

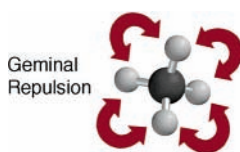
## An Alternative Interpretation of the C–H Bond Strengths of Alkanes

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A new model based on 1,3 repulsive steric interactions (geminal repulsion) is proposed for explaining the variation in the C–H bond strengths of the alkanes. The model builds from the assumption that 1,3 repulsive interactions are the major factor in determining the stability of a C–C or C–H bond in an alkane. From this simple premise, the model successfully reproduces the effect of branching on the stability of alkanes, alkyl radicals, and alkenes. The results suggest that geminal repulsion can provide a simple, unified explanation for these fundamental stability trends. Although previous explanations have been widely accepted, it is shown that the theoretical support for them is relatively shallow and that the current hyperconjugative stabilization model is inconsistent with several experimental and computational results concerning alkyl radicals. In contrast, an explanation based on geminal repulsion provides a general conceptual framework for rationalizing each of these stability trends and is based on a physical effect that is known to play a role in the stability of alkanes and related species.

### Introduction

The variation of C–H bond strengths at 1°, 2°, and 3° centers in simple alkanes is one of the best-known substituent effects in organic chemistry. Moreover the differences are often invoked to explain reactivity patterns and regioselectivity in reaction processes. The bond strength order (1° > 2° > 3°) has almost universally been explained on the basis of the stability of the resulting radicals under the assumption that the attachment of alkyl groups to a radical center provides stabilization. Although this paradigm is well accepted and has allowed chemists to rationalize a variety of chemical behavior, the evidence supporting this interpretation is surprisingly shallow and open to sharp criticism.

In this paper, an alternative explanation is presented which is consistent with the available data. The new bonding model explains the difference in bond strengths on the basis of differential steric strain relief as a result of bond cleavage. Specifically, the model focuses on repulsive 1,3 interactions (geminal repulsion) and takes into account the steric strain that is released when a bond is broken. Dunitz and Schomaker<sup>1</sup> identified repulsive 1,3 interactions over 50 years ago and later

Bartell<sup>2–5</sup> used them to explain variations in C–C bond lengths as well as vibrational spectra. In the 1970s and 1980s, Bauld<sup>6</sup> and Wiberg<sup>7</sup> used them to explain trends in small ring stability. Bickelhaupt, Ziegler, and Schleyer<sup>8</sup> have used them to explain the preference for planarity in alkyl radicals. They are a part of molecular mechanics force fields either through explicit terms<sup>9,10</sup> (i.e., Urey–Bradley field<sup>11,12</sup>) or indirectly through a stretch–bend term.<sup>13</sup> Here, we take a logical step forward and suggest that the 1,3 repulsive interactions are not uniform and vary in magnitude depending on the nature of the groups involved. This hypothesis directly leads to the conclusion that 1,3 repulsive

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- (4) Bartell, L. S. *Tetrahedron* **1962**, *17*, 177.
- (5) Bartell, L. S.; Kuchitsu, K. *J. Chem. Phys.* **1962**, *37*, 691.
- (6) Bauld, N. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8140.
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- (8) Bickelhaupt, F. M.; Ziegler, T.; Schleyer, P. v. R. *Organometallics* **1996**, *15*, 1477.
- (9) Fitzwater, S.; Bartell, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 5107.
- (10) Derreumaux, P.; Dauchez, M.; Vergoten, G. *J. Mol. Struct.* **1993**, *295*, 203.
- (11) Urey, H. C.; Bradley, C. A., Jr. *Phys. Rev.* **1931**, *38*, 1969.
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(1) Dunitz, J. D.; Schomaker, V. J. *Chem. Phys.* **1952**, *20*, 1703.

TABLE 1. Bond Dissociation Energies of Alkyl Radical Precursors

R	bond dissociation energy (kcal/mol) <sup>a</sup>			
	R–H	R–Cl	R–OH	R–CH <sub>3</sub>
CH <sub>3</sub>	105.0	84.0	92.3	89.8
CH <sub>3</sub> CH <sub>2</sub>	101.1	84.8	94.5	88.8
(CH <sub>3</sub> ) <sub>2</sub> CH	98.6	84.5	96.0	88.3
(CH <sub>3</sub> ) <sub>3</sub> C	96.5	84.3	96.3	87.2

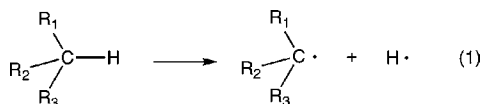
<sup>a</sup> References 15 and 16.

interactions will cause variations in bond strengths depending on the substitution pattern. After completing this work, we later discovered that in 1932, Eyring<sup>14</sup> put forward a similar suggestion in a short passage of a paper focused on steric hindrance. In the present study, it will be shown that geminal repulsion can be used to explain the variations in C–H bond strengths as well as the effect of branching on the relative stabilities of alkanes and alkenes. The discussion begins with a description of the conventional interpretation, its inherent assumptions, and several inconsistencies that it has with experimental and computational data. An explanation of the new bonding model, an examination of its predictive capabilities, and finally an analysis of its conceptual value follow.

## Results and Discussion

**I. The Conventional Model.** The conventional interpretation of the variation in C–H bond strengths is that alkyl substituents stabilize radical centers and consequently weaken the corresponding C–H bond in the precursor. The stabilization derived from the alkyl substituent is believed to result from hyperconjugation of the partially filled orbital with C–H or C–C bonds on the adjacent carbon(s). This interpretation has been widely accepted, but two aspects warrant careful consideration.

**1. Two-State Problem.** The variation in C–H bond strengths in going from 1° to 3° centers generally has been attributed exclusively to the stability of the resulting radicals. However, bond scission is fundamentally a two-state problem (eq 1), and



consequently, one must consider the effect of substitution on both the radical and the alkane. A hidden assumption in the present interpretation is that alkyl substitution has no effect on the relative stability of the alkanes and therefore this component can be ignored. Although this assumption may seem reasonable on the surface, it does suffer from some critical liabilities. First, it is well-known that different isomers of alkanes (e.g., *n*-butane vs isobutane) have different heats of formation, so substitution patterns do matter in the stability of an alkane. Second, there are notable examples of bond scissions resulting in alkyl radicals that do not follow this trend in bond dissociation energies (BDE).<sup>15,16</sup> In Table 1, bond dissociation energies for forming alkyl radicals from alkanes (R–H or C–CH<sub>3</sub> scission), alcohols (R–O scission), and alkyl chlorides (R–Cl scission) are listed.

(14) Eyring, H. *J. Am. Chem. Soc.* **1932**, *54*, 3191.

(15) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69 (<http://webbook.nist.gov>); Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2005.

(16) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

Although the same alkyl radicals are formed in these processes, the reactivity patterns are strikingly different. In fact, data from the alcohols might lead one to believe that methyl radicals are the *most* stable. Nicholas and Arnold<sup>17</sup> pointed out this inconsistency over 20 years ago, and more recently, Zavitsas<sup>18,19</sup> as well as Pross, Radom, and co-workers<sup>20</sup> have probed this issue in great detail. Overall, these examples point out that alkyl substitution can have a significant effect on reactant stabilities and that using alkane bond dissociation energies as a measure of radical stabilities relies heavily on the questionable assumption that the relative stabilities of the precursors are totally unaffected by structural variations.

**2. Hyperconjugation.** The variation in the stabilities of the alkyl radicals has been rationalized with an argument that parallels the accepted explanation for the variation in the stabilities of carbocations. In short, the alkyl substituents can act as electron donors (via hyperconjugation) and stabilize the electron deficient center. In early work, Mulliken<sup>21</sup> showed that a simple molecular orbital model that included terms for hyperconjugation could be parametrized to fit the then observed variations in radical stability.<sup>22</sup> In ESR spectra, hyperfine splitting to the  $\beta$ -hydrogens of alkyl radicals also has been used as evidence of hyperconjugation.<sup>23</sup> It is important to note that both of these results only indicate that hyperconjugation is a possible explanation, but they do not provide any evidence that it provides the observed bond weakening effects in alkanes. From a perturbation theory viewpoint, the hyperconjugative interaction involves mixing the radical center orbital with the  $\sigma$  and  $\sigma^*$  orbitals of the adjacent bonds. Overall, this is a potentially stabilizing, 3-electron interaction (i.e., two electrons in a bonding and one in an antibonding MO), but the magnitude of the stabilization might be quite limited given the relative energies of the mixing orbitals. Below, several challenges to the hyperconjugative model are presented.

**A. Geometries.** If there is a strong hyperconjugative interaction between the singly occupied orbital on the radical center and a bond on an adjacent carbon, the geometry should reflect this interaction. Therefore in a species such as the ethyl radical, one expects that the C–H bond should tilt toward the radical center (i.e., reduced H–C–C bond angle) because if there is a significant shift in the electron density of the C–H bond, the hydrogen should follow. The opposite is true for alkyl radicals and calculated H–C–C angles are greater than 109.5° (>111° in the ethyl radical).<sup>24</sup> This geometry suggests that this is a repulsive, not a stabilizing interaction with the adjacent bond.<sup>25</sup> As a point of comparison, C–H bonds adjacent to carbocations either lean toward it (H–C–C < 109.5°) or collapse onto it to give a bridged structure in the gas phase.<sup>26,27</sup> As for other geometric measures, hyperconjugation also should result in a lengthening of the C–H bond involved in the interaction. In the ethyl radical, this lengthening is very limited (0.007 Å

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(19) Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158.

(20) Coote, M. L.; Pross, A.; Radom, L. *Org. Lett.* **2003**, *5*, 4689.

(21) Muller, N.; Mulliken, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 3489.

(22) At the time, the variation in C–H bond strengths from 1° to 3° was believed to be much larger. Presumably, Mulliken's model could have been successfully parametrized to fit the modern bond strength values.

(23) Smaller, B.; Matheson, M. S. *J. Chem. Phys.* **1958**, *28*, 1169.

(24) Richter, U. NIST Computational Chemistry Comparison and Benchmark Database. In *NIST Chemistry WebBook*; NIST Standard Reference Database No. 101 (<http://srdata.nist.gov/cccbdb>); Johnson, R. D., Ed.; National Institute of Standards and Technology: Gaithersburg, MD, 2005.

**TABLE 2. Relative Bond Dissociation Energies (kcal/mol)<sup>a</sup>**

species	pyramidal radical <sup>b</sup>	unconstrained radical <sup>c</sup>
methane	0.0	0.0
isobutane (3°)	–7.1	–7.2
propene	–10.3	–16.0

<sup>a</sup> CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level. No thermal or zero-point energy corrections. <sup>b</sup> Radical center's angles constrained to 109.5°. <sup>c</sup> Full optimization. The *tert*-butyl radical prefers a slightly pyramidal structure.

relative to ethane). The C–C bond to the radical center is shorter than normal in the ethyl radical (1.492 Å), but this effect is also consistent with the rehybridization of the radical center as well as a reduction in 1,3 repulsive interactions (see below). Overall, geometric evidence argues against significant hyperconjugative stabilization of radical centers.

**B. Radical Pyramidalization Energies.** Hyperconjugative stabilization should be maximized when the radical center is planar because this orientation allows for the greatest  $\pi$ -orbital overlap. As a result, the energy needed to force a radical into a pyramidal geometry should provide a relative measure of the impact of hyperconjugative stabilization. To gain a measure of this effect, one can compare the energies of the radicals in their optimum geometries and in geometries where the carbon is forced to be pyramidal (i.e., internal angles of 109.5°). At the CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) level (Supporting Information, Table S1), the following pyramidalization energies are obtained: methyl (6.7 kcal/mol), ethyl (6.7 kcal/mol), isopropyl (6.9 kcal/mol), and *tert*-butyl (6.8 kcal/mol).<sup>28</sup> There is little difference across the series despite the prediction that the more highly substituted radicals should suffer the greatest loss of hyperconjugation during pyramidalization. In other words, methyl and *tert*-butyl radicals pay the same cost for pyramidalization although one cannot and one can participate in hyperconjugation. The small differences between these pyramidalization energies require that the impact of hyperconjugative stabilization must be already fully realized in a pyramidal radical, a conclusion that is wholly at odds with expectations based on other instances of hyperconjugation. For example, pyramidalization of the allyl radical (one terminal carbon) costs over 12 kcal/mol. To put this in better perspective, Table 2 lists relative energies for forming pyramidal and planar radicals from methane, isobutane (3° center), and propene. In the case of propene, about 6 kcal/mol of the net 16 kcal/mol of bond weakening (35%) occurs as a result of planarization of the allyl radical. For isobutane, only 0.1 kcal/mol of the net 7.2 kcal/mol of bond weakening (1.5%) occurs as a result of removing the pyramidal constraint on the *tert*-butyl radical. It is logical to assume that hyperconjugation in the *tert*-butyl radical should have at least crudely the same orbital interaction

(25) One might argue that the major hyperconjugative interaction is with the C–H  $\sigma^*$  orbital and that weakening of the bond could increase the H–C–C angle. This would be energetically unfavorable (trading a strong C–H bond for a weaker partial  $\pi$ -bond) and is not supported by computational evidence. If an adjacent C–H bond in the ethyl radical is weakened by stretching it to 1.35 Å (i.e., this type of hyperconjugation is facilitated), the H–C–C angle contracts in response (110.5° vs 111.5° at the MP2/6-31+G\*\* level).

(26) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(27) Trinquier, G. *J. Am. Chem. Soc.* **1992**, *114*, 6807.

(28) The *tert*-butyl radical prefers a very slightly pyramidalized geometry with internal C–C–C angles of about 118°: Griller, D.; Ingold, K. U.; Krusic, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 6750.

dependencies as that in the allyl radical. That assumption indicates that 0.1 kcal/mol represents roughly  $\frac{1}{3}$  of the hyperconjugative stabilization in the *tert*-butyl radical and therefore hyperconjugation can only account for less than 0.5 kcal/mol of net bond weakening in isobutane. *Even if one assumes that hyperconjugation could reach 90% of its potential in a pyramidal radical, this analysis suggests that it represents no more than 1 kcal/mol of the 7 kcal/mol of bond weakening found in the formation of a 3° radical.* The remainder of the bond weakening must come from some other effect. Similar arguments could be developed with the ethyl and isopropyl radicals.

**C. Silyl Radicals.** The  $\pi$ -bonds between carbon and silicon are reasonably strong (about 70% of a C–C  $\pi$ -bond)<sup>29</sup> so one expects that if hyperconjugative stabilization is important in alkyl radicals it should have a similar, but somewhat reduced impact on substituted silyl radicals. Because good experimental numbers are not available for a wide variety of Si–H bond strengths, we have turned to G3 theory (Supporting Information, Table S2). At this level, (CH<sub>3</sub>)<sub>3</sub>SiH and SiH<sub>4</sub> have silicon–hydrogen bond strengths of 95.2 and 92.3<sup>30</sup> kcal/mol (G3 enthalpies), respectively. In contrast to alkanes, the more highly substituted system has the stronger bond. Clearly, hyperconjugation is not an important factor in stabilizing silyl radicals despite the fact that it is viable and potentially significant based on the strengths of C–Si  $\pi$ -bonds.

It is possible to challenge individually these criticisms and offer rationalizations, but taken together, they deeply weaken the argument that the variation in C–H bond strengths is driven by differences in hyperconjugation. Although hyperconjugation is orbitally allowed and its impact should increase with substitution on the radical center, predictions based on this explanation fail on several important tests with respect to radical geometries and energetics. *Each of these tests suggests that hyperconjugation provides negligible stabilization to alkyl radicals.* The most damaging of the criticisms comes from the pyramidalization energies because they provide direct energetic evidence that hyperconjugation can only play a very minor role in the bond weakening found at 3° centers. This is not meant to be a criticism of hyperconjugation in general, just of its role in weakening C–H bonds in alkanes. Given these failings, there is a compelling need to investigate alternative interpretations based on other premises.

**II. A New Model.** To present the new model, its foundation first must be described in detail. The model hinges on strain terms that are present in the alkane, but absent in the alkyl radical. The following sections will identify these strain terms and justify their importance.

**1. 1,3 Repulsive Interactions (Geminal Repulsion).** While studying a series of ring closures to thiirane and cyclopropane derivatives,<sup>31,32</sup> it became apparent to us that the low cyclization barriers in these systems were a direct result of converting a repulsive interaction in the substrate (steric strain) into a bonding interaction in the transition state/product. This strain was identified as a 1,3 repulsive interaction between the nucleophile and the carbon bearing the leaving group. As the reaction

(29) Avakyan, V. G.; Guseynikov, S. L.; Guseyn'nikov, L. E. *J. Organomet. Chem.* **2003**, *686*, 257.

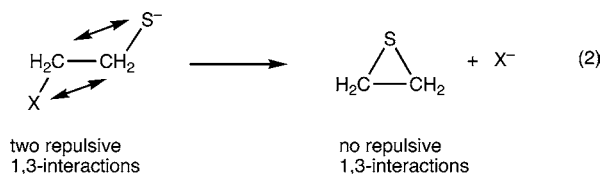
(30) The experimental value for SiH<sub>4</sub> is 91.8 kcal/mol: Jasinski, J. M.; Becerra, R.; Walsh, R. *Chem. Rev.* **1995**, *95*, 1203.

(31) Gronert, S.; Azizian, K.; Friedman, M. *J. Am. Chem. Soc.* **1998**, *120*, 3220.

(32) Gronert, S.; Lee, J. M. *J. Org. Chem.* **1995**, *60*, 6731.



progresses, this repulsive 1,3 interaction is converted into a bond and the steric strain is released. An example leading to thiirane is shown in eq 2. The substrate actually loses two 1,3 interactions



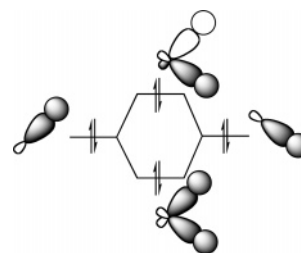
in the process, but only one is relevant in terms of reducing the reaction barrier relative to an acyclic system (here, only heavy atom interactions are considered).<sup>33</sup> Much earlier, Wiberg<sup>7</sup> and Bauld<sup>6</sup> had identified repulsive 1,3 interactions as important factors in understanding the strain found in small rings. For example, Wiberg<sup>7</sup> noted that the absence of repulsive 1,3 interactions in cyclopropane partly explains why its total strain energy is less than one would expect based on its anticipated angular strain. The importance of repulsive 1,3 interactions has been appreciated in small ring systems because the total number of 1,3 interactions changes during ring formation/opening. However, this is not the case in most reactions involving acyclic systems. As a result, it has been possible to ignore the role that 1,3 interactions play in the stability of alkanes and other substrates when analyzing reaction energies. However, it should be noted that in a series of papers, Bartell<sup>2-4</sup> argued that 1,3 repulsive interactions (nonbonded interactions in his words) are important in alkane structure and play a key role in determining C–C bond lengths. Of course, there is a correlation between bond length and strength for a given type of bond. In the remainder of the text, the strain resulting from these interactions will also be referred to as *geminal repulsion*.

The existence of significant geminal repulsion should not be surprising because the distances between the groups are rather short and there are no bonding interactions. For example, the methyl–methyl distance in propane is only  $\sim 2.5$  Å, whereas the combined van der Waals radii of two methyls is 4 Å. The problem is not limited to carbon–carbon interactions. For example, the H–H distance in methane is  $\sim 1.8$  Å, but the combined van der Waals radii amounts to 2.4 Å. It is hard to imagine that these interactions do not result in some degree of steric repulsion. The repulsion also is indicated by a simple MO picture of the 1,3 interaction. If one considers localized orbitals for the C–H bonds in methane, bonding between the two C–H orbitals is a filled–filled interaction with both the bonding and antibonding combinations being doubly occupied (Scheme 1).

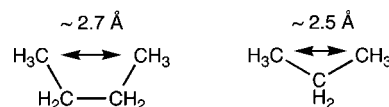
Finally, 1,4 repulsions are a well-accepted fact and are routinely used to discuss conformational equilibria and barriers to rotation in alkanes. However, the distances involved are significantly greater than those for the 1,3 repulsive interactions described above. For example, in butane, the methyl–methyl distance in the eclipsed, synperiplanar form is  $\sim 2.7$  Å or about 0.2 Å longer than the methyl–methyl distance in propane (Scheme 2). The difference in stability of *cis*- and *trans*-2-butene also highlights the importance of steric interactions at these distances. In short, although chemists have been able to ignore geminal repulsion in most cases, there is little doubt that they exist and could have significant energetic consequences.

(33) In an acyclic system, an extra 1,3 interaction is developed as the nucleophile approaches the reaction center. In the cyclization system, the price of this added 1,3 interaction has already been paid in the form of steric strain (1,3 repulsion) in the substrate.

## SCHEME 1



## SCHEME 2



### 2. A Simple Additivity Scheme Based on 1,3 Interactions.

If 1,3 repulsive interactions are important strain terms, it is logical that they would have an effect on the stabilities of alkanes and therefore play a role in determining their heats of formation. We are not the first to make this assumption and additivity schemes have been built that include these terms.<sup>34-37</sup> Here, however, we wish to explore whether these terms alone can be used to account for the effect of branching on the bond dissociation energies and stabilities of alkanes. To test this conceptual model, an exceptionally simple additivity scheme was developed for the prediction of heats of formation. The key assumptions are listed below:

1. The heats of formation of alkanes are determined solely by 1,2 bonding interactions and 1,3 repulsive interactions.
2. All C–H bonding interactions provide the same stabilization.
3. All C–C bonding interactions provide the same stabilization.
4. The 1,3 repulsive interactions can be grouped into C–C–C, C–C–H, and H–C–H interactions.

The resulting formula follows:

$$\Delta H_f = n_{\text{C-C}}E_{\text{C-C}} + n_{\text{C-H}}E_{\text{C-H}} + n_{\text{C-C-C}}E_{\text{C-C-C}} + n_{\text{C-C-H}}E_{\text{C-C-H}} + n_{\text{H-C-H}}E_{\text{H-C-H}} - f(\text{C,H}) \quad (3)$$

where  $f(\text{C,H}) = (170.6 + E_{\text{C}})n_{\text{C}} + 52.1n_{\text{H}}$ .

The “*n*” terms refer to the number of each type of interaction or atom and the “*E*” terms give the stabilization/destabilization per interaction. The final term is needed to convert to heats of formation from values that are fundamentally atomization energies. The known heats of formation of gaseous carbon (170.6 kcal/mol) and hydrogen atoms (52.1 kcal/mol) are contained in this term<sup>15</sup> as well as the free parameter,  $E_{\text{C}}$ . This parameter is a correction term for electron pairing in atomic carbon and will be discussed in more detail below. Overall, the model contains six parameters (the “*E*” terms) that can be determined by fits to experimental data. The model is akin to Benson’s approach<sup>38-40</sup> for estimating alkane heats of formation.

(34) Somayajulu, G. R.; Zwolinski, B. J. *Trans. Faraday Soc.* **1966**, *62*, 2327.

(35) Brown, R. D. *J. Chem. Soc.* **1953**, 2615.

(36) Allen, T. L. *J. Chem. Phys.* **1959**, *31*, 1039.

(37) Skinner, H. A. *J. Chem. Soc.* **1962**, 4396.

(38) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

(39) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.

(40) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

TABLE 3. Data for Simple Alkanes and Radicals<sup>a</sup>

compd <sup>b</sup>	interactions						$\Delta H_f$	calcd $\Delta H_f$	error
	C	C–C	C–H	H–C–H	H–C–C	C–C–C			
<b>methane</b>	1	0	4	6	0	0	–17.9	–17.3	0.6
<b>ethane</b>	2	1	6	6	6	0	–20.0	–20.4	–0.4
<b>propane</b>	3	2	8	7	10	1	–25.0	–25.3	–0.3
<b><i>n</i>-butane</b>	4	3	10	8	14	2	–30.4	–30.2	0.2
<b>isobutane</b>	4	3	10	9	12	3	–32.1	–31.9	0.2
<b><i>n</i>-pentane</b>	5	4	12	9	18	3	–35.1	–35.1	0.0
<b>isopentane</b>	5	4	12	10	16	4	–36.7	–36.8	0.1
<b>neopentane</b>	5	4	12	12	12	6	–40.1	–40.3	–0.2
<b><i>n</i>-hexane</b>	6	5	14	10	22	4	–40.0	–39.9	0.0
<b>cyclohexane</b>	6	6	12	6	24	6	–29.4	–29.3	0.1
<b>methyl radical</b>	1	0	3	3	0	0	35.0	34.9	–0.1
<b>ethyl radical</b>	2	1	5	4	5	0	29.0	29.1	0.1
propyl radical	3	2	7	5	9	1	23.9	24.2	0.3
<b>isopropyl radical</b>	3	2	7	6	8	1	21.5	21.6	0.1
<i>sec</i> -butyl radical	4	3	9	7	12	2	16.1	16.7	0.6
<b><i>tert</i>-butyl radical</b>	4	3	9	9	9	3	12.3	12.2	–0.1
<sup>3</sup> CH <sub>2</sub>	1	0	2	1	0	0	93.3	93.8	0.5
<sup>4</sup> CH	1	0	1	0	0	0	159.2	159.2	0.0
<i>E</i> <sub>interaction</sub>	60.7 <sup>c</sup>	–146.0	–124.2	6.6	9.3	10.2			

<sup>a</sup> kcal/mol. See refs 15, 16, and 43 for experimental data. <sup>b</sup> Compounds in bold print used in establishing the parameters. <sup>c</sup> Value for *E*<sub>c</sub>, see eq 3 in text.

However, instead of breaking the molecule into fragments, we have chosen 1,2 and 1,3 interactions as our basis set.

Data from Table 3 have been used to fit the parameters needed in eq 3. The data set contains a variety of simple alkanes, including cyclohexane. Strained alkanes are not included because the basic model does not incorporate terms for angular distortions or 1,4 repulsions (torsional strain). Like the Benson model, extra terms would be necessary to account for these types of strain effects. Table 3 also contains simple radicals. It should be noted that not all of the data in Table 3 have been used in the fitting procedure (see below).

**3. Alkanes.** To be able to determine the C–H bond strengths, the model must be able to accurately predict heats of formation for the alkanes and their corresponding radicals. The model was trained with a set of 10 simple alkanes ranging from methane to hexane. Included in the set is the whole array of connectivities from primary to quaternary carbons. Systems with numerous gauche interactions are excluded because the model is not designed to handle 1,4 interactions. The results are listed in Table 3. The average absolute error is less than 0.3 kcal/mol and the largest deviation is 0.6 kcal/mol for methane. Overall the fit is very good and is of comparable quality to results with a Benson additivity approach.<sup>38</sup> However, it should be noted that the Benson approach requires only five free parameters (values for CH<sub>4</sub>, CH<sub>3</sub>, CH<sub>2</sub>, CH, and C groups) whereas our model is using six. Nonetheless, the results are satisfactory. A plot of the data is given in Figure 1.

**4. Radicals.** The same set of free parameters can be used to estimate heats of formation of radicals. Here it is assumed that the singly occupied orbital plays no role in terms of 1,3 repulsive interactions. Four simple radicals (methyl, ethyl, isopropyl, and *tert*-butyl) were included in the training set. The results in Table 3 indicate that the model does an excellent job on the heats of formation of these radicals. In addition, the propyl and *s*-butyl radicals are included in the table and are well fit by the model. The average absolute error is only 0.3 kcal/mol and the greatest deviation is limited to 0.6 kcal/mol for the *s*-butyl radical. *It must be stressed that the same free parameters that fit the alkanes are being used to fit the alkyl radicals.* The overall quality of the fit is clearly shown in Figure 2 where the estimated

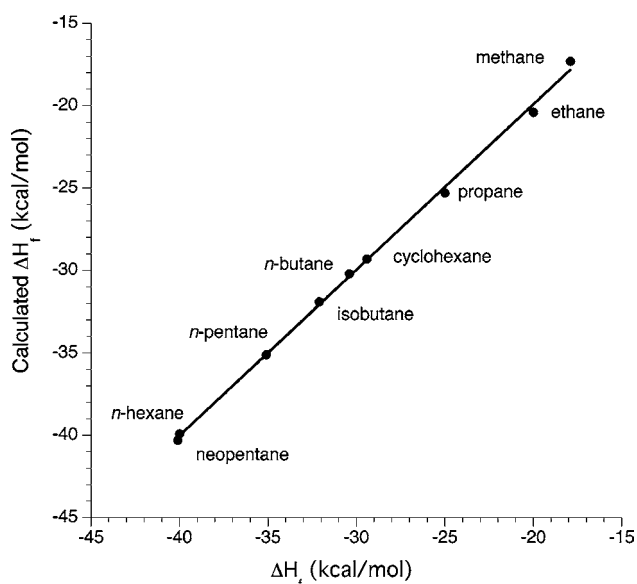
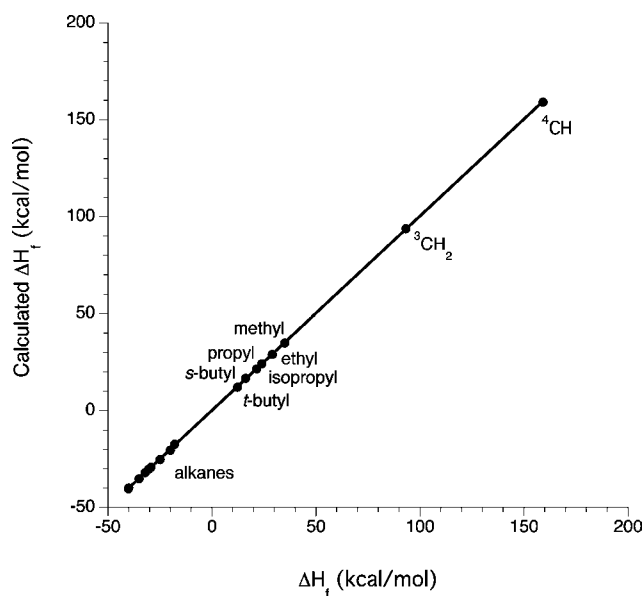


FIGURE 1. Plot of  $\Delta H_f$  values calculated with eq 3 vs literature values for alkanes. See Table 3 for references.

heats of formation of the radicals and alkanes are plotted against the experimental values. The correlation is striking given the simplicity of the model. The Benson approach also fits these data very well, but requires more parameters. In addition to the five noted above, additional parameters are needed for methyl, primary, secondary, and tertiary radical centers (a total of nine parameters).<sup>38</sup> In short, the present model is very efficient and fits a wide range of data with a small number of parameters.

Two other radical species are included in Table 3, but were not used in the training set, <sup>3</sup>CH<sub>2</sub>, and <sup>4</sup>CH. The high spin states are necessary for these species because the model does not incorporate any terms to account for spin pairing energies<sup>41</sup> (i.e., it assumes that each broken bond leads to an unpaired electron). Methylene is a ground-state triplet, but the heat of formation

(41) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.



**FIGURE 2.** Plot of  $\Delta H_f$  values calculated with eq 3 vs literature values for radical species. See Table 3 for references.

for an excited state of methyne (quartet) is included in the table. Surprisingly, the parameters in Table 3 also fit these species.<sup>42</sup> If the doublet state of CH is used in this comparison, an error of about 17 kcal/mol results.<sup>43</sup> The last C–H bond cleavage in this series would lead to atomic carbon. To exclude electron pairing, the carbon would have to be formed as a quintet. The correction factor,  $E_c$ , is meant to account for the difference in energy between ground-state carbon and the fully unpaired carbon that would be formed by sequential bond cleavages. The value of  $E_c$ , 60.7 kcal/mol, is well below the energy needed to excite carbon to its quintet state (96 kcal/mol).<sup>44</sup> This is an inconsistency in the model; however, it represents an extreme and unrealistic expectation. For example, quintet carbon explicitly restricts the occupancy of the 2s orbital to a single electron whereas all the bonded species are allowed to include a greater contribution from this low-energy orbital. In any case, the ability of the model to fit methylene and methyne so well suggests some fortuitous cancellations of errors because the bond angles and lengths in these species are quite different from those in the training set.<sup>45, 46</sup>

**5. Bond Energies.** Since the model can successfully reproduce the heats of formation of the alkanes and their corresponding radicals, it obviously does a reasonable job on the C–H and C–C bond dissociation energies (BDE). The values for C–H bonds are given in Table 4. The average absolute error is

(42) It should be noted that the value for  $E_c$  is not well defined by the energies of the alkanes and simple radicals (i.e., changes in the C–H and C–C bond terms can balance changes in  $E_c$ ). Inclusion of methylene and methyne in the data set puts a much tighter restriction on the value of  $E_c$ . The values in Table 3, including  $E_c$ , were obtained from a fit using only the bold-labeled species, but the fitting process began using a value for  $E_c$  that was appropriate for methylene and methyne.

(43) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Vol. IV, Constants for Diatomic Molecules; Van Nostrand Reinhold: New York, 1979.

(44) Ralchenko, Y.; Kramida, A. E.; Reader, J. *NIST Atomic Spectra Database*; NIST Standard Reference Database No.78, Version 3.0 (<http://physics.nist.gov/PhysRefData/ASD/index.htm>); National Institute of Standards and Technology: Gaithersburg, MD, 2005.

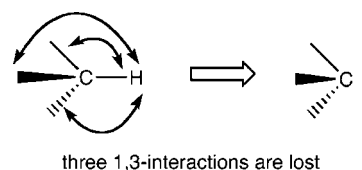
(45) Undoubtedly the terms for the 1,3 interactions also contain some energetic contribution from changes in geometry that occur with bond cleavage.

**TABLE 4.** R–H Bond Dissociation Energies

R–H	bond dissociation energy (kcal/mol)		
	calcd <sup>a</sup>	exptl <sup>b</sup>	error
CH <sub>3</sub> –H	104.3	105.0 ± 0.1	–0.7
CH <sub>3</sub> CH <sub>2</sub> –H	101.6	101.1 ± 0.4	0.5
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> –H	101.6	101.0 ± 0.4	0.6
(CH <sub>3</sub> ) <sub>2</sub> CH–H	99.0	98.6 ± 0.4	0.4
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>3</sub> )CH–H	99.0	98.2 ± 0.5	0.8
(CH <sub>3</sub> ) <sub>3</sub> C–H	96.2	96.5 ± 0.4	–0.3

<sup>a</sup> Equation 3. <sup>b</sup> Reference 16.

**SCHEME 3**



0.4 kcal/mol with the largest error being 0.8 kcal/mol. However, it should be noted that the experimental values have significant uncertainties. In any case, it is safe to say that the model is capable of reproducing the variation in C–H bond strengths for the alkanes. *The remarkable aspect of this result is that the model assumes that all C–H bonds have the same fundamental strength and therefore any variation in bond strength is a result of differences in geminal repulsion.*<sup>47</sup> The mechanism for generating this variation can be seen from the values listed in Table 3 for the 1,3 repulsive interactions. As one might expect, the H–C–H, H–C–C, and C–C–C repulsive interactions have different energetic costs and increase along the series. The values vary from 6.6 for the H–C–H interaction to 10.2 kcal/mol for the C–C–C interaction. When a C–H bond is broken, three 1,3 repulsive interactions are lost in our model. In other words, along with the loss of the C–H bond energy, three strain terms are lost. It is the relative size of these strain terms (1,3 repulsive interactions) that determines the bond strength in this model (Scheme 3). For example, cleavage of a C–H bond in methane releases three H–C–H interactions (6.6 kcal/mol each), whereas cleavage of the 3° C–H bond in isobutane releases three H–C–C interactions (9.3 kcal/mol each). Thus, cleavage of the 3° bond is less endothermic by 8.1 kcal/mol.

**6. Values of the Parameters.** The C–C and C–H bond strength parameters in Table 3 appear to be large in comparison to accepted bond dissociation energies. However, this is simply a consequence of dissecting the bond dissociation energy into two components, an endothermic bond cleavage and an exothermic release of geminal repulsion. It may seem surprising that the C–C bond strength parameter is considerably larger than the C–H parameter (C–H BDE's generally are greater

(46) A referee was interested in whether the model would fit diamond accurately. For a diamond structure, each carbon experiences 4 C–C bonds and 12 C–C–C geminal interactions. However, each of these terms are shared with another carbon, so per carbon, there are 2 C–C interactions and 6 C–C–C interactions. Using the parameters in Table 3, eq 3 gives a heat of formation of 0.6 kcal/mol for diamond. This is very close to the experimental value (0.5 kcal/mol). However, the model does not include corrections for gauche interactions and therefore a close fit to experiment suggests some error in the value from eq 3.

(47) Schleyer has shown that bond electron density measures indicate surprisingly similar intrinsic bond energies for most C–H bonds. However, the absolute values from the study are much different than those reported here because they were parametrized in a conventional way without including terms for 1,3 repulsions: Exner, K.; Schleyer, P. v. R. *J. Phys. Chem. A* **2001**, *105*, 3407.

than C–C BDE's), but this is a consequence of the fact that more 1,3 steric interactions are lost when a C–C bond is broken (6) than when a C–H bond is broken (3). Of course, the 1,3 steric repulsion terms are the key to the model. The progression from H–C–H to H–C–C to C–C–C follows the pattern 6.6, 9.3, 10.2 kcal/mol. As expected, the geminal repulsion increases as the sizes of the interacting groups increase. Unfortunately, estimating the energetic impacts of 1,3 repulsive interactions by other, independent means is exceptionally difficult because there are no good model systems where this energetic term can be isolated. In the past, Bauld has estimated a value of  $\sim 8$  kcal/mol for the C–C–C interaction by extracting the repulsive terms in an AM1 calculation on propane.<sup>6</sup> One can also probe the magnitude of a 1,3-methyl interaction by examining the energy needed to bring two methyl groups together in a triplet state. By doing so, one prevents bonding between them and the repulsive terms can be judged. When this is done with two methyl groups locked into the alignment found in propane (i.e., deleting the central CH<sub>2</sub> group of propane), a CCSD(T)/6-311+G(d,p) calculation on the triplet suggests 12.2 kcal/mol of destabilization relative to two separated methyl groups retaining the same geometry as in propane (Supporting Information, Table S3). Using a similar approach, Bickelhaupt, Ziegler, and Schleyer<sup>8</sup> used theory to estimate that there is 19.7 kcal/mol of geminal repulsion (6.6 kcal/mol per H–C–H interaction) in a pyramidal methyl radical. Although none of the three measures of geminal repulsion presented above is expected to be highly accurate, they provide solid support for the general magnitude of the geminal repulsion terms found in the fitting parameters.

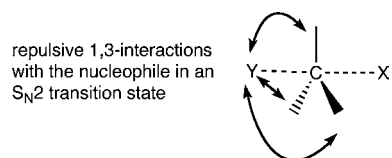
**7. Justification of the Model.** Conceptually, the most appealing aspect of the model is that the variation in C–H bond strengths can be explained solely on the basis of geminal repulsion. In other words, the data can adequately be reproduced without invoking hyperconjugation. *Of course this does not prove that geminal repulsion is responsible for the variation in BDE's, but it does make geminal repulsion a viable alternative for explaining the behavior.* The next question is whether this is a rational way of interpreting the data.

First, geminal repulsion is expected. As noted above, the atoms (groups) are separated by less than the combination of their van der Waals radii and 1,4 steric interactions (longer range) are widely accepted. Moreover, computational estimates (see above) suggest that they are significant and of the proper magnitude to match the observed variations.

Second, a good deal of evidence suggests that 1,3 repulsive interactions are important in determining structures. For example, the C–C–C angle in propane is slightly larger than normal (112.4°), presumably to reduce the repulsive interaction between the two methyl groups.<sup>48</sup> This effect is not limited to C–C–C angles, and the H–C–C angles in ethane are opened to 110.9° at the expense of the H–C–H angles. Bickelhaupt, Ziegler, and Schleyer<sup>8</sup> have argued that the preference for a trigonal planar structure in the CH<sub>3</sub> radical is caused by the resulting reduction in geminal repulsion. In contrast, analogous radicals for heavier elements (e.g., SiH<sub>3</sub>, GeH<sub>3</sub>) remain pyramidal because the attached groups have much longer bonds and consequently there is negligible geminal repulsion. As noted in the discussion of hyperconjugation, silanes do not follow the

(48) Hellwege, K. H.; Hellwege, A. M. *Atomic and Molecular Physics, Structure Data of Free Polyatomic Molecules*; Springer-Verlag: Berlin, Germany, 1976; Vol. 7.

## SCHEME 4



same pattern as alkanes in bond strengths and increasing substitution does not reduce Si–H bond strengths. This is consistent with the notion that 3rd period elements suffer less from 1,3 repulsive interactions.

Third, there are data that point to the effect of geminal repulsion on relative reactivity. The sharp drop in S<sub>N</sub>2 reaction rates in going from 1° to 2° to 3° centers is universally explained on the basis of increasing steric repulsion between the nucleophile/leaving group and the substituents on the α-carbon. However, this repulsion is simply another manifestation of repulsive 1,3 steric interactions (Scheme 4). In addition, we have shown that the loss of repulsive 1,3 interactions is the key to the low enthalpic barriers found for cyclizations to three-membered rings.<sup>31,32</sup>

If repulsive 1,3 interactions exist and are on the order of 5–10 kcal/mol, it would be surprising if they did not play a role in determining the physical properties of alkanes. This conclusion also is supported by the examples cited in the previous paragraphs. Therefore, a model based on geminal repulsion is justifiable. The conceptual value and validity of the model will be discussed in a later section.

**III. Other Applications of the Model. 1. Branched Alkanes.** Although not stated explicitly above, the model is able to handle the variation in the stability of alkane isomers. For example, the increase in stability across the series pentane, isopentane, neopentane is reproduced (Figure 1). This result implies that the variation can be explained on the basis of geminal repulsion. The key is the relative values of the three-center interactions. The E<sub>H–C–H</sub> value is significantly smaller than the other repulsive terms, but more importantly, the E<sub>H–C–C</sub> value is greater than the average of the E<sub>H–C–H</sub> and E<sub>C–C–C</sub> values. This is critical because for each new branching point in an alkane, two H–C–C interactions (the most common interaction in linear alkanes) are replaced by a H–C–H and a C–C–C interaction. From the values in Table 3, it can be seen that each such branching (e.g., pentane vs isopentane) results in 1.8 kcal/mol of stabilization (2 × 9.3 vs 6.6 + 10.2). If the E<sub>H–C–C</sub> value were the average of the E<sub>H–C–H</sub> and E<sub>C–C–C</sub> values, there would be no variation in the predicted stability of the isomeric alkanes. Therefore it is the asymmetry in the 1,3 repulsive terms that allows the model to reproduce the experimental observation that the combination of a CH<sub>3</sub> and CH group is more stable than two CH<sub>2</sub> groups. However, the experimental trends are somewhat more complicated. Benson<sup>49</sup> noted that the stabilization gained by branching is not constant and drops off as the branching becomes more extensive (i.e., less is gained in the conversion from isopentane to neopentane than in the conversion from pentane to isopentane). This subtle variation represents a higher order effect that cannot be accounted for with the model outlined in eq 3 (i.e., it requires 4-center interaction terms). Of course, correction terms could be added to build this variation into the model, but the goal of the present study is not to develop an accurate molecular mechanics approach, but rather to explore

(49) Benson, S. W.; Luria, M. *J. Am. Chem. Soc.* **1975**, *97*, 704.



TABLE 5. Data for Alkenes<sup>a</sup>

compd	interactions					$\Delta H_f$	calcd $\Delta H_f$	error
	C–C <sup>b</sup>	C–H	H–C–H	H–C–C	C–C–C			
ethene	1 (1)	4	2	4	0	12.5	12.5	0.1
propene	2 (1)	6	4	7	1	4.9	4.9	0.1
<i>E</i> -2-butene	3 (1)	8	6	10	2	–2.6	–2.6	–0.1
1-butene	3 (1)	8	5	11	2	–0.2	0.1	0.3
2-methylpropene	3 (1)	8	7	8	3	–4.3	–4.4	0.1
2-methyl-2-butene	4 (1)	10	9	9	6	–9.9	–10.1	–0.2

<sup>a</sup> kcal/mol. See ref 15 for experimental data. <sup>b</sup> Number of  $\pi$  bonds given parenthetically.

the conceptual value of invoking repulsive geminal repulsion as a way to explain reactivity and stability trends in alkanes. Because many higher order effects are being neglected, one does not expect the model to provide a perfect match to experimental data. Its ability to provide a simple explanation for the gross trends in alkane stability as well as C–H bond strength is the principal virtue of the model.

The effect of branching on the stability of alkanes has lacked a compelling explanation in the past. In early work, Pitzer and Catalano<sup>50</sup> suggested that increased intramolecular van der Waals attractions in branched alkanes (electron correlation in their words) could explain the enhanced stability of branched alkanes. Although their model fits the data, it lacks repulsive terms, thus all steric strain is ignored (i.e., all molecular crowding is favorable). As a result, the model predicts that gauche conformations of alkanes are much *more stable* than anti conformations. To remedy this situation, they assumed that gauche interactions would impose a large steric penalty, thus overwhelming the van der Waals attraction. However, they did not take into account 1,3 repulsive interactions. As noted above (Scheme 2), the distances are shorter in 1,3 interactions as compared to 1,4 interactions so steric penalties should be larger in the former. Bartell<sup>4</sup> noted this inconsistency not long after Pitzer's paper appeared. The key issue is that Pitzer's argument depends on exceedingly large van der Waals attractions, which can only be attained at very short distances, but these distances are deep into the repulsive portion of a molecular interaction surface. Therefore, the Pitzer and Catalano explanation requires selectively turning off some potent steric repulsions while retaining others. There is simply no justification for that interpretation and it is counter to the data presented above. More recently, Laidig<sup>51</sup> used Bader's atomic partitioning approach<sup>52</sup> to analyze the effect of branching. The data provide some insight into the impact of branching on electron distributions, but provide limited insight into the structural factors related to the enhanced stability of branched alkanes.<sup>53</sup> Finally, arguments based on the strengths of the C–H bonds in the alkane (i.e., branched alkanes have a higher fraction of strong 1° C–H bonds) are certainly valid, but they do not address the underlying cause (i.e., why those bonds are stronger). In fact, that argument, when followed up by conventional logic on bond strengths, leaves one with the unfulfilling conclusion that neopentane is more stable than pentane because it yields less stable radicals after C–H bond scissions. A model based on geminal repulsion provides a straightforward explanation for the effect of branching

on alkane stability. The steric advantage of methyl groups, in terms of 1,3 interactions, is sufficient that they are preferred over methylene and methyne groups despite the added steric strain that is developed at the branching carbon. Therefore, the alkane isomer with the most methyl groups (ignoring gauche interactions) is the most stable.

**2. Branched Alkenes.** A similar approach can be applied to alkenes. To maintain the simplicity of the model, it has been assumed that the same 1,3 interaction parameters can be used in aliphatic and vinylic situations. As a result, only one new parameter needs to be added ( $E_\pi$ ), the strength of the  $\pi$ -bond in an alkene (the double bond is assumed to be the combined strength of the a standard C–C bond and an added  $\pi$ -bond). Data for the alkenes in Table 5 were used to fit the added parameter and a value of 66.2 kcal/mol was obtained for the  $\pi$ -bond. This value is very close to the barrier to rotation in ethane (65 kcal/mol).<sup>54</sup> This is expected because in the absence of the  $\pi$ -bond energy term, the model treats ethene as a singly bonded pair of CH<sub>2</sub> groups. The errors listed in Table 5 are small (~0.2 kcal/mol) and it is clear that the extended model is capable of predicting reasonably accurate values for the heats of formation of alkenes.

The data also indicate that the model reproduces the key trend in alkene stability, more highly substituted alkenes are more stable. For example, the model predicts that *E*-2-butene is 2.7 kcal/mol more stable than 1-butene. This result is simply an extension of the preference for methyl groups noted for alkanes and 2-butene is favored by the conversion of an H–C–C interaction into an H–C–H interaction, which reduces the net destabilization from geminal repulsion. The conventional arguments related to alkene stability have focused on a preference for C<sub>sp<sup>2</sup></sub>–C<sub>sp<sup>3</sup></sub> bonds. The stabilization has been attributed to hyperconjugation as well as a disproportionate strengthening of C<sub>sp<sup>2</sup></sub>–C<sub>sp<sup>3</sup></sub> bonds relative to C<sub>sp<sup>2</sup></sub>–H bonds to the double-bonded carbons.<sup>55–58</sup> However, computational data cited earlier indicate that the latter argument is flawed. In forming a radical, an aliphatic carbon becomes nearly planar and effectively shifts from sp<sup>3</sup> to sp<sup>2</sup> hybridization. Therefore, the pyramidalization energies presented in the discussion of hyperconjugation can also be viewed as measures of the energy involved in the rehybridization of a carbon. If there is an inherent preference for C–C bonds to sp<sup>2</sup>-hybridized carbons, then the more highly substituted radicals (e.g., isopropyl and *tert*-butyl) should have the greatest preference for a planar, sp<sup>2</sup>-hybridized radical center, especially because they have the most to gain sterically by

(50) Pitzer, K. S.; Catalano, E. *J. Am. Chem. Soc.* **1956**, *78*, 4844.

(51) Laidig, K. E. *J. Phys. Chem.* **1991**, *95*, 7709.

(52) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

(53) Unfortunately, Laidig's level of theory did not reproduce the experimental preference for branching. As a result, no quantitative interpretations of the data are possible.

(54) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(55) Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41.

(56) Deasy, C. *Chem. Rev.* **1945**, *36*, 145.

(57) Dewar, M. J. S. *Hyperconjugation*; Ronald Press: New York, 1962.

(58) Whangbo, M.-H.; Stewart, K. R. *J. Org. Chem.* **1982**, *47*, 736.



increasing the bond angles on the radical. However, this is not the case and the methyl, ethyl, isopropyl, and *tert*-butyl radicals all have similar preferences for a planar central carbon. As a result, it is difficult to argue that C–C bonds are preferentially stabilized by the conversion to  $sp^2$  hybridization. As for hyperconjugative stabilization in substituted alkenes, Dewar<sup>57,59</sup> presented persuasive arguments over 40 years ago that this effect is not important. Another problem with the conventional arguments is that they cannot account for the enhanced stability of 2-methylpropene relative to *E*-2-butene. Both are doubly substituted, yet the former is more stable by 1.7 kcal/mol. However, the model based on 1,3 interactions does reproduce this variation in stability. It is a result of converting two H–C–C interactions into an H–C–H and a C–C–C interaction. This conversion is the same one that is seen when an alkane incorporates a branch point. The most important result is that the new model can explain all the basic features of alkene stability with the same logic that was applied to the alkanes. This is an exceptional conceptual advantage of the model.

It is well-known that bonds to vinylic carbons are stronger than analogous bonds to aliphatic carbons. It may not be obvious how this effect is incorporated into the present model. Part of the effect is built into the term added for the  $\pi$ -bond. This term was included to account for the added stability of an alkene due to  $\pi$ -bonding, but also incorporates some of the added strength of its  $\sigma$ -bonds. However, the model does require that the combined strengthening of the four vinylic  $\sigma$ -bonds be the same for all alkenes. This approximation breaks down for vinylic radicals because there are only three vinylic bonds. For example, if eq 3 is applied to the vinyl radical, the estimated heat of formation, 68.7 kcal/mol, leads to a C–H bond strength, 108.3 kcal/mol, that is too low by 2.4 kcal/mol. Nonetheless, the model naturally accounts for much of the bond strengthening observed in ethene.<sup>60</sup>

**IV. Comparisons to Other Additivity Schemes.** Aside from molecular mechanics computer packages, the best-known additivity scheme is Benson's.<sup>38–40</sup> In this method, the molecule is partitioned into components (e.g. CH<sub>3</sub>, CH<sub>2</sub>, and CH groups) and energy values for these groups are summed. In addition, terms are included for various types of strain. The approach is exceptionally versatile and has had great success in estimating heats of formation for a wide variety of species. The aim of Benson's approach is to provide accurate heats of formation. It was not developed around a conceptual model and relies on an empirical partitioning of the heat of formation into contributions from convenient molecular subsets (i.e., atom-centered groups). In comparison to the present model, Benson's approach is more accurate, but requires far more parameters to describe the species in this study (12 vs 7).

In a series of papers, Zwolinski and co-workers<sup>34,61–64</sup> presented an additivity scheme that includes repulsive 1,3

interactions as well as many higher order terms. This method also focuses on the accuracy of predicting heats of formation of alkanes rather than the underlying factors that affect the stability of the alkanes. The approach contains some of the concepts put forward in earlier studies by Brown,<sup>35</sup> Allen,<sup>36</sup> Skinner,<sup>37</sup> and Zahn.<sup>65</sup> Zwolinski's approach does not address radical stability or C–H bond strengths. More recently, Jackson<sup>66</sup> put forward an additivity scheme that included some 1,3 interactions and used differences in rehybridization energies to reproduce variations in C–H bond strengths.

In the mid 1970s, Benson presented an intriguing model based on electrostatic interactions in hydrocarbons.<sup>49,67,68</sup> Although this model did not gain widespread recognition, it offers an interesting insight into the factors that stabilize alkanes. It provides reasonably accurate predictions of heats of formation for the same general set of compounds (i.e., alkanes, alkenes, and alkyl radicals) in this study. Moreover, it uses remarkably few free parameters (essentially only three for the heats of formation of the alkanes). The basic premise is that C–H bonds are polarized and therefore stabilized by electrostatic interactions. Benson and co-workers assumed that all C–H bonds have the same polarization (i.e., same partial positive charge on all the hydrogens) and all C–C bonds had no polarization in alkanes. The net electrostatic stabilization of the alkane then can be calculated by using the resulting charges and the alkane's geometry; however, the short-range electrostatic interactions between bonded atoms dominate the analysis. In a methyl group, the carbon is attached to three hydrogens, each with a charge of  $+y$ . To balance the charges, the carbon must have a charge of  $-3y$ . As a result, the electrostatic interaction energy for each of the three C–H bonds is proportional to  $-3y \times y$  for a total of  $-9y^2$  of stabilization in the methyl group. A CH<sub>2</sub> group has a charge of  $-2y$  on the carbon and each C–H provides only  $-2y^2$  stabilization ( $-4y^2$  for the CH<sub>2</sub> group). Finally a CH group has a charge of  $-y$  on the carbon and its C–H bond provides only  $-y^2$  stabilization. Benson's electrostatic model can explain the variation in the stability of isomeric alkanes because like the present model, it also predicts that two CH<sub>2</sub> groups (net stabilization of  $-8y^2$ ) are less stable than the combination of a CH<sub>3</sub> and a CH group (net stabilization of  $-10y^2$ ). The model is also able to deal with radicals and bond dissociation energies by including terms to account for changes in charge distributions related to radical formation.

Given its abilities, why did Benson's electrostatic additivity scheme not gain wider acceptance? There are several reasons. First, the need to account for all the pairwise electrostatic interactions in a molecule is a demanding task and requires a knowledge of all the interatomic distances. The awkwardness of the model in this respect is even more pronounced for radical species. Second, some aspects are counterintuitive. For example, methyl groups act as electron-withdrawing groups (relative to hydrogen) and as a result in this model, the carbon in CH<sub>3</sub> appears to be more electron-rich than the central carbon of (CH<sub>3</sub>)<sub>3</sub>C. Third, the terms needed to correct for the heats of formation of the radical do not have a strong physical foundation

(59) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *11*, 96.

(60) One might wonder about how this simple model would perform in predicting C<sub>sp</sub>–H bond strengths, such as in ethyne. If it is assumed that all repulsive 1,3 interactions are missing in ethyne due to the linear geometry, eq 3 predicts a C–H bond strength of 124.2 kcal/mol. This is well below the experimental bond strength (133.3 kcal/mol). A good fit is not expected because the model contains no terms to account for the changes that occur in the transition to  $sp$ -hybridization, but it does indicate that the majority of the bond strengthening found in ethyne might be the result of its lack of geminal repulsion.

(61) Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1971.

(62) Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 973.

(63) Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 967.

(64) Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 2213.

(65) Zahn, C. T. *J. Chem. Phys.* **1934**, *2*, 671.

(66) Jackson, R. A. *Tetrahedron* **1991**, *47*, 6777.

(67) Benson, S. W.; Luria, M. J. *Am. Chem. Soc.* **1975**, *97*, 3337.

(68) Benson, S. W.; Luria, M. J. *Am. Chem. Soc.* **1975**, *97*, 3342.

and in contrast to other theories on radical stability require that adjacent alkyl groups act as electron-withdrawing groups with respect to a radical. Fourth, the model really does not faithfully represent its key premise, carbon is more electronegative than hydrogen and this difference strengthens C–H bonds. In practice, the model predicts that the polarization of bonds is reduced (and bonds weakened) for more highly substituted carbons; however, adding more electronegative atoms to a center should enhance its electronegativity, not reduce it. Finally, the model makes no accommodation for the fact that the build-up of charge on a carbon has an energetic cost and will not increase linearly with the addition of more electron-releasing groups.<sup>69</sup> These issues, particularly the last three, greatly weaken the conceptual value of the model.

Initially it might seem surprising that Benson's electrostatic model and the present geminal repulsion model could fit the data equally well despite having completely different conceptual foundations. The answer is in the regular patterns found in heats of formation and the fact that many seemingly unrelated parameters can be used to represent fundamental changes in alkane structure. For example, any parameter set that is able to identify the number of primary, secondary, and tertiary carbons in a molecule can reproduce, at least crudely, the trends in heats of formation. In the 1,3 interaction model, the number of H–C–H, H–C–C, and C–C–C terms defines the number of primary, secondary, and tertiary carbons in the molecule. In Benson's electrostatic model, the charge on the carbon,  $-3y$  for primary,  $-2y$  for secondary, and  $-y$  for tertiary, serves as the basis for identifying the substitution patterns on the carbons in the molecule. Therefore, both models are essentially using the same fundamental terms to reproduce the patterns in heats of formation of the alkanes. In this respect, both models share common characteristics with Benson's original additivity scheme. As this discussion suggests, fitting the energetic patterns is not a unique feature of any particular model and does not indicate that a model is accessing the physical factors that are responsible for the patterns. This critical issue will be addressed in the final section of the paper.

**V. Geminal Repulsion vs Hyperconjugation.** In an earlier section, the conventional hyperconjugative stabilization argument was tested against three challenges involving the geometries and energies of radical species. It effectively failed each. Can a geminal repulsion argument pass these tests? As noted earlier, the geometries of simple radicals are consistent with geminal repulsion and a C–H bond on an adjacent carbon tilts away from a radical center (H–C–C angle  $>109.5^\circ$ ), suggesting geminal repulsion. At first glance, it might be surprising that the geminal repulsion model would be consistent with the fact that radical pyramidalization energies are similar for 1°, 2°, and 3° centers; however, it is important to note that pyramidalization also involves an increase in the bond lengths to radical centers, so the distances between the geminal groups do not change by large amounts. For example, the distance between the methyl groups in the *tert*-butyl radical only decreases from 2.562 Å to 2.475 Å in the pyramidalization

process (MP2/6-311+G(d,p) level) so negligible changes in geminal repulsion are expected. As a result, the concept of geminal repulsion can accommodate similar pyramidalization energies for 1°, 2°, and 3° radicals. Finally, there is the issue of Si–H bond strengths not following the same pattern as alkanes (e.g., trimethylsilane has a stronger Si–H bond than silane). As shown by Bickelhaupt, Ziegler, and Schleyer,<sup>8</sup> geminal repulsion is negligible in silanes because of the long bonds to silicon. In fact, they used an argument based on geminal repulsion to explain why carbon-centered radicals prefer planar geometries whereas silicon-centered radicals are pyramidal. As a result, other factors must determine the small differences in the Si–H bond strengths. Overall, the geminal repulsion explanation can pass the tests that the hyperconjugation explanation failed. *Moreover, the fact that the model in eq 3 can 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.*

**VI. Value of the Model.** As noted above, there are suitable ways of accurately estimating the heats of formation of alkanes and related radicals, so this aspect of the model is not of great importance. The real value of the new model is in its ability to address a conceptual question—is geminal repulsion the cause of the stability trends in these species? If so, the model provides a simple conceptual framework for explaining the effects of branching on C–H bond strengths and alkane stability, obviously a highly desirable result. Factors supporting the model are enumerated below.

1. There is no doubt that repulsive 1,3 interactions exist and the available estimates indicate that they have a significant energy impact. In the context of bond dissociation energies, the only way that they would not have an effect on relative C–H bond strengths would be if they were equal for H–C–H, H–C–C, and C–C–C interactions. This is not likely. The only question is how much do they contribute to the changes in bond strengths.

2. Branching has a strong effect on the stabilities of alkanes, not just on the bond dissociation energies. For example, the difference in the heats of formation of neopentane and pentane (5 kcal/mol) is about the same as the difference in bond dissociation energies of 1° and 3° centers (5.3 kcal/mol for ethane vs isobutane). As a result, there is no compelling evidence to support the conclusion that differences in bond strengths are solely controlled by factors exclusive to the resulting radical. A model that can simultaneously address both issues (alkane and radical stability) is preferred.

3. The model relies on an interaction that has been documented in a variety of systems and is known to affect both structure and reactivity. Its foundation is based on the well-accepted concept that close-range, nonbonding interactions are repulsive (i.e., steric strain).

4. The conventional explanation for the variation in C–H bond strengths requires two major leaps of faith. First, one must assume that hyperconjugation between a radical and an alkyl group does not obey the same orbital orientation effects normally found in  $\pi$ -type interactions (i.e., as in the allyl radical). Second, one must assume that 1,3 steric repulsions are nonexistent, despite the short distances, or that they perfectly cancel, despite the differences in the sizes of the groups as well as geometric deformations that suggest greater repulsion between larger groups. These leaps of faith seem unwarranted given the available data.

(69) In this model, bond polarization is treated as being solely stabilizing. As a result, the most stable C–H bond would be ionic,  $C^-H^+$ . The failing of the model is a lack of terms to account for electron–electron repulsion as the carbon takes on additional electron density. It is true that atomic charges from MO calculations indicate that the carbon charge linearly increases with each hydrogen, but this analysis involves partitioning shared electron density and it is not appropriate to use these values as if they were point charges centered at nuclei.

**Summary**

A model based on geminal repulsion in hydrocarbons can successfully reproduce the basic stability trends in alkanes, alkyl radicals, and alkenes. In this model, the reduction in C–H bond strengths in going from 1° to 3° centers is the result of a greater release of 1,3 repulsive energy during the bond cleavage. The model is consistent with experimental data and provides a conceptual framework for explaining a broad set of stability trends. Currently, a separate explanation is used to rationalize each of the stability trends and none of them is firmly supported by an unambiguous theoretical framework. Models based on hyperconjugative stabilization of radicals lead to predictions that are not consistent with available data. The effect of branching on alkane stability has lacked a compelling explanation since Bartell countered Pitzer's rationalization over 40 years ago. As a result, the new model fills a critical void by providing a unified framework, based on a rational physical effect, for explaining an important set of fundamental stability trends.

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**Note added in proof:** In early work, Bartell also showed that 1,3 repulsive interactions could account for the variation in stability of branched alkanes (Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736 and Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754).

**Supporting Information Available:** Tables of data from the Gaussian03<sup>70</sup> ab initio calculations reported in text and complete ref 70. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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