Estimation of Bond Dissociation Energies and Radical Stabilization Energies by ESR Spectroscopy

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Correlations of various indices of the stability and reactivity of carbon-centered radicals with ESR hyperfine splitting constants have been examined. For a large number of mono- and disubstituted radicals there is a moderately good linear correlation of α-proton hyperfine splitting constants ($a(H_\alpha)$) with radical stabilization enthalpies (RSE) and with BDE(C−H), the C−H bond dissociation energies for the corresponding parent compounds determined from thermodynamic and kinetic studies of C−C homolysis reactions. There is a similarly satisfactory linear correlation of $a(H_\alpha)$ with BDE-(C−H) determined by Bordwell's electrochemical and acidity function method. In all cases the correlations fail for nonplanar radicals. As expected, β-proton hyperfine splitting constants ($a(H_\beta Me)$) for radicals with a freely rotating methyl substituent are less sensitive to deviations from planarity and give better linear correlations with RSE and BDE(C−H). The correlations cover a range of more than 20 kcal/mol and are reliable predictors of RSE and BDE(C−H) for a variety of radicals including captodative species. However, the correlations fail for significantly nonplanar radicals and for radicals with cyclic delocalized systems, e.g., cyclopentadienyl. The ratio $a(H_\beta Me)/a(H_\alpha)$ for suitably substituted radicals provides an index of pyramidalization and allows one to decide for which compounds values of RSE and BDE(C−H) can be confidently estimated.

Introduction

Radical stabilization energies and bond dissociation enthalpies (BDE) are useful for the prediction or interpretation of reactivity and selectivity in free radical chemistry. Values of stabilization energy or of BDE(C−H) cannot be measured directly but must be deduced indirectly from the results of thermochemical, kinetic, or electrochemical experiments. Thus the quality and comparability of values measured by different techniques depend both on the accuracy of the experimental data and on their interpretation. Consequently, it is sometimes difficult to assess the validity of a new method or even the accuracy of a single value in a series obtained by similar measurements. This is particularly so if no appropriate comparable data are available in the literature.

In a recent paper,[1] we examined the relationship of radical stabilization enthalpy (RSE) to the α-proton ESR hyperfine splitting constant ($a(H_\alpha)$) for 15 different radicals including unsaturated and captodative species. The values of RSE ranged over 22 kcal/mol and of $a(H_\alpha)$ over 14 G. A good linear correlation was observed. In the present study, we extend this approach to further examples and show that it is possible to use both α- and β-proton hyperfine splitting constants to predict values of RSE and BDE(C−H) and to estimate the consistency of a series of data.

Early work[2] on the factors affecting the magnitudes of $a(H_\alpha)$ and $a(H_\beta)$ showed that for planar carbon-centered radicals

$$a(H_\alpha) = Q_\alpha \rho(C_\alpha) \tag{1}$$

$$a(H_\beta Me) = Q_\beta \rho(C_\alpha) \tag{2}$$

where $\rho(C_\alpha)$ is the spin density on the radical center, Q_α and Q_β are constants, and $a(H_\beta Me)$ is the β-proton hyperfine splitting constant for a freely rotating methyl group attached directly to the radical center. On the basis of eqs 1 and 2, it should be possible to use either $a(H_\alpha)$ or $a(H_\beta Me)$ to determine values of α-spin density, and hence the degree of delocalization of the free electron. However, the development of quantitative relationships between hyperfine coupling constants and radical stabilization or BDE is complicated by the fact that eqs 1 and 2 are not valid for nonplanar radicals. Deviations from planarity due to strain, such as occurs for cyclopropyl and other small cyclic radicals,[3] or from the effect of electronegative α-substituents, e.g., halogen,[3] oxygen,[4] or nitrogen,[5] lower the values of Q_α and Q_β. Nevertheless, there have been a number of earlier attempts to correlate stabilization energies or bond dissociation energies with $a(H_\alpha)$ or $a(H_\beta Me)$. Most such studies have involved $a(H_\alpha)$.

In one of the earlier papers, Green and Walton[6] reported that stabilization energies (SE[ESR]) derived ex-

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(1) Welle, F. M.; Beckhaus, H.-D.; Rüchardt, C. *J. Org. Chem.* **1997**, *62*, 552−558.
(2) Fischer, H. *Z. Naturforsch.* **1964**, *19a*, 855−867. Fischer, H. *Z. Naturforsch.* **1965**, *20a*, 428−432.
(3) For a discussion of factors affecting deviations from planarity of radicals including the cyclopropyl and oxiranyl radicals, see ref 4.

(4) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **l971**, 124−135.
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clusively from experimental ESR rotational barriers gave a linear relationship when plotted against $\log(a(H_\alpha))$, where $a(H_\alpha)$ is the proton hyperfine splitting for the terminal methylene groups of polyenyl radicals. In contrast, Nicholas and Arnold[7] found a linear relationship between $a(H_\alpha)$ and SE^{ESR} for similar species. Nonhebel and Walton[8] examined the relationship between the rotational barriers and $a(H_\alpha)$ for some saturated radicals and found a linear correlation, while Leroy et al.[9] showed that there also exists a linear relationship between the $\rho(C_\alpha)$ of six captodative radicals and their relative stabilization energies determined by ab initio calculations. Other examples of attempts to correlate hyperfine splitting constants with factors related to stabilization energies include Stein's linear correlations of the kinetically determined $BDE(C-C)$ of substituted ethylbenzenes with the benzylic hyperfine splitting constant[10] and of the $BDE(C-O)$ of substituted anisoles with the hyperfine splitting constants for the ortho and para protons in substituted phenoxy radicals.[11]

For aromatic compounds, Arnold et al.[12] have published extensive lists of substituent constants $\sigma_\alpha{}^\bullet(X)$ for meta- and para-substituted benzyl radicals. $\sigma_\alpha{}^\bullet(X)$ is defined by $\sigma_\alpha{}^\bullet(X) = 1 - a(H_\alpha(X))/a(H_\alpha(0))$, where $a(H_\alpha(X))$ is the hyperfine splitting of the benzylic proton in the substituted benzyl radical and $a(H_\alpha(0))$ is the corresponding splitting for the benzyl radical. The $\sigma_\alpha{}^\bullet$ scale gives good linear correlations with the rates of various radical reactions in Taft equations. Similar results involving extensive tables of $\sigma^\bullet$ have been reported by Jackson et al.[13] Very recently a $\sigma^\bullet$ scale based on the ESR D parameter for substituted 1,3-arylcyclopentane-1,3-diyl radicals has been published.[14]

As Q_β (eq 2) is less diminished by pyramidalization of the radical center than is Q_α (eq 1), one might expect that values of $a(H_\beta Me)$ would give a better correlation with indices of radical stabilization than do values of $a(H_\alpha)$.[2,4] Although Norman et al.[4] had earlier noted that there is a good correlation of $a(H_\beta Me)$ with $\rho(C_\alpha)$, the only correlation of $a(H_\beta Me)$ with radical reactivity appears to be that of Afanas'ev who developed a Taft equation for the rates of radical substitution reactions.[15] He found that there is a good linear correlation between $\sigma^\bullet$ and $a(H_\beta Me)$ for radicals of the type $X(CH_3)HC^\bullet$.

Despite the undoubted utility of some of the correlations outlined above, there remains the question of which type of hyperfine splitting gives the best correlations with consistent and reliable indicators of radical stability and

reactivity. In the present work we have compared correlations of $a(H_\alpha)$ and of $a(H_\beta Me)$ with $BDE(C-H)$ and with Rüchardt's radical stabilization enthalpies (RSE).[16]

Results and Discussion

Indices of Radical Stability and Reactivity. Although it is clear that a decrease in α-spin density represents delocalization of the free electron, it is not axiomatic that different mechanisms of spin distribution, such as π-delocalization, hyperconjugation, spin polarization, and anomeric interactions, will each lead to the same increase in radical stabilization for the same degree of spin delocalization.[17] Furthermore, there are other factors that may influence the stabilization energy as estimated from $\Delta BDE(C-H)$ or $\Delta BDE(C-C)$. They include interactions between substituents such as van der Waals repulsions, dipolar effects, hydrogen bonding, and hydrophobic interactions, all of which contribute to the difference in strain enthalpy between a radical and its precursor. To minimize the importance of such effects, we have used radical stabilization enthalpy (RSE) defined as the difference in stability between a purely hydrocarbon radical $^\bullet CXYZ$ (X, Y, Z = H or alkyl) and the corresponding substituted radicals $^\bullet CXYZ$ (X = H or alkyl; Y = H, alkyl or functional group; Z = functional group), i.e., the difference in stability between a purely hydrocarbon radical and its analogue in which one or more of the *alkyl* groups have been replaced by substituents. One of the advantages of the use of RSE's is that they avoid the problem that values of differences in $BDE(C-H)$ clearly do not correspond accurately to the differences in stability between primary, secondary, and tertiary alkyl radicals. Extensive compilations of values of RSE based on thermochemical and kinetic data for the homolysis of $C-C$ bonds are available.[16]

Despite the fact that they include contributions arising from the release of strain in the precursor molecule and differences between other nonbonded interactions in the precursor and the radical, values of $BDE(C-H)$ for the parent compound are widely used to estimate the relative stabilities and reactivities of radicals. McMillen and Golden's early review[18] includes extensive lists of BDE-$(C-H)$ values taken from the literature, while more recently Tsang[19] has published a selection of "best" values. An excellent self-consistent series of $BDE(C-H)$ has been experimentally determined by Bordwell using a combination of electrochemical and acidity function measurements.[20] Values of $BDE(C-H)$ are also

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Table 1. RSE, BDE(C–H), ESR Parameters, and Pyramidalization Quotients for the Radicals •CXYZ

no.	X	Y	Z	RSE[a]/ kcal mol^{-1}	BDE(C–H)[b]/ kcal mol^{-1}	a_α/G	$a(H_\beta Me)$/G	P^{t} [c]	P^{sec} [d]
1a	Me	Me	Me	≡ 0	95.7[e]		22.71[f]		
1b	Me	Me	H	≡ 0	98.7[e]	22.1[f]	24.7[f]	1.03	1.12
2a	Ph	Me	Me	−8.4[g]	87.3		16.5[f]		
2b	Ph	Me	H	−8.4[g]	90.3	16.25[h]	17.69[h]	1.02	1.09
3a	OPr^i	Me	Me	−5.9[i]	93.9		19.37[j]		
3b	OBu^t	Me	H	−5.9[i]	96.9	13.5[k]	21.6[k]	1.45	1.6
4a	NH$_2$	Me	Me	−3.9[l]	94.2		17.9[j]		
4b	NH$_2$	Me	H	−3.9[l]	97.1	14.7[k]	20.7[k]	1.22	1.41
5a	COPh	Me	Me	−6.0[m]	89.9		19.13[k]		
5b	COPh	Me	H	−6.0[m]	92.9	18.7[k]	21.86[k]	1.04	1.17
6a	CO$_2$Et	Me	Me	−2.8[m]	92.6		21.56[f]		
6b	CO$_2$Et	Me	H	−2.8[m]	95.6	20.48[j]	24.68[j]	1.05	1.21
7a	CN	Me	Me	−3.4[n]	91.9		20.6[k]		
7b	CN	Me	H	−3.4[n]	94.9	20.3[f]	23.1[f]	1.01	1.13
8a	CO$_2$Et	Ph	Me	−10.1[o,p]	85.6		16.60[q]		
8b	CO$_2$Et	Ph	H	−10.1[o,p]	88.6	14.8[q]		1.12	
9a	COMe	COMe	Me	−11.4[r]	84.7		21.52[j]		
9b	COMe	COMe	H	−11.4[r]	87.7	18.0[j]		1.16	
10a	CN	CN	Me	−2.5[n]	84.6		20.64[j]		
10b	CN	CN	H	−2.5[n]	87.6	19.22[j]			
11a	CN	OH	Me	−8.1[i]	87.3		17.88[f]	0.97	
11b	CN	OMe	H	−8.1[i]	90.3	18.4[k]			
12a	-CONBuCHMeCONBu-		Me	−6.3[s,p]	89.4		17.8[j]	1.04	
12b	-CONBuCH$_2$CONBu-		H	−6.3[s,p]	92.4	17.1[j]			
13	CN	NH$_2$	H	−13.8[t]	84.9	14.9[k]			
14a	CO$_2$Bu^t	NH$_2$	Me	−14.8[u]	81.3		13.2[v]	1.02	
14b	CO$_2$Me	NH$_2$	H	−14.8[u]	84.3	13.0[v]			
15	COPh	NMe$_2$	H	−21.6[w]	78.3	8.5[x]			
16a	Ph	Ph	Me	−12.9[y]	82.8		15.1[f]	1.03	
16b	Ph	Ph	H	−12.9[y]	85.8	14.7[f]			
17	9,10-dihydroanthryl-9-yl			−15.2[y]	83.5	13.4[g]			
18a	9-methylfluoren-9-yl			−16.0[z]	79.7		14.56[j]	1.05	
18b	fluoren-9-yl			−16.0[z]	82.7	13.9[f]			
19a	9-methylxanth-9-yl			−18.1[y]	77.6		12.2[f]	0.96	
19b	xanth-9-yl			−18.1[y]	80.6	12.7[f]			
20a	CH=CH$_2$	Me	Me	−12.6[y]	83.1		13.8[f]	0.99	
20b	CH=CH$_2$	Me	H	−12.6[y]	86.1	14.0[f]	15.2[f]		1.09
21	pentamethylcyclopentadienyl			−13.7[y]	82.0[aa]		6.4[f]		
22	inden-1-yl			−15.7[y]	83.0	11.9[f]			
23	anthron-10-yl			−17.8[bb]	80.9	12.12[bb]			

[a] Reference 16. In most cases RSE is the mean value of RSE for several radicals •CXYZ with different alkyl substituents. [b] Reference 1. [c] $P^{t} = a(H_\beta Me)(XYMeC•)/a(H_\alpha)(XYHC•)$. [d] $P^{sec} = a(H_\beta Me)(XHMeC•)/a(H_\alpha)(XHMeC•)$. [e] Reference 19. [f] Reference 23a. [g] Kratt, G.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1748–1764. [h] Arnold, D. R.; de P. Nicholas, A. M.; Young, K. M. *Can. J. Chem.* **1986**, *64*, 769–772. [i] Reference 23b. [j] This work. [k] Reference 23b. [l] Schüle, U. Ph.D. Thesis, University of Freiburg, 1992, ref 1. [m] Gleissner, R. Ph.D. Thesis, University of Freiburg, 1988, ref 16. [n] Pakusch, J.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1991**, *124*, 1191–1198. [o] Rausch, R. Ph.D. Thesis, University of Freiburg, 1984. Schulze, R.; Beckhaus, H.-D.; Rüchardt, C. *J. Pract. Chem.* **1990**, *332*, 325–330. [p] Geminal interactions in the saturated radical precursor are neglected. [q] Korth, H.-G.; Lommes, P.; Sustman, R.; Sylander, L.; Stella, L. *New. J. Chem.* **1987**, *11*, 365–375. [r] Nölke, M.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Liebigs Ann.* **1995**, 41–51. [s] Brocks, J. J.; Welle, F. M.; Beckhaus, H.-D.; Rüchardt, C. in preparation. [t] Welle, F. M.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Liebigs Ann.* **1997**, 155–163. [u] Schulze, R.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1993**, *126*, 1031–1038. [v] MacInnes, I.; Walton, J. C.; Nonhebel, D. C. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1789–1794. [w] Reference 1. [x] Welle, F.; Verevkin, S. P.; Keller, M.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 697–710. [y] Herberg, C. Ph.D. Thesis, University of Freiburg, 1992. [z] Rakus, K.; Schätzer, J.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 1095–1103. [aa] Strain enthalpy is implied. [bb] Wurche, F. Diploma Thesis, University of Freiburg, 1996.

available from Rüchardt's kinetic and thermochemical studies.[16] Also, a variety of theoretical approaches at various levels of theory, e.g., UHF or ROHF 4-31G,[21a] Density Functional Theory,[22a] and MP4 methods,[22b] have been used to obtain values of BDE(C–H).

ESR Hyperfine Coupling Constants. Many of the values of $a(H_\alpha)$ and of $a(H_\beta Me)$ required for the present study were obtained from the literature.[23] Although the spectra were recorded in a wide range of solvents, our analysis of more than 200 hyperfine splitting constants showed that the values of $a(H_\alpha)$ and $a(H_\beta Me)$ for any single radical vary within a range of <0.3 G if measured in different nonpolar solvents. Measurements in aqueous solutions show variations of up to 0.5 G from those made in nonpolar solvents, while splittings obtained from solid samples show much larger variability, and hence are not suitable.

Some values of $a(H_\alpha)$ and $a(H_\beta Me)$ in nonpolar solvents required for the present study were not available and were therefore measured in these laboratories. The radicals **3a**, **4a**, **9a**, **9b**, **10a**, **10b**, **12a**, **12b**, and **27** (the structures of radicals **1**–**23** are given in Table 1) were each generated in the cavity of the ESR spectrometer by

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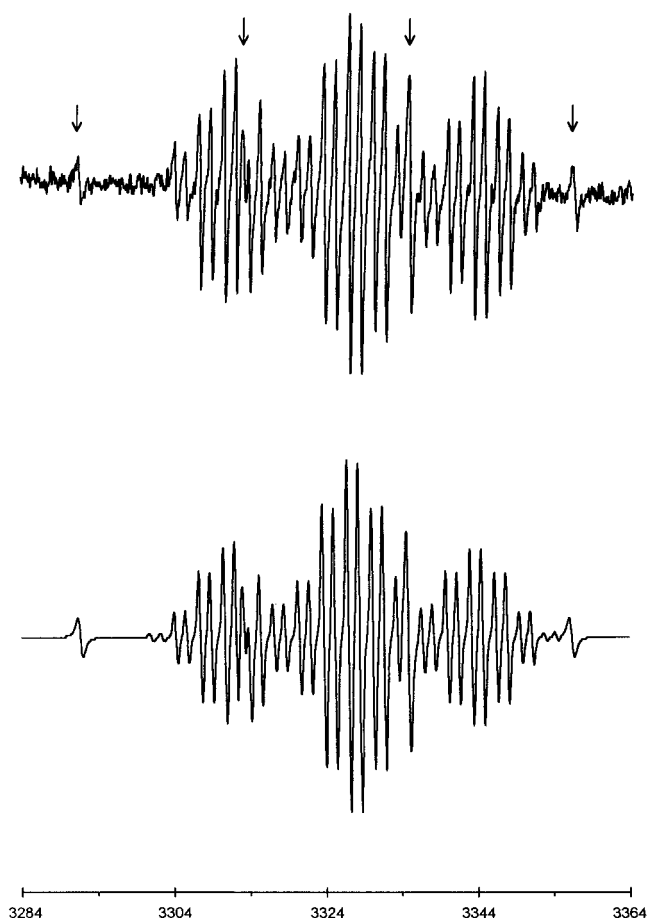
Figure 1. ESR spectrum of radicals **25** and **9a** and its simulation (below); the arrows indicate the quadruplet of **9a**.
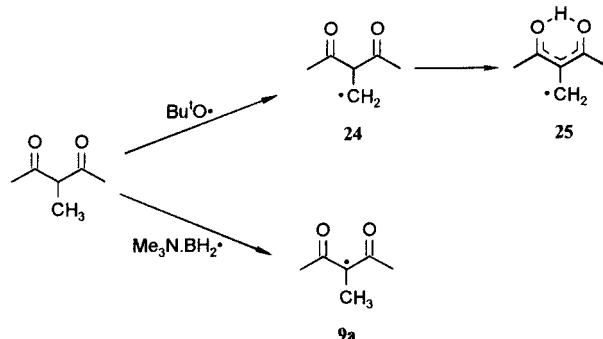
UV irradiation of a solution of the corresponding C−H compound and di-*tert*-butyl peroxide in a nonpolar solvent. Similar irradiation of a mixture of di-*tert*-butyl peroxide, triethylsilane (or hexamethylditin), and ethyl 2-bromopropionate afforded the 1-(ethoxycarbonyl)ethyl radical **6b** via abstraction of the bromine atom by Et$_3$Si$^\bullet$ or Me$_3$Sn$^\bullet$. The 9-methylfluoren-9-yl radical **18a** was generated by thermal homolysis of the dimer in diphenyl ether. Malononitrile and methylmalononitrile, the chosen precursors for the radicals **10a** and **10b**, were insufficiently soluble in nonpolar solvents to give suitable ESR spectra. However, satisfactory signals were obtained by irradiation of saturated solutions of the two precursors in a 1:1 mixture of benzene and di-*tert*-butyl peroxide, even though in the case of methylmalononitrile a two-phase system was formed.

3-Methyl-2,4-pentanedione, when irradiated in di-*tert*-butyl peroxide solution, gave a complex ESR signal comprised of two overlapping spectra (Figure 1). The major spectrum (80%), a doublet (a(H) = 1.46 G) of triplets (a(H) = 16.25 G) of septets (a(H) = 3.23 G), was tentatively assigned to the radical **25**, while the minor component (20%) was a quartet (a(H) = 21.5 G) assigned to the radical **9a**.

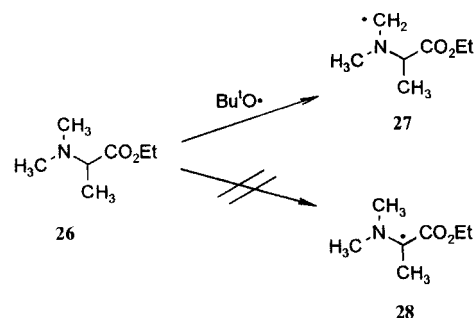We suggest that formation of **25** initially involves hydrogen-atom abstraction by the electrophilic Bu^{t}O$^\bullet$ radical from the 3-methyl substituent, the C−H bonds of which are the least affected by the electron-withdrawing nature of the carbonyl groups. The β-proton in the species **24** so formed is more acidic than it is in the

precursor because of the adjacent radical center. Hence **24** undergoes rapid enolization to form the symmetrical radical **25**.

As the preferential formation of **25** could be reasonably attributed to polar effects, the experiment was repeated in the presence of the polarity reversal catalyst trimethylamine−borane complex.[24] As expected, the intermediate nucleophilic Me$_3$N·BH$_2$$^\bullet$ radical abstracted hydrogen with high selectivity from the electrophilic 3-position of the precursor to afford only **9a**, the spectrum of which appeared as a clean quartet (a(H) = 21.5 G), although the spectral simulation showed that it was necessary to include a very small septet coupling (a(H) = 0.1 G) to account for the line width. The same method involving catalysis by Me$_3$N·BH$_3$ was effective for generating the radical **9b** from the parent dione.

An attempt to form the radical **28** gave what appears to be another example of polar effects on hydrogen-atom abstraction. When the precursor **26** in di-*tert*-butyl peroxide was subjected to UV irradiation, the ESR spectrum with hfc's a(1H) = 1.34 G, a(2H) = 14.30 G, a(3H) = 4.04 G, and a(1N) = 7.00 G was assigned to the radical **27**. Apparently the selectivity of the reaction is affected not only by statistical factors but also by the preference of the electrophilic Bu^{t}O$^\bullet$ radical for attack on the methyl C−H bonds adjacent to the electron-donating nitrogen rather than on the 2-CH position, even though the latter would afford the more stabilized product **28**.

The hyperfine splitting constants of **9a**, **25**, **27**, and the other radicals generated in the course of this work were all determined by computer simulation.

Correlation of Radical Stabilization Enthalpy with a(H$_o$) and a(H$_\beta$Me). Table 1 gives a list of values of RSE for 40 radicals determined by the Rüchardt method from changes in the values of BDE(C−C) by comparison with alkyl-substituted ethanes with the same

(24) Paul, V.; Roberts, B. P.; Willis, J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1953−1261. Paul, V.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1322−1324.
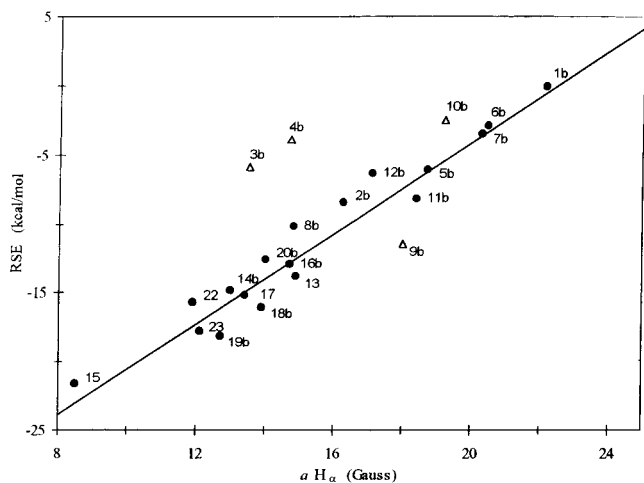
Figure 2. Plot of RSE against $a(H_\alpha)$ showing the line of eq 3 in Table 4: ($\triangle$) outliers for the calculation of eq 3. Compound numbers are shown in Table 1.

strain dissociation enthalpy.[16] A consequence of this method is that all saturated acyclic tertiary and secondary radicals are defined as having RSE = 0. Furthermore, similarly substituted radicals, whether secondary or tertiary, all have the same value of RSE, e.g., $^\bullet CR^1R^2COPh$ and $^\bullet CHR^3COPh$ have RSE = −6.0 kcal/mol no matter what the structures of the saturated alkyl substituents R^1, R^2, and R^3 are. Hence, the values of RSE given in Table 1 are not necessarily those determined for the particular radical specified but are the mean values obtained for a number of radicals of the same type. However, to maintain consistency, ESR data are given only for those radicals in which the saturated alkyl substituent(s) is methyl. Also it should be noted that Table 1 differs from that in our earlier paper[1] in that it contains RSE data for five new radicals **8**, **12**, **21**, **22**, and **23**, improved values of RSE for radicals **9** and **10** corrected for strain in the precursor, and more recent ESR splitting constants determined in nonpolar solvents for most of the radicals listed.

A plot of $a(H_\alpha)$ against RSE for all the appropriate (i.e., secondary) radicals in Table 1 is shown in Figure 2. Linear regression affords eq 3 (see Table 4) with coefficients very similar to those given in our earlier paper. Figure 2 shows that all the species studied lie reasonably close to the line of best fit except **3b** ($^\bullet$CHMeOBu^t) and **4b** ($^\bullet$CHMeNH$_2$), the two radicals expected to be somewhat pyramidalized. Each has a value of $a(H_\alpha)$ about 5 G less than those estimated from eq 3.

Since in the Rüchardt method values of BDE(C−H) are obtained by combination of values of RSE with thermochemical data for the parent hydrocarbon, a plot of $a(H_\alpha)$ against BDE(C−H) should also give a similar linear correlation. Equation 5, obtained by linear regression of the appropriate data in Table 1, shows the standard deviation to be much the same as those for eq 3. Once again the two nonplanar radicals **3b** and **4b** are outliers.

We suggested above that $a(H_\beta Me)$ might be a better indicator of RSE and BDE(C−H) than $a(H_\alpha)$ because the former is less sensitive than the latter to deviations from planarity of the radical center.[4] The plot of $a(H_\beta Me)$ for tertiary radicals against RSE (Figure 3) shows the validity of this hypothesis. The data point for the oxygen-substituted radical $^\bullet$CMe$_2$OPr^i **3a** lies very close to the line of best fit (eq 4 in Table 4) while that for the amino-

Table 2. BDE(C−H) for H−CHXY Determined by the Bordwell Method and $a(H_\alpha)$ for the Corresponding Radicals

no.	X	Y	BDE(C−H)[a]/ kcal mol^{-1}	$a(H_\alpha)$/G
33	CO$_2$Me	CO$_2$Me	98.3[b]	20.15[c]
34	COMe	H	97[b]	19.7[d]
35	COBu^t	H	96.3[e]	20.95[d]
36	COMe	CO$_2$Et	96[f]	18.96[c]
37	SR	H	96[g]	16.9[d]
38	COPh	H	96[c]	19.5[d]
39	COPh(p-OMe)	H	96[c]	19.25[c]
40	COPh(p-CN)	H	96[c]	17.5[c]
41	-CO$_2$CMe$_2$OCO-		95.6[b]	19.30[h]
9b	COMe	COMe	95[i]	18.0[k]
42	-COCH$_2$CH$_2$CH$_2$CO-		95[i]	20.1[d]
43	NO$_2$	Me	94.4[i]	21[d]
44	CN	CO$_2$Et	94[f]	19.80[c]
10b	CN	CN	93[j]	19.22[k]
45	COEt	Me	91.2[e]	18.6[d]
46	Ph	H	91[c]	16.30[d]
5b	COPh	Me	91[i]	18.70[c]
47	-COCH$_2$CH$_2$CH$_2$-		91[l]	17.96[d]
48	-COCH$_2$CH$_2$CH$_2$CH$_2$-		91[i]	18.1[d]
49	SEt	CO$_2$Et	90.0[m]	15.0[c]
50	SMe	CN	89[m]	15.1[c]
51	S^{t}Bu	CN	88.9[m]	15.02[c]
52	CH=CH$_2$	H	88.8[n]	14.35[d]
53	SPh	CO$_2$Et	88.8[m]	15.0[c]
8b	Ph	CO$_2$Et	87.0[b]	14.94[o]
54	COPh	Ph	85.5[c]	14.04[p]
55	Ph	CN	84.9[j]	15.29[q]
16b	Ph	Ph	84.8[r]	14.7[d]
18b	fluorene (9-H)		83[c]	13.9[d]
56	cyclopentadiene (1-H)		81.8[r]	6.06[d]
17	dihydroanthracene (9-H)		81[h]	13.4[s]
22	indene (9-H)		81[r]	11.9[d]
19b	xanthene (9-H)		78.5[j]	12.73[d]
15	COPh	NMe$_2$	75[i]	8.3[t]
57	phenalen (1-H)		67[j]	6.3[d]

[a] The BDE(C−H) data in this table is 3.0 kcal/mol higher than given in the original literature (see text). [b] Reference 20b. [c] Reference 23b. [d] Reference 23a. [e] Reference 20d. [f] Reference 20c. [g] Reference 20b. [h] Kaushal, P.; Pearl, L. H.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1663−1670. [i] Reference 20e. [j] Reference 20j. [k] This work. [l] Reference 20f. [m] Reference 20g. [n] Reference 20i. [o] Korth, H.-G.; Lommes, P.; Sustman, R.; Sylander, L.; Stella, L. *New. J. Chem.* **1987**, *11*, 365−375. [p] Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575−1588. [q] Korth, H.-G.; Lommes, P.; Sicking, W.; Sustmann, R. *Chem. Ber.* **1985**, *118*, 4627−4631. [r] Reference 20h. [s] Herberg, C. Ph.D. Thesis, University of Freiburg, 1992. [t] Welle, F.; Verevkin, S. P.; Keller, M.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 697−710.

Table 3. BDE(MeXYC−H) Determined by the Bordwell Method and $a(H_\beta^{Me})$ for the Corresponding Radicals

no.	X	Y	BDE(C−H)[a]/ kcal mol^{-1}	$a(H_\beta^{Me})$/G
43	NO$_2$	H	94.4[b]	25[c]
45	COEt	H	91.2[d]	22.5[c]
5b	COPh	H	91[b]	21.86[e]
58	-CO$_2$CH$_2$OCO-		90.5[f]	22.8[e]
59	NO$_2$	Me	89.8[b]	19.8[c]
5a	COPh	Me	89[b]	19.13[e]
60	COPr^i	Me	87[b]	19.9[c]
21	pentamethylcyclopentadiene		80[g]	6.4[c]
18a	9-methylfluorene		78.4[h]	14.56[i]

[a] The BDE(C−H) data in this table are 3.0 kcal/mol higher than given in the original literature. See text. [b] Reference 20e. [c] Reference 23a. [d] Reference 20d. [e] Reference 23b. [f] Reference 20k. [g] Reference 20i. [h] Reference 20g. [i] This work.

substituted radical $^\bullet$CMe$_2$NH$_2$ **4a** is much closer than it is in the plot of Figure 2. However, as Figure 3 shows, there are serious discrepancies for the $^\bullet$CMe(COMe)$_2$

Table 4. Linear Correlations of RSE and BDE(CH) with ESR Parameters

eq	data collection[a]	linear correlations[b]/kcal mol^{-1}	r[c]	n[d]
3	Rüchardt	$RSE^{sec} = 1.65a(H_\alpha) - 37.1(\pm 1.3)$[e]	0.97	18
4	Rüchardt	$RSE^t = 1.61a(H_\beta{}^{Me}) - 36.8(\pm 1.4)$[f]	0.97	13
5	Rüchardt	$BDE(C-H) = 1.61a(H_\alpha) + 62.4(\pm 1.6)$	0.96	18
6	Rüchardt	$BDE(C-H) = 1.58a(H_\beta{}^{Me}) + 59.4(\pm 1.3)$	0.97	13
7	Bordwell	$BDE(C-H) = 1.93a(H_\alpha) + 57.8(\pm 2.3)$	0.95	33
8	Bordwell	$BDE(C-H) = 1.45a(H_\beta{}^{Me}) + 59.4(\pm 1.7)$	0.95	8
9	McMillen/Golden	$BDE(C-H) = 1.57a(H_\alpha) + 65.2(\pm 3.2)$	0.93	22
10	McMillen/Golden	$BDE(C-H) = 1.45a(H_\beta{}^{Me}) + 62.8(\pm 1.4)$	0.98	9
11	Tsang	$BDE(C-H) = 1.92a(H_\alpha) + 57.8(\pm 1.0)$	0.96	8
12	Tsang	$BDE(C-H) = 1.21a(H_\beta{}^{Me}) + 68.5(\pm 0.3)$[g]	0.99	5
13	Pasto	$BDE(C-H) = 1.68a(H_\alpha) + 64.7(\pm 1.8)$	0.95	16
14	Timberlake	$BDE(C-H) = 1.90a(H_\alpha) + 55.1(\pm 3.0)$	0.93	5

[a] For citations see text. [b] $a(H_\alpha)$ and $a(H_\beta{}^{Me})$ in G. [c] Correlation coefficient. [d] Number of data points. [e] Only valid for secondary radicals. [f] Only valid for tertiary radicals. [g] The maximum deviation (0.3 kcal/mol) is smaller than the biggest error estimated by Tsang (0.7 kcal/mol) in ref 19.
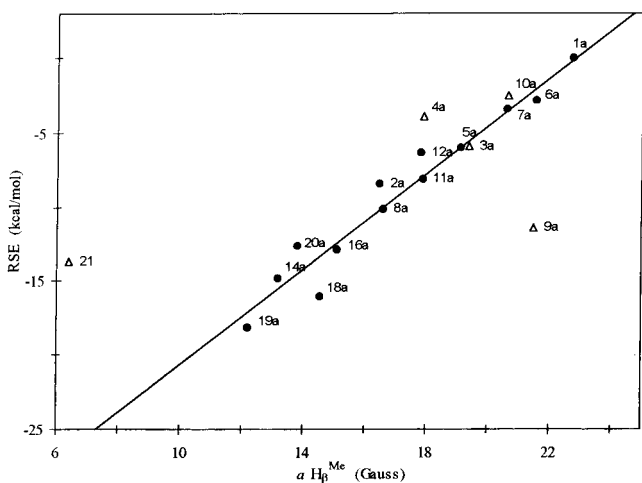

Figure 3. Plot of RSE against $a(H_\beta Me)$ for tertiary radicals showing the line of eq 4 in Table 4: (△) outliers for the calculation of eq 4. Compound numbers are shown in Table 1.

Figure 4. Plot of BDE(C−H) against $a(H_\beta Me)$ showing the line of eq 6: (△) outliers; (s) secondary radicals; (•) tertiary radicals. Only the tertiary radicals were used to calculate eq 6 in Table 4. Compound numbers are shown in Table 1.

radical **9a** and the pentamethylcyclopentadienyl radical **21** which have a values of $a(H_\beta Me)$ about 6 G higher and 8 G lower than that expected from eq 4. The case of radical **9a** is discussed below. The anomalous behavior of **21** arises from the orbital degeneracy of the cyclopentadienyl radical.[25] It is noteworthy that when the degeneracy is broken by monoalkyl substitution, the value of $a(H_\beta Me)$ is aproximately doubled. Thus the methylcyclopentadienyl radical has $a(H_\beta Me) = 12.7$ G[26a] or 14.8 G.[26b] The latter value would place **21** very close to the line of eq 4 in Figure 3.

A pleasing feature of Figure 3 is that the data for a wide variety of radicals including captodative radicals, e.g., **14a**, unsaturated species, e.g., **20a**, and numerous substituted alkyl radicals lie close to the line of best fit over a range of 18 kcal/mol. This engenders confidence both in the validity of the correlations and in the reliability of the experimental data.

In the Rüchardt method, each secondary radical ·CHXY has the same value of RSE as the corresponding tertiary radical ·CMeXY. However, the values of $a(H_\beta Me)$ for the latter are always smaller than those for the former. Consequently eq 4 must be modified for secondary
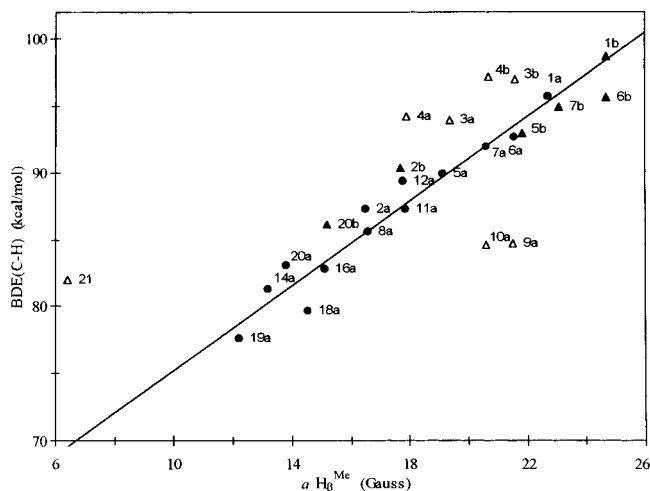
radicals of the type ·CHMeX. Unfortunately there are not sufficient data available to enable a reliable correlation to be established. However, the relationship $RSE^{sec} = 1.17a(H_\beta Me) - 30.4$ gives satisfactory agreement with all the data available.

The correlation (Figure 4) of $a(H_\beta Me)$ against Rüchardt's values of BDE(C−H) (eq 6) is somewhat less satisfactory than that against RSE (eq 4) although better than it is for the correlation of $a(H_\alpha)$ with BDE(C−H) (eq 5). The nonplanar radicals **3a**, **3b**, **4a**, and **4b**, the dicyano and the diacyl radicals **9a** and **10a**, and the pentamethylcyclopentadienyl radical **21** all lie off the line of eq 6. There is considerable divergence between the values of BDE(C−H) for **9b** and **10b** obtained from Rüchardt's data (87.7 and 87.6 kcal/mol, respectively) and those obtained by Bordwell's method (95 and 93 kcal/mol, respectively). The fact that the latter values lie close to the line of best fit (eq 7) in Figure 5 suggests that the former require reevaluation. It is noteworthy that for values of BDE(C−H), unlike those of RSE, the same correlation (eq 6) applies to both secondary and tertiary radicals.

We examined next the correlation of $a(H_\alpha)$ and $a(H_\beta Me)$ with BDE(C−H) determined by Bordwell's cyclovoltametry/acidity function method.[20] These data were originally calibrated by reference to a scale of 15 values of BDE(C−H) measured in the gas phase.[20j] However, the

(25) For a discussion of the orbital degeneracy of cyclopentadienyl radical, see ref 26.
(26) (a) Kira, M.; Watanabe, M.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5202. (b) Barker, P. J.; Davies, A. G.; Tse, M.-W. *J. Chem. Soc., Perkin Trans. 2* **1980**, 941−948.
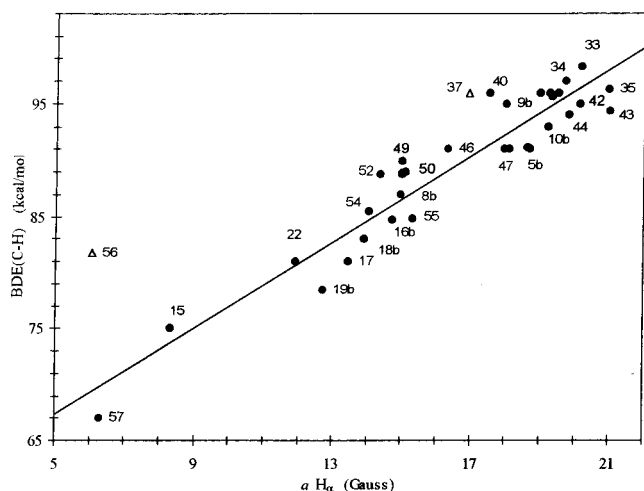
Figure 5. Plot of Bordwell's values of BDE(C−H) against $a(H_\alpha)$ showing the line of eq 7 in Table 4: (△) outliers. Compound numbers are shown in Tables 1 and 2.

Figure 6. Plot of BDE(C−H) against $a(H_\beta Me)$ showing the line of eq 8 in Table 4: (△) outlier. Compound numbers are shown in Tables 1 and 3.

gas-phase data were in turn based on values for the isopropyl and ethyl radical[18] that have been shown by more recent work to be too low.[19] Accordingly, for the present study the Bordwell values of BDE(C−H) have each been increased by 3.0 kcal/mol.

Tables 2 and 3 show the data for 44 radicals bearing various combinations of the substituents COR, CO_2R, SR, NO_2, CN, and NR_2 as well as for a variety of unsaturated radicals. A plot (Figure 5) of $a(H_\alpha)$ against BDE(C−H) for 35 radicals shows a reasonably good linear correlation expressed by eq 7, the most serious anomaly being the cyclopentadienyl radical **59** which, as discussed above, has a value of $a(H_\alpha)$ about 6 G less than that expected. The sulfur-substituted radical, $\cdot CH_2SR$ **37**, has an $a(H_\alpha)$ about 3 G less than that calculated from eq 7, but the value of BDE(C−H) for this radical is open to doubt because it was derived from an *estimate* of the acidity of the parent compound.

For the nine radicals for which appropriate data are available, there is a good linear correlation of $a(H_\beta Me)$ with Bordwell's BDE(C−H) expressed by eq 8, the only serious anomaly being the pentamethylcyclopentadienyl radical **21** which has $a(H_\beta Me)$ about 8 kcal/mol lower than that calculated (Figure 6).

An extensive set of data is available in the review by McMillen and Golden.[18] Not surprisingly, in view of the wide range of sources, there is considerable scatter in a plot of $a(H_\alpha)$ against BDE(C−H). The line of best fit is given by eq 9. A feature of this correlation is that the values of $a(H_\alpha)$ for methyl and some of the primary radicals deviate considerably from those calculated. The same is true of a plot of Tsang's best values of BDE(C−H)[19] against $a(H_\alpha)$ (eq 11). However, in both cases the linear correlation is much better for the lesser number of data available for plots of BDE(C−H) against $a(H_\beta Me)$ (eqs 10 and 12).

Finally, we examined the correlation of $a(H_\alpha)$ against values of BDE(C−H) obtained by theoretical methods by Pasto[21] and Timberlake[22a] and their co-workers. In both cases rather poor linear correlations were observed, with data for radicals expected to be nonplanar lying well away from the lines of best fit (eqs 13 and 14). The theoretical values of BDE(C−H) reported by Leroy et al.[22b] did not show a linear correlation with $a(H_\alpha)$.
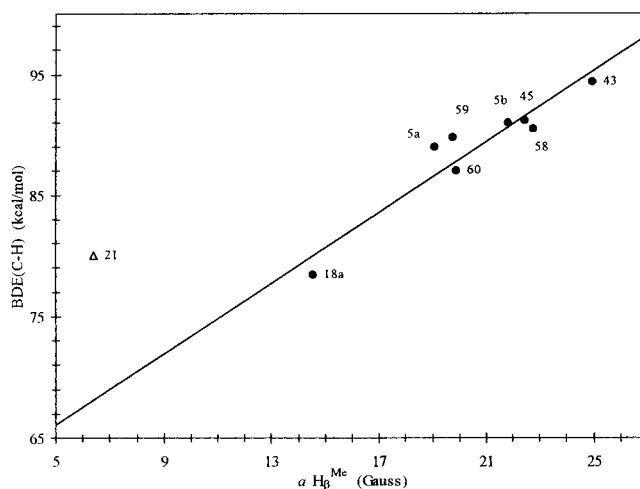
Prediction of RSE and BDE(C−H) from ESR Data. The results described above indicate that appropriate ESR hyperfine splitting constants correlate well with RSE's determined by the Rüchardt method which are useful indices of radical stability. Except for nonplanar radicals, e.g., $\cdot CR^1R^2NR^3_2$, and the radicals **9a** or **21**, the special features of which are discussed above, they are predictable from values of $a(H_\alpha)$ or $a(H_\beta Me)$ by eqs 3 and 4 with the latter generally giving somewhat more accurate results. The correlations cover a range of about 22 kcal/mol and appear to be particularly suitable for estimating the RSE's of captodative and benzylic radicals. For all such radicals, values of RSE predicted from eqs 3 or 4 should be accurate to within 2.0 kcal/mol. For radicals containing an α-methyl substituent, eq 4 is preferred.

The prediction of the C−H bond dissociation enthalpies of the parent compounds, which are widely used as indices of radical stability and reactivity, is more problematic. Values of BDE(C−H) calculated from $a(H_\alpha)$ by eqs 5, 7, 9, and 11 are all in reasonable agreement, but eqs 13 and 14 based respectively on theoretical approaches give higher and lower values of BDE(C−H). Values obtained from eq 9 are uniformly ca. 2.0 kcal/mol above those derived from eq 5, while those calculated from eq 7 (and eq 11) show a slightly larger divergence at the top of the range (>22 G) but coincide at about 24.5 G. We consider that either eq 5 based on Rüchardt's data[16] or eq 7 based on Bordwell's data[20] can confidently be used to obtain reliable values of BDE(C−H) for planar or very nearly planar radicals to within a range of 2 kcal/mol.

Reasonably consistent values of BDE(C−H) can be obtained by substitution of the appropriate $a(H_\beta Me)$ into eqs 6, 8, and 10 but eq 12 gives markedly higher values at the lower end of the scale. Equations 6 and 8 based respectively on Rüchardt's and Bordwell's results[16,20] are derived from the widest range of experimental data, but values of BDE(C−H) calculated from eq 8 tend to be about 2.0−2.5 kcal/mol lower than those obtained from eq 6, probably because of systematic differences in the experimental data. Since $a(H_\beta Me)$ is less sensitive than $a(H_\alpha)$ to nonplanarity of the radical center, eq 6 is to be preferred over eq 5 if the appropriate ESR hyperfine coupling constants are available.

Table 5. Pyramidalization Quotients for Radicals ·CHMeX

X	$a(H_\alpha)$/G	$a(H_\beta Me)$/G	P^{sec}
NH_2	14.7[b]	20.7[b]	1.41
NH_3^+	22.7[a]	26.7[a]	1.18
$NHCOCH_3$	18.9[b]	21.8[b]	1.15
$NHCONH_2$	16.9[b]	21.9[b]	1.30
$NHEt$	14.6[a]	20.0[a]	1.37
NH_2Et^+	22.6[a]	26.9[a]	1.19
$NEtCHO$	18.8[a]	22.0[a]	1.17
OEt	13.9[b]	21.6[b]	1.55
$OCOCH_3$	18.8[a]	24.0[a]	1.28
$OCHO$	19.6[a]	24.5[a]	1.25
$OP(OEt)_2$	16.5[a]	22.3[a]	1.35
$OPO(OEt)_2$	18.1[a]	22.6[a]	1.26
$OCONH_2$	17.6[a]	24.0[a]	1.36
OCO_2Et	18.9[a]	23.9[a]	1.26
SEt	16.5[a]	20.3[a]	1.23
$S(O)Et$	20.2[a]	25.3[a]	1.25
$S(O_2)Et$	21.6[c]	27.3[c]	1.26
Br	20.5[a]	24.7[a]	1.20
F	17.3[a]	24.5[a]	1.42

[a] Reference 23b. [b] Reference 23b. [c] Carton, P. M.; Gilbert, B. C.; Laue, H. A. H.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1245.

Although the satisfactory correspondence between the correlations based on experimental data suggest that values of $a(H_\alpha)$ and $a(H_\beta Me)$ should be suitable for the prediction of BDE(C−H), the plots in Figures 4−6 show that this is not valid for all radicals. The question arises, therefore, of how one might assess whether values of BDE(C−H) obtained in this way are likely to be accurate. The radicals that deviate most from values predicted by the appropriate equations are simple saturated hydrocarbon radicals, radicals that may have unusual strain or dipolar effects, e.g., **9a**, cyclic delocalized radicals, e.g., **21**, and radicals that are nonplanar. The first group presents no problem as accurate experimental values of BDE(C−H) are already available. As the experimental data for some of the radicals in the second group, e.g., **9a**, are in discord, the accurate prediction of BDE(C−H) for such species must await agreement on correct values of BDE(C−H). For the last group (nonplanar radicals), since values of $a(H_\alpha)$ are much more sensitive to pyrimidalization than are values of $a(H_\beta Me)$, we suggest that the ratio $a(H_\beta Me)/a(H_\alpha)$ be used as an index of deviation from planarity.[27] Table 1 gives values of pyramidalization quotients P defined as

$$P^t = a(H_\beta Me(·CMeXY))/a(H_\alpha(·CHXY)) \quad (15)$$

$$P^{sec} = a(H_\beta Me(·CHXMe))/a(H_\alpha(·CHXMe)) \quad (16)$$

where X and Y are any substituents. Further values of P^{sec} obtained from literature data are shown in Table 5. Our survey of the data presented in the figures and tables indicates that if $P^t < 1.05$ or if $P^{sec} < 1.25$, then values of RSE and BDE should be obtainable from ESR data. We recommend that for this purpose eqs 3−6 be used, with preference given to eqs 4 and 6 since $a(H_\beta Me)$ is less sensitive to pyramidalization of the radical center than is $a(H_\alpha)$. For radicals that meet the criteria, the calculated values of RSE and BDE(C−H) should be accurate to within about 2.0 kcal/mol.

In general the values of P^t and P^{sec} listed in Tables 1 and 5 confirm that a wide range of substituted secondary

(27) For the first suggested use of this ratio as a measure of radical pyrimidalization, see ref 4.

and tertiary radicals including unsaturated radicals, benzylic radicals, radicals bearing a single electron-withdrawing substituent, and a large number of captodative species are either planar or sufficiently close to planar to allow values of BDE(C−H) and RSE to be calculated from ESR data by means of eqs 4 and 6. Radicals bearing fluoro or amino substituents are nonplanar and do not meet the criteria for application of eqs 3−6. Although $·CR^1R^2OR^3$ are nonplanar and do not meet the criteria, eq 4 *may* be applicable. Thus for **3a** eqs 4 and 6 give an RSE of −5.6 kcal/mol and a BDE-(C−H) of 93.9 kcal/mol in fair agreement with experiment (−5.9 and 93.9 kcal/mol, respectively). However, when the value of $a(H_\alpha)$ for **3b** is substituted into eq 3, the RSE obtained (−14.8 kcal/mol) is far too large.

Radicals **29−32** show how the above criteria may be applied to the estimation of RSE and BDE(C−H). Radical **29** has $a(H_\beta Me) = 15.0$ G while **30** has $a(H_\alpha) = 15.1$ G.[23b] As the pyramidalization quotient $P^t = 0.99$, the values calculated from eqs 3−6 of RSE = −12.7 kcal/mol and BDE(C−H) = 83.1 kcal/mol for compound **29**, and RSE = −12.2 kcal/mol and BDE(C−H) = 86.7 kcal/mol for compound **30** may confidently be accepted as correct to within 2 kcal/mol. In accord with this conclusion, the two values of RSE are in close agreement, while the difference of 3.6 kcal/mol between the two values of BDE(C−H) is about what would be expected between a secondary and a tertiary compound. Conversely, the values of $a(H_\beta Me) = 16.9$ G for **31** and $a(H_\alpha) = 13.4$ G for **32**[23b] give $P^t = 1.26$ well outside the acceptable range. Clearly, **31** and **32** are significantly pyramidalized and the values calculated from eqs 3−6 for RSE (−9.6 and −15.0 kcal/mol for **31** and **32**) and BDE(C−H) (86.1 and 84.0 kcal/mol for **31** and **32**) must be erroneous.

29 R = Me	**31** R = Me
30 R = H	**32** R = H
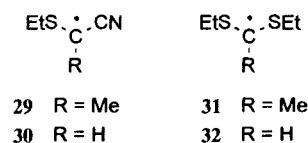
The data in Table 5 show some interesting trends. For example, protonation of α-amino radicals removes the lone pair from conjugation with the SOMO and virtually restores planarity. It should be possible to predict values of RSE and BDE(C−H) for such species. Delocalization of the lone pair by acylation has a similar effect. Thus the 1-(acetamido)ethyl radical $·CHMeNHCOCH_3$ meets the criteria for application of eqs 3−6 as does the formamido radical $·CHMeNEtCOH$. However, when the electron-attracting power of the carbonyl group is reduced by a second donor group as in the radical $·CHMeNH-CONH_2$, the nonplanarity is increased.

For oxygenated radicals the situation is less clear-cut. The radicals $·CHMeOCHO$ and $·CHMeSEt$ just meet the critera, while the acetate, carbonate, carbamate, phosphate, and sulfoxy substituted radicals are slightly outside. The α-bromo radical, $·CHMeBr$, although possibly somewhat nonplanar, just meets the criteria.

Conclusion

The above discussion of the correlation of ESR hyperfine splitting constants with indices of radical stability and reactivity indicates that eqs 3 and 5 relating $a(H_\alpha)$ to RSE and BDE(C−H) are applicable to a reasonable variety of substituted planar carbon-centered radicals

including captodative radicals. Equation 7 relating $a(\text{H}_\alpha)$ to BDE(C−H) determined by Bordwell's method is also satisfactory over a similar range of radicals. Each of these equations fails for nonplanar radicals.

Values of $a(\text{H}_\beta\text{Me})$ significantly less sensitive to derivations from planarity of the radical center provide more reliable indicators of RSE and BDE(C−H) when substituted into eqs 4, 6, and 8. Although they can be applied to radicals which deviate slightly from planarity, they give erroneous results for *significantly* pyramidalized radicals. An indication of the degree of planarity and hence of the applicability of eqs 3−8 can be obtained from pyramidalization quotients (P^t and P^{sec}) derived from the ratio $a(\text{H}_\beta\text{Me})/a(\text{H}_\alpha)$ as shown in eqs 15 and 16. Values of RSE and BDE(C−H) can be confidently predicted within a range of 2 kcal/mol when $P^{\text{sec}} < 1.25$ or $P^t < 1.05$. All of the correlations fail for cyclic delocalized radicals, e.g., cyclopentadienyl, while significant differences between the literature values of BDE(C−H) for some disubstituted species, e.g., $\cdot\text{CH(COR)}_2$, make it difficult to assess the accuracy of the correlations.

Since extensive compilations of ESR hyperfine splitting factors are now available, it should be possible to confidently estimate RSE and BDE(C−H) for a very large number of radicals to within 2 kcal/mol.

Experimental Section

ESR spectra were obtained on a Bruker ESR 420 spectrometer at an operation frequency of 9.3 GHz. All samples were recorded in quartz tubes. The samples were degassed by three cycles of freeze, pump, and thaw and filling with pure nitrogen. For photochemical reactions, the sample was irradiated with UV light inside the cavity of the spectrometer by means of a 1000 W high-pressure mercury lamp (Philips). The beam was passed through a water filter and then focused onto the sample by a system of two quartz lenses and a mirror. The temperature was controlled by a cooled or heated nitrogen flow (Bruker). Di-*tert*-butyl peroxide and halogenated solvents were filtered over basic alumina. All chemicals were purified by distillation or recrystallization. The spectra were simulated with the program NIEHS-WINSIM-EPR version 0.95.[28] The abbreviations are as follows: DTBP, di-*tert*-butyl peroxide; Mod, modulation; Pow, microwave power; T, temperature (K); CF, center field; LS, line shape (% Gaussian); LW, line width.

1-Methyl-1-(isopropoxy)ethyl (3a). Generated by UV irradiation of 200 μL of diisopropyl ether with 200 μL of DTBP: Mod, 0.32 G; T, 240; Pow, 6.4 mW. Simulation parameters: LS, 34%; LW, 0.35 G; $a(6\text{H}) = 19.37$ G, $a(1\text{H}) = 0.93$ G.

1-Amino-1-methylethyl (4a). Generated by UV irradiation of 60 μL of isopropylamine with 170 μL of DTBP: Mod, 1.0 G; T, 225; Pow, 6.4 mW. Simulation parameters: LS, 78%; LW, 0.35 G; $a(6\text{H}) = 17.90$ G, $a(\text{N}) = 3.87$ G, $a(2\text{H}) = 2.20$ G.

1-(Ethoxycarbonyl)ethyl (6b). Generated by UV irradiation of 50 μL of ethyl 2-bromopropionate with 50 μL of hexamethylditin in 150 μL of DTBP: Mod, 0.5 G; T, 293; Pow, 6.4 mW. Simulation parameters: LS, 100%; LW, 0.11 G; $a(3\text{H}) = 24.68$ G, $a(2\text{H}) = 1.31$ G, $a(1\text{H}) = 20.48$ G. During the irradiation a white precipitate accumulated. The same radical

could also be generated by UV irradiation of 150 μL of ethyl 2-bromopropionate with 150 μL of Et₃SiH and 150 μL of DTBP.

3-Methyl-2,5-pentanedion-3-yl (9a). Generated by UV irradiation of 30 μL of 3-methyl-2,4-pentanedione with 150 μL of DTBP and 2.4 mg of trimethylamine−borane in 170 μL of chlorobenzene: Mod, 1.0 G; T, 195; Pow, 10.1 mW. Simulation parameters: LS, 52%; LW, 0.43 G; $a(3\text{H}) = 21.52$ G, $a(6\text{H}) = 0.1$ G.

2,5-Pentanedion-3-yl (9b). Generated from 30 μL of 2,5-pentanedione by the method used for **9a**: Mod, 1.0 G; T, 195; Pow, 6.4 mW. Simulation parameter: $a(1\text{H}) = 18.0$ G. The intensity of the signal decreased rapidly during irradiation.

2-Acetyl-1-hydroxy-1-methylallyl (25). Generated by UV irradiation of 30 μL of 3-methyl-2,4-pentanedione with 80 μL of DTBP in 90 μL of chlorobenzene: Mod, 0.5 G; T, 195; Pow, 10.1 mW. Simulation parameters: CF, 3327.7 G; LS, 59%; LW, 0.20 G; $a(2\text{H}) = 16.25$ G, $a(1\text{H}) = 1.46$ G, $a(6\text{H}) = 3.23$ G. The spectrum also showed the presence of 21% of **9a**: CF, 3324.1 G.

1,1-Dicyanoethyl (10a). Generated by UV irradiation of a saturated solution of methylmalononitrile[29] in 200 μL of 1:1 benzene/DTBP. The two layers so formed were irradiated inside the cavity of the spectrometer without separation: Mod, 0.5 G; T, 305; SW, 90 G; Pow, 6.4 mW. Simulation parameters: LS, 0%; LW, 0.11 G; $a(3\text{H}) = 20.64$ G, $a(2\text{N}) = 2.64$ G.

Dicyanomethyl (10b). Generated by UV irradiation of a saturated solution of malononitrile in 200 μL of 1:1 benzene/DTBP: Mod, 0.5 G; T, 280; Pow, 8.1 mW. Simulation parameters: LS, 55%; LW, 0.15 G; $a(3\text{H}) = 19.22$ G, $a(2\text{N}) = 2.78$ G. The solution became brown and the signal intensity decreased very rapidly.

1,4-Dibutyl-2,4-diketo-3,6-dimethylpiperazin-3-yl (12a). Generated by UV irradiation of 50 mg of 1,4-dibutyl-3,6-dimethylpiperazine-2,5-dione with 150 mg of DTBP: Mod, 1.0 G; T, 225; Pow, 9.96 mW. Simulation parameters: LS, 100%; LW, 1.2 G; $a(3\text{H}) = 17.8$ G. After 10 min the solution became red and a second, persistent radical was formed.

1,4-Dibutyl-2,4-diketopiperazin-3-yl (12b). Generated by UV irradiation of 32 mg of 1,4-dibutylpiperazine-2,5-dione with 220 mg of DTBP in 30 mg of CHCl₃: Mod, 0.4 G; T, 253; Pow, 4 mW. Simulation parameters: LS, 10%; LW, 0.4 G; $a(\text{H}) = 17.1$ G, $a(2\text{H}) = 5.7$ G, $a(\text{N}) = 1.2$ G, $a(2\text{H}) = 1.0$ G, $a(\text{N}) = 0.2$ G.

9-Methylfluoren-9-yl (18a). Generated by heating of 70 mg of 9,9′-bis(9-methylfluorene) in 300 μL of biphenyl ether: Mod, 0.4 G; T, 475; Pow, 5.1 mW. Simulation parameters: LS, 100%; LW, 0.21 G; $a(3\text{H}) = 14.56$ G, $a(2\text{H}) = 0.83$ G, $a(2\text{H}) = 3.73$ G, $a(2\text{H}) = 0.81$ G, $a(2\text{H}) = 3.62$ G.

N-(1-Ethoxycarbonylethyl)-N-(methyl)aminomethyl (27). Generated by UV irradiation of 50 μL of the ethyl ester of DL-*N,N*-dimethylalanine in 150 μL of DTBP: Pow, 8.1 mW; T, 222. Simulation parameters: LS, 35%; LW, 0.44 G; $a(2\text{H}) = 14.30$ G, $a(3\text{H}) = 4.04$ G, $a(\text{N}) = 7.00$ G, $a(1\text{H}) = 1.34$ G.

(28) NIEHS WINSIM EPR Version 0.95, Dave Duling, Laboratory of Molecular Biophysics NHEIOS, NIH, DHHS.

(29) Diez-Barra, E.; de las Hoz, A.; Moreno, A.; Sánchez-Verdú, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2589−2592.