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Bond Strengths: The Importance of Hyperconjugation

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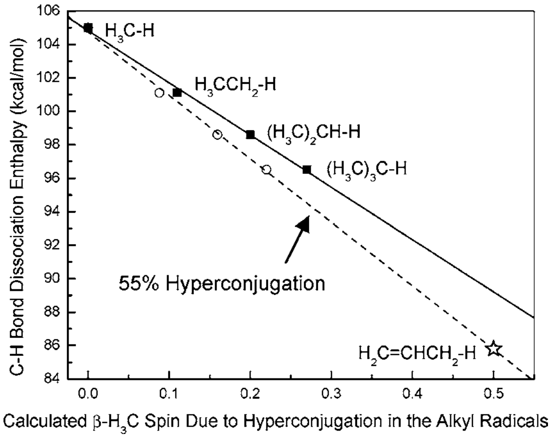
ABSTRACT



Gronert (*J. Org. Chem.* 2006, *71*, 1209) has challenged the importance of hyperconjugation in determining C–H bond dissociation enthalpies (BDEs) in alkanes. Electron paramaganetic resonance spectra of $H_3CCH_2^{\bullet}$, $(H_3C)_2CH^{\bullet}$, and $(H_3C)_3C^{\bullet}$ show significant positive spin on their *β*-H_3C groups' hydrogens. A 55%/45% partitioning of these spins between hyperconjugation and spin polarization mechanisms linearly correlates with the C–H BDEs in methane, ethane, propane, isobutane and propene. Hyperconjugation is an important factor determining alkane C–H BDEs.

The decrease in C−H bond dissociation enthalpies (BDEs) along the series H_3C−H > H_3CCH_2−H > $(H_3C)_2CH$−H > $(H_3C)_3C$−H has conventionally been attributed to electron donation from the *β*-H_3C groups to the radical center via hyperconjugation. Furthermore, 1,3-methyl/methyl interactions have conventionally been viewed as attractive and hence as stabilizing methyl-branched hydrocarbons compared with the unbranched analogue (e.g., ΔH_f neopentane = −40 kcal/mol and ΔH_f *n*-pentane = −35 kcal/mol). These conventional views were recently challenged by Gronert,[1] who put forward a group additivity model to explain the decrease in C−H BDEs from methane to isobutane that is based on the relief of 1,3 repulsive (i.e., destabilizing) H/H, H/H_3C, and H_3C/H_3C interactions in forming the radicals from the alkanes. Gronert challenged the hyperconjugative stabilization concept and stated that the fact that his model "could adequately fit the heats of formation of alkanes, alkenes and alkyl radicals indicates that hyperconjugation need not be invoked to explain any energetic trends involving these species."

Such iconoclastic views were quickly challenged by Wodrich and Schleyer.[2] These workers developed a new isodesmic additivity scheme that reproduced experimental heats of formation of a broad range of unstrained alkanes, alkenes, alkynes, and alkyl radicals. Moreover, their scheme uses only four adjustable parameters, whereas Gronert used seven. Wodrich and Schleyer noted that the "stabilization of radicals, double and triple CC bonds by alkyl substituents (hyperconjugation), as well as the stabilization by 1,3-alkyl

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(1) Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209−1219. See also, Gronert, S. *J. Org. Chem.* **2006**, *71*, 7045−7048.

(2) Wodrich, M. D.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 2135−2138.

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Table 1. Some C−H BDEs (kcal/mol), EPR hfcc (G), and Calculated Spin Densities

		hfcc at radical center		hfcc at β-H_3C group(s)		spin on all H in all β-H_3C group(s)		
radical, R•	R−H BDE	^{13}C	H	^{13}C	H	total	spin-polarization	hyperconjugation
$H_3C^\bullet$	105.0	+38.3	−23.0			0.00	0.00	0.00
$H_3CCH_2^\bullet$	101.1	+39.1	−22.4	−13.6	+26.9	+0.16	+0.05	+0.11
$(H_3C)_2CH^\bullet$	98.6	+41.3	−22.1	−13.2	+24.7	+0.29	+0.09	+0.20
$(H_3C)_3C^\bullet$	96.5	+45.2		−12.4	+22.7	+0.40	+0.13	+0.27

group interactions at the same carbon (branching), support conventional interpretations."

Hyperconjugation in radicals is a fact attested to by electron paramagnetic resonance (EPR) spectroscopy. For example, the ethyl radical has significant unpaired spin density on the β-H_3C group's three equivalent hydrogen atoms. Insofar as this spin arises from hyperconjugative delocalization of the unpaired electron, it must stabilize $H_3CCH_2^\bullet$ relative to $H_3C^\bullet$. By convention, the spin in the 2p orbital at the formal radical center, $CH_2^\bullet$, is labeled "positive" (also α, or "up"). In ethyl, the β-H_3C group's carbon atom lies in the (average) nodal plane of the unpaired electron's 2p orbital. This carbon acquires spin of the opposite sign to the radical center, i.e., negative spin, by a process termed spin polarization.[3] The H_3C group's hydrogens in $H_3CCH_2^\bullet$ acquire positive spin both by hyperconjugation from $C^\bullet$ and by spin polarization from the H_3C group's carbon atom. The three hydrogen atoms in the H_3C group produce a characteristic EPR pattern of four lines (intensities 1:3:3:1) with a splitting between adjacent lines that is called the hyperfine coupling constant (hfcc), a quantity that is generally given in Gauss (G). Like hydrogen, carbon-13 has a nuclear spin of 1/2 and gives rise to EPR hfcc. The H and ^{13}C hfcc for four simple alkyl radicals are given in Table 1.[4] In this Letter we will use EPR hfcc's to demonstrate that hyperconjugation would appear to account for the decrease in C−H BDEs for the methane, ethane, propane, and isobutane series in a more or less quantitative manner. Our conclusions support the views of Wodrich and Schleyer, not those of Gronert.

There have been numerous attempts in the past to correlate radical stabilities with a single EPR H-hfcc using the values found in $RCH_2^\bullet$, $RR'CH^\bullet$, and particularly, $H_3CC^\bullet RR'$.[5] However, our analysis differs from all earlier analyses (so far as we are aware) because we believe that the stabilities of $(H_3C)_nC^\bullet(H)_{3-n}$ ($n = 0-3$) radicals must depend on the sum of the H-hfcc of all the hydrogen atoms in all the β-H_3C groups rather than the hfcc of one single β-H_3C hydrogen atom. Because positive spin leaves the formal radical center by hyperconjugation, the C−H BDE of the parent alkane will decrease and would decrease to zero if 100% of the spin left the formal radical center by hyperconjugation, or in any other manner, for elsewhere in the radical.

The hydrogen atom, $H^\bullet$, has 100% spin in its 1s orbital, and this gives rise to a hfcc of +507 G. The ethyl radical has β-H_3C H-hfcc's of +26.9 G. Since there are three hydrogen atoms on this methyl group, the total positive spin on ethyl's β-H_3C group is $(3 \times 26.9)/507 = 0.16$. Similarly, the total positive spin on the six hydrogen atoms in the two β-H_3C groups of isopropyl is $(6 \times 24.7)/507 = 0.29$, and on the nine hydrogen atoms in the three β-H_3C groups of *tert*-butyl it is $(9 \times 22.7)/507 = 0.40$ (see Table 1). As a simple but admittedly very approximate estimate of the spin polarization contribution to these β-H_3C H-hfcc's, we will employ the methyl radical's ^{13}C-hfcc[6] and H-hfcc to model the H_3C groups in the other alkyl radicals. For the ethyl radical, this procedure yields a positive spin polarization contribution to the β-H_3C H-hfcc's of $(-13.6/38.3) \times -23.0 = +8.2$ G, i.e., $(3 \times 8.2)/507 = +0.05$ spin (see Table 1). The remaining contribution, $26.9 - 8.2 = +18.7$ G, i.e., $(3 \times 18.7)/507 = +0.11$ spin (see Table 1), presumably comes from hyperconjugation. Similar calculations of the isopropyl and *tert*-butyl radicals' positive spin densities on all of the hydrogen atoms of all of their β-H_3C groups that come from hyperconjugation yield values of +0.20 and +0.27, respectively. These hyperconjugative spin densities, including 0.00 for methyl, have been plotted against the C−H BDEs for methane, ethane, propane, and isobutane in Figure 1. That a straight line is obtained is not really surprising. What will surprise those who doubt that hyperconjugation is important in determining C−H BDEs along this alkane series, is that when this line is extrapolated, it suggests that the parent molecule of a hydrocarbon radical that had 50% of its positive spin delocalized would have a C−H BDE = 89.5 kcal/mol. Propene (see the asterisk in Figure 1) has a C−H BDE = 85.8 kcal/mol and the radical formed from propene is allyl,


H_2CCHCH_2

which has 50% of its positive spin on each of its terminal carbon atoms.

Using the methyl radical as a model, the spin polarization contribution to the β-H_3C hydrogen atom hfcc's in the other

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(3) This is also the process that gives the methyl radical's three hydrogen atoms negative spin, i.e., spin of the opposite sign as the spin at its $C^\bullet$.

(4) All EPR data are from: Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 19.

(5) See, for example: Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935−1943 and references therein.

(6) The theoretical ^{13}C hfcc for a system in which 100% of an unpaired electron occupies this carbon's 2s orbital is 1110 G.[4] Thus, the ^{13}C hfcc at the alkyl radical centers (Table 1) imply that only ca. 4% of the unpaired electron is in the 2s orbital of $C^\bullet$. Small changes in $^{13}C^\bullet$ hfcc between alkyl radicals are difficult to interpret, and this difficulty is compounded by the fact that the potential energy surface for the in-and-out "umbrella" motion of, e.g., methyl, has a single minimum, whereas the "umbrella" potential for *tert*-butyl has a double minimum.[7]

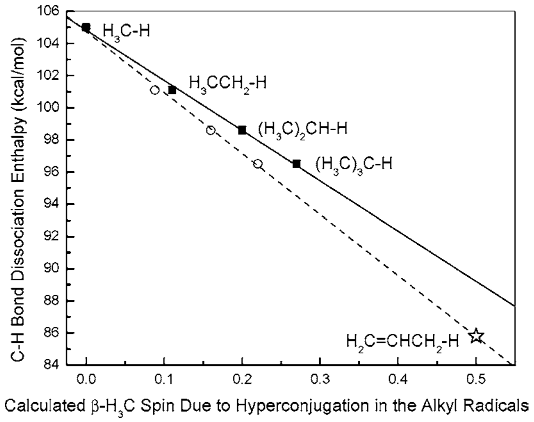

Figure 1. Plot of C−H bond dissociation enthalpies versus calculated fraction of unpaired spin due to hyperconjugation on all H atoms in β-H_3C groups. Filled squares (solid line) are based on the model described in the text (32% spin polarization/68% hyperconjugation). Open circles (dashed line) are based on a model using 45% spin polarization/55% hyperconjugation. The asterisk represents the propene/allyl radical point.

three alkyl radicals were calculated to contribute ∼32% to their measured positive spin density, leaving a 68% share to hyperconjugation. A model that used 45% spin polarization and 55% hyperconjugation (open circles in Figure 1) yields the dotted line, i.e., a line that correlates the four alkanes *and* propene.[8] Of course, delocalization in the allyl radical is generally called resonance. However, the different names we bestow on conceptually different mechanisms of delocalization of an unpaired electron should not mislead us into thinking that one mechanism has different energetic consequences from another mechanism. Delocalization is stabilizing and similar extents of delocalization by any mechanism should produce the same degree of radical stabilization.[9]

There is a second argument that would appear to favor the hyperconjugative stabilization of $H_3CX^\bullet$ radicals. The F_3C group should produce as much, or more, 1,3 steric repulsion as the H_3C group. Therefore, the C−H BDE in F_3CCH_3 would be expected, by Gronert's arguments, to be similar to that in ethane. However, it has a value of 106.7[11] to 106.5[12] kcal/mol, which is similar to the C−H BDE in methane (105.0 kcal/mol). This result might well be due to the absence of significant hyperconjugative stabilization by the F_3C group in the $F_3CCH_2^\bullet$ radical.[10] Similarly, the O−H BDE in F_3-COH (118.2 kcal/mol)[12,14] and in water (118.8 kcal/mol)[15] are almost the same and significantly greater than the O−H BDE in H_3COH (104.2 kcal/mol).[16] In addition, the $HOCH_2$-CH_2−H BDE of 103.1 kcal/mol[12] is larger than in ethane. This could be attributed to the loss of one β-H atom. These facts could only be reconciled with Gronert's suggestions by "special pleading", i.e., by special but probably not quantifiable "polar effects", an argument we cannot and do not discount. However, the lack of hyperconjugative stabilization in $F_3CX^\bullet$ radicals does provides a simple explanation for F_3CX−H BDEs being similar to HX−H BDEs rather than to H_3CX−H BDEs.

In conclusion, EPR spectroscopy and the difference in the X−H BDEs in H_3CX−H and F_3CX−H provide support for the traditional role of hyperconjugation as an important and possibly as the major factor determining C−H BDEs in alkanes.[17]

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[7] Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978**, *100*, 6750−6752.

[8] If 100% spin is attributed to hyperconjugation, a straight-line fit of the BDE data would predict the propene C-H BDE to be 94.2 kcal/mol, too high by 8.4 kcal/mol, and if 39% of the spin is attributed to hyperconjugation, the predicted BDE is too low by 8.4 kcal/mol.

[9] In the ethyl radical, the conventional valence bond picture of hyperconjugation ascribes significant double bond character to the H_3C−$CH_2^\bullet$ bond. However, the amount of double bond character in this and in the C-$C^\bullet$ bond of other alkyl radicals must be very small because the barriers to rotation about these bonds are very much less (∼1 kcal/mol) than the barrier to rotation in the allyl radical (15.7 kcal/mol).[10] Hyperconjugative interactions in the ethyl radical are maximzed when the nominally planar $CH_2^\bullet$ moiety is perpendicular to the plane defined by a H, the C atom of the β-H_3C group, and the C atom of the $CH_2^\bullet$ group. However, upon rotation of the $CH_2^\bullet$ group, overlap can be achieved between the radical center's singly occupied p-orbital and linear combinations of the β-H_3C group's σ- and σ*-orbitals, resulting in a very small barrier to rotation. Molecular orbital calculations also provide evidence for the importance of hyperconjugation because deleting the principal natural bond orbital hyperconjugative interactions in the ethyl radical causes the HF/6-31.G(d) C−C bond length to increase by 0.05 Å.

[10] Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483−4489. See also: Walton, J. C. *Rev. Chem. Intermed.* **1984**, *5*, 249−291.

[11] Stein, S. E. *Thermochemical Data Base 25*, NIST Structures and Properties Database and Estimation Program; U.S. Department of Commerce: Washington, DC,1992.

[12] Calculated using the B3P86/6-311G(2d,2p)//B3P86/6-31G(d) method described in ref 13. This approach has been shown to predict X−H bond dissociation enthalpies in very good agreement with experimental values, as is also seen in this example.

[13] Johnson, E. R.; Clarkin, O. J.; DiLabio, G. A. *J. Phys. Chem. A* **2003**, *107*, 9953−9963.

[14] Experimental values as high as 124.7 and as low as 109.0 kcal/mol have been published; see: Ingold, K. U., Wright, J. S. *J. Chem. Educ.* **2000**, *77*, 1062−1064.

[15] Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, A.; Ng, C.-Y.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727−2747.

[16] Calculated from heats of formation from the NIST database: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Mallard, W. G., Linstrom, P. J., Eds.; June 2005; National Institute of Standards and Technology: Gaithersburg MD, 20899 (http://webbook.nist-.gov).

[17] Using the isodesmic scheme developed in reference 2 reveals that C-H BDEs in ethane, propane, and butane decrease solely as a result of hyperconjugation. A similar analysis of the C-C BDEs in of propane, isobutane, and neopentane, relative to ethane, reveals that hyperconjugative stabilizations are present in the radicals but these are effectively cancelled by attractive branching interactions present in both the parent and radical species. For additional information, see Supporting Information of ref 2.