$F–BH_2$	170.1	171.4, 169.7±1.5	
$CH_3C(O)–SH$	69.7	Not found	
$H_2NC(O)–SH$	72.6	Not found	
$H_2NC(O)–CH_2Ph$	75.7	Not found	
cyclo-C_3H_5–$CH_2C{\equiv}CH$	83.4	Not found	
cyclo-C_3H_5-CH_2–OH	91.1	Not found	
Ph–S(O)CH_3	63.5	Not found	

[a] A full list of 234 D[R–R´]$_{calc}$ values are compared to available literature values in the ESI,† with the provenance of all D[R–R´]$_{lit}$ values, including the above. [b] Theoretical values by W1w theory from reference 3g.

Use of radical stabilities values to predict bond energies

If the RSE$_{Et}$ values represent radical stabilization energies that are inherent to the radical and transferable to species other than those from which they were derived, equation (8) should produce accurate values of D[R–R´]. This is assuming of course there are no effects present in R–R´ that are absent in CH_3–R and Cl–R, i.e., effects that are not inherent to the radical and are brought about by their particular combination.

$$\begin{aligned} D[R–R']_{calc} &= D[CH_3–CH_3] - RSE_{Et}[R\cdot] \\ &\quad - RSE_{Et}[\cdot R'] + 23(\chi[R] - \chi[R'])^2 \qquad (8) \end{aligned}$$

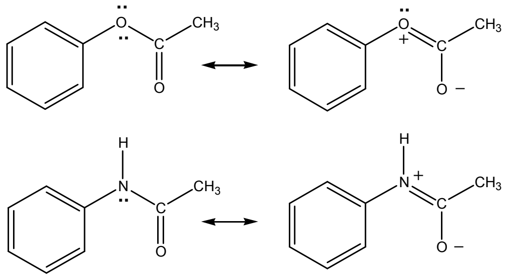
Equation (8) was used with the RSE$_{Et}$ and χ values of Table 1 to predict values of D[R–R´]$_{calc}$ for a broad set of C–C and non C–C bonds, which are not expected to be subject to the complicating effects of strain, resonance, etc. These were compared with corresponding bond energies from the literature, D[R–R´]$_{lit}$, as reported either from experimental data or from direct high-level ab initio calculations. In all, we were able to compare D[R–R´]$_{calc}$ values with 234 corresponding literature values we were able to locate. We also calculated a smaller set of D[R–R´]$_{calc}$ values for which bond dissociation energies are not currently available in the literature for future testing.

A set of typical results is provided in Table 2. The full set of 234 bonds and the provenance of all D[R–R´]$_{lit}$ values (including those in Table 2) is provided in Table S2 of the ESI†. For comparing D[R–R´] values with literature values, the mean absolute deviation of available literature values was used, without any consideration of their provenance, experimental or theoretical, and without consideration of any reported uncertainties. This avoids possibly subjective judgments regarding the accuracy of such values, which differ substantially sometimes. Literature values from high level W1w calculations[3g] in common with the bonds shown in Table 2 are specifically identified in the Table and constitute an internally self-consistent set at a very high level of theory.

The 66 values of D[R–R´]$_{calc}$ obtained by equation (8) in Table 2 show a mean absolute deviation of 1.3 kcal mol^{-1} from the available literature values and of 1.2 from the 30 W1w values in common. For all 237 bonds given in Table S2 of the ESI, the mean absolute deviation of D[R–R´]$_{calc}$ from the average literature value is 1.6 kcal mol^{-1}. This type of agreement validates the inherent nature and transferability of radical stabilization energies defined according to equation (2), which bear no calculational relation to directly calculated (or measured) bond energies. The good agreement also confirms that the χ values obtained are inherent to the radicals and transferable. The success of equation (8) is particularly noteworthy as it is easily applicable to molecules larger than those amenable to very-high-level theoretical calculations at the present time.

Only two of the 234 bonds in Table S2 deviate from an available *experimental* value (including its reported uncertainty) by more than 3 kcal mol^{-1}. D[N≡C–C$(CH_3)_3$]$_{calc}$ is greater by 6.4 kcal mol^{-1} from the single available experimental value. D[O_2N–F]$_{calc}$ = 37.1 is much smaller than either of two quite different available values of 46.0 and 52.9. The strong stabilization for O_2N–F is understood in the same way as the strong resonance stabilizing effects that have been shown to be present for the groups HO, RO, H_2N, and R_2N bonding to sp^2 and sp hybridized atoms.[6,19] For example, D[Ph–OH]$_{calc}$ = 105.9 kcal mol^{-1} is 7 kcal mol^{-1} lower than the experimental value 113.3 ± 2, while D[$CH_3C(O)$–OH]$_{calc}$ = 95.4 lies some 15.0 kcal mol^{-1} below the experimental value of 109.9. In both cases these differences are not failures but rather they reveal the stabilization due to resonance between OH and π-accepting R-groups. Such bonds have not been included in Table 2 or in S2 of the ESI. Equation (8) and any approaches using RSE values cannot account for conjugation or resonance because such effects are not inherent to the radical groups involved but result from their particular combinations. In such cases, the value of equation (8) lies not in predicting accurate bond energies but in quantifying the extent of stabilization or destabilization caused by specific interactions between the bonded groups.

Interestingly, Tables 2 and S2 contain several examples of formally conjugated double-single-double bonds that do not exhibit significant thermodynamic stabilization, as might have been expected. For example, the D[R–R']$_{calc}$ values, which do not account for conjugation stabilization, are not very different from the experimental values for acrolein ($\mathrm{CH_2{=}CH{-}CH{=}O}$), 1-butene-3-yne ($\mathrm{HC{\equiv}C{-}CH{=}CH_2}$), 1-pentyn-3-ene ($\mathrm{HC{\equiv}C{-}CH{=}CHCH_3}$), phenylacetylene (HC≡C–Ph), and acrylonitrile ($\mathrm{N{\equiv}C{-}CH{=}CH_2}$). The lack of directly measurable (e.g. by enthalpies of hydrogenation) thermodynamic stabilization mentioned above for 1,3-butadiyne is not unique. Other examples include the $C(sp^2)$–O bond in phenyl acetate and the $C(sp^2)$–N bond in acetanilide which do not show stabilizations comparable to those of about 8 kcal mol^{-1} for the corresponding bonds in phenol and aniline.[6] From Table S2, $D[Ph–OC(O)CH_3]_{calc}$ = 98.0 kcal mol^{-1} versus experimental 98.8 and 99.8; $D[Ph–NHC(O)CH_3]_{calc}$ = 109.2 versus experimental 112.1 ± 2.4. The lack of any significant stabilization in these cases is understood in terms of the resonance structures in Scheme 3, where the lone electron pairs on oxygen and nitrogen are delocalized onto the oxygen of the electron withdrawing carbonyl group, rather than onto the ring.



Scheme 3

The generally excellent performance of the RSE_{Et} values for bond energy predictions contrasts with that of the corresponding RSE_H values. If the RSE_H values obtained by equation (1) accurately represented actual radical stabilization energies, then one could use equation (9) to obtain fairly accurate bond dissociation energies of the C–C bonds of various R–R', because bond dipole effects between carbon atoms are small, generally contributing less than 2 kcal mol^{-1} to D[R–R'].

$$D[R–R'] = D[CH_3–CH_3] – RSE_H[R] – RSE_H[R'] \quad (9)$$

When compared with $D[R–R']_{lit}$, the values obtained by equation (9) with RSE_H show an average unsigned deviation of ±10.6 kcal mol^{-1} and all so calculated values are smaller than $D[R–R']_{lit}$. These underestimates range from a low of 2.0 for $\mathrm{HC{\equiv}CCH_2{-}CH_3}$ to a high of 18.9 kcal mol^{-1} for CH3CH=CH–CH(O). When compared with $D[R–R']_{lit,}$ values obtained by equation (8) with RSE_{Et} show an average unsigned deviation of only ±1.4 kcal mol^{-1}. In these 84 cases, 49 values obtained by RSE_{Et} are greater than $D[R–R']_{lit}$ and 35 are smaller, thus indicating no great trend in their distribution. As noted above, RSE_H values are certainly useful for representing trends of relative stabilities of carbon-centred radicals, but they are not inherent and transferable quantitative measures of actual stability.

Comparison of RSE_{Et} with the De Vleeschouwer Model[8]

Recently, De Vleeschouwer et al.[8] introduced an alternative inherent radical stability scheme that is also based on Pauling's equation, but with some additional corrections so that radical electrophilicities and polarizabilities are used in addition to electronegativities.[8] Also, Pauling's equation was not used in the form of equation (4) but rather the arithmetic mean of D[A–A] and D[B–B] is replaced with the geometric mean, $(D[A–A] \times D[B–B])^{0.5}$. This is a form that was also considered by Pauling and by others. In addition, the Δχ term was not used as $23(\chi[A] – \chi[B])^2$ of equation (4) but in an form termed enhanced electronegativities, $|2.83(\chi[A] - \chi[B])|^{(a[A]+a[B])}$, where the exponents a[A] and a[B] are empirical polarizability parameters, possibly to account for an unexpectedly strong $F–NO_2$ bond. The work was based on a large number of theoretical calculations with various DFT functionals, with the B3P86/6-311+G(d,p) method selected for their recommended "best procedure", described as "model 2".[8] All of their reported results for D[R–R′] bond energies in common with the present work are included in Table 2, denoted as $D[R–R′]_V$.

The 54 values in Table 2 of $D[R–R′]_V$ as reported by De Vleeschouwer et al.[8] show a mean absolute deviation of 4.5 kcal mol^{-1} from the literature values and a similar deviation of 4.6 from the 30 W1w values in common. These deviations are considerably larger than those from RSE_{Et} values (1.3 and 1.2 kcal mol^{-1}, respectively). The larger $D[R–R′]_V$ deviations are likely to arise in part from the level of theory used in Ref 8, which has been shown elsewhere to fail to predict the accurate qualitative as well as quantitative bond energies for many compounds.[20] However, there also appear to be a number of larger differences related to the original parameterisation of the scheme, which we now discuss.

In five cases deviations from literature values exceed 10 kcal mol^{-1}, with the largest deviation, that of calculated $D[F–F]_V$ = 23.3, being 14.7 kcal mol^{-1} lower than the experimental value. For comparison the corresponding value based on RSE_{Et} = 36.6 lies within 2.2 kcal mol^{-1} of experiment. Interestingly, the situation is reversed for $D[O_2N–F]$, which was the largest outlier for equation (8) but is predicted by De Vleeschouwer et al. to lie within 2 kcal mol^{-1} of one of the available experimental values (54.9 versus 52.9 kcal mol^{-1}). As noted above, equation (8) is not expected to provide a good match for this compound, as the O_2N–F bond is strengthened by resonance interactions that are not inherent to the radical groups involved but arise from their particular combination. De Vleeschouwer et al.[8] attempted to account for such resonance interactions between fluorine and groups exhibiting electron-withdrawing effects by applying corrections to Pauling's equation. However, by making such effects an inherent and transferrable property of the radical, the predictability of the scheme is compromised for other compounds involving these groups that don't exhibit such strong resonance interactions. For instance, in acetyl fluoride the proposed resonance effect with the electron-withdrawing carbonyl is not significant: equation (8) yields $D[CH_3C(O)–F]_{calc}$ = 119.3 kcal mol^{-1} versus experimental values of 120.7 and 122.3, while De Vleeschouwer et al. obtained 111.7.[8] The proposed resonance effect also is not found for $F–BH_2$ with equation (8) in Table 2, where the fluorine is bonded to the electropositive BH_2 group (sp^2 hybridized boron).

More generally, in applying the RSE_{Et} scheme to determine radical stabilities, the R-Cl and $R–CH_3$ bond energies were chosen as lacking specific steric or resonance interactions between R and the Cl or CH_3 groups. However, in applying the

RSE_V scheme, De Vleeschouwer et al.[8] included a more general range of R–X bond types, including X-groups such as HO, RO, and F which, as noted above, are able to undergo strong resonance interactions with certain types of R-group. As a result, the RSE_V values obtained from such bond energies may reflect in part these resonance interactions, rather than the inherent radical stability. This in turn limits their applicability to cases where the resonance interactions are different in magnitude or indeed absent, and may explain the generally higher deviations over the bond energies in the current study, which were deliberately chosen avoid these direct interactions.

A universal standard of reference

Rather than the traditional focus on radical stabilization energies it is conceptually advantageous to think in terms of destabilization energies. The RSE_{Et} values of Table 1, by their derivation, are relative to $RSE_{Et} = 0$ for the methyl radical from D[CH_3–CH_3] and of $RSE_H = 0$ from D[CH_3–H]. However, it is not necessary to use H_3C•, or any one other particular radical, as a reference standard.[21] An unstable radical will couple head to head with itself in an exothermic reaction. One half of the energy released measures the absolute radical destabilization energy relative to itself as measured by ½D$[R–R]_{calc}$ of Table 1. A radical with zero destabilization will not couple exothermically, unless there is some specific interaction stabilizing R–R that is not an inherent and transferrable property of the radical. With low D values, usually less than 10 kcal mol^{-1}, the reaction will be exothermic but not exergonic at room temperature because of the unfavourable entropy change. The standard of reference for all radicals thus becomes a bond dissociation energy of zero as the universal standard. For example, the destabilization energy of the methyl radical becomes ½ (88.6) = 43.3 kcal mol^{-1} based on the G3(MP2)-RAD value of D[CH_3–CH_3] or ½(89.85 ± 0.25) = 44.9 based on experimental values. Based on the D$[R–R]_{calc}$ values, the destabilization energy of HC≡C• is ½(156.2) = 78.1; of Ph•, ½(117.4) = 58.7; of •$CH_2CHC{=}CH_2$, ½(59.0) = 29.5; of •Cl, ½(57.2) = 28.6; of •F, ½(36.7) = 18.3; of O_2N•, ½(11.2) = 5.6; of $CH_3S(O)$• ½(7.3) = 3.6; of HO•, ½(46.4) = 23.2, and so forth. The destabilization energy of the phenoxy radical is near zero[21] and the antioxidant properties of various phenols, such as α-tocopherol, are due to the fact that ArO• radicals do not couple head to head. So defined destabilization energies, of course, are the values of D[A–A] and D[B–B] in Pauling's equation (4). Even negative values of bond dissociation energies are suitable for obtaining correct D values with equation (4). The bond dissociation energy of ONO–ONO is –11.3 kcal mol^{-1} due to spin-forbidden barrier to dissociation into ground state NO_2.[22] The molecule exists, but the energy of this peroxide is greater than that of two ground state NO_2 molecules, which is the definition of bond dissociation energy. The peroxide dissociates into the excited $^2B_2$ state, which falls to the $^2A_1$ ground state releasing energy. The value of –5.7 kcal mol^{-1} (i.e., half of –11.3) has been used successfully to calculate correct D[R–ONO] of nitrites.[21] The use of destabilization energies dispenses with any one particular bond or radical as the reference standard.

Conclusions

The definition of radical stabilization energies by equation (2) and its variants allows the calculation of: (a) stabilization energies that are inherent to the radical and transferable, whether the radical is carbon-centred or not; and (b) the calculation of group electronegativities that are inherent and transferable. Theoretically calculated values of bond dissociation energies of R–CH_3, R–Cl, and R–R used with Pauling's electronegativity equation allow the successful calculation of bond dissociation energies for combinations of R–R´. These are major advantages of the RSE definition by equation (2), which places successfully all stabilization or destablization energies on the same scale, unlike other alternative approaches. The methods used are not applicable to R–R´ species that are subject to effects of stabilization by conjugation or resonance and destabilization by steric strain or electrostatic repulsion, because such effects are not inherent to the radicals but to their combination in each specific whole molecule. In these cases comparison of predicted R–R' bond energies with actual ones (from direct theoretical calculation or experiment) allows the magnitude of these interactions to be evaluated. The use of theoretically calculated values of dissociation energies of R–CH_3, R–Cl, and R–R allows for the prediction of a wide range of bond dissociation energies, including those for which reliable experimental or theoretical values are not available.

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Notes and references

[a] *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.; E-mail: michelle.coote@anu.edu.au*
[b] *Department of Chemistry and Biochemistry, Long Island University, University Plaza, Brooklyn, New York 11201, USA; E-mail: Andreas.Zavitsas@liu.edu*

† Electronic Supplementary Information (ESI) available: experimental bond dissociation energies and their sources, further computational details including optimized geometries and total energies. See DOI: 10.1039/b000000x/

‡ There are actually two solutions to the quadratic equation but we take the one that is consistent with Pauling's original scale.

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