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STABILIZATION EFFECTS IN ALKANES AND IN PRIMARY, SECONDARY AND TERTIARY ALKYL RADICALS

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Abstract - Heats of formation of alkanes and alkyl radicals, along with kinetic and spectroscopic data, are used to derive appropriate group parameters: two atom parameters related to intrinsic bond energies and three atom parameters related to van der Waals interactions. The decrease in bond dissociation energies along the series CH_3-H, CH_3CH_2-H, $(CH_3)_2CH$-H, $(CH_3)_3C$-H is deduced to be mainly due to differences in intrinsic bond energies on rehybridization, with electron delocalization playing only a minor role.

INTRODUCTION

The trend in bond dissociation energies D(Me-H)>D(Et-H)>(Pr^i-H>(Bu^t-H) is long established, and has led to the concept of stabilization of secondary and tertiary alkyl radicals, sometimes attributed to hyperconjugation or inductive effects. An alternative explanation of the 'stabilization' is in terms of differing intrinsic strengths of C-C and C-H bonds depending on the hybridization of the carbon. Rüchardt[1] has pointed out the importance of considering stabilization or destabilization of the parent alkane. Now that there is considerable agreement on the bond dissociation energies of simple alkyl radicals[2] (to within ±3 kJ mol^{-1}), a thermochemical analysis of stabilization effects in radicals becomes possible. First we consider the thermochemistry of simple alkanes, then that of the derived radicals.

HEATS OF FORMATION OF ALKANES

A number of bond energy schemes have been proposed for estimation of heats of formation of organic compounds, for example those of Laidler[3], Allen[4] and Benson and Buss[5]. These schemes are parameterized from data on simple organic molecules: Cox and Pilcher[6] have shown these three schemes to be equivalent. In essence, the heats of formation of simple organic compounds (or their heats of atomization) can be expressed as a sum of contributions from two-atom interactions, which may be regarded as 'intrinsic' bond strengths, and three-atom terms which are necessary to account for such features as the greater stability of branched alkanes compared with their straight chain isomers.

This is the approach which is developed further in this paper. The two-bond terms are seen as intrinsic bond energies, which differ on changes in hybridization, whilst the three-bond terms are rationalized in terms of van der Waals interactions. The contribution of pi and sigma bonds to the C=C linkage is evaluated, and free alkyl radicals are brought into the scheme. It should be noted that calculations of heats of formation and heats of atomization are entirely equivalent and differ only in the datum point for calculation of the energies. Heats of atomization relate more directly to intrinsic energies of bonds rather than 'contributions' to heats of formation which are less readily visualized. However, experimental data relate more closely to heats of formation, and estimates of error of derived quantities can be determined more readily, so the majority of the arguments developed in this paper are based on contributions to heats of formation.

To simplify notation, in this paper sp^2 and sp^3 hybridized carbon will be represented as 2 and 3 respectively, so that 3-H represents the two atom contribution of an sp^3 hybridized C-H bond and 2-2-3 represents the three atom C_{sp2}-C_{sp2}-C_{sp3} contribution to -ΔH_f. A single bond between two sp^2 hybridized carbon atoms is 2-2 as in the central bond of 1,3-butadiene, the double bond in ethene is represented as 2=2, and the π-bond contribution to a double bond is 2$^-$2. All heats of formation and reaction in this paper are in kJ mol^{-1}, and units will not be routinely expressed in the text. Thermochemical references are given in the computational details section.

$$\Delta H$$

$$CH_4 \longrightarrow C(s) + 2\,H_2 \qquad 74.4\pm0.4 \tag{1}$$

$$CH_4 \longrightarrow C + 4\,H \qquad 2297.9 \tag{2}$$

$$C_2H_6 \longrightarrow 2\,C(s) + 3\,H_2 \qquad 83.8\pm0.4 \tag{3}$$

$$C_2H_6 \longrightarrow 2\,C + 6\,H \qquad 4094.8 \tag{4}$$

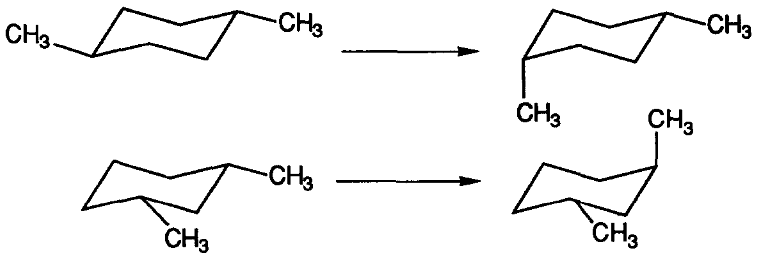
$$2\,C_2H_6 \longrightarrow CH_4 + C_3H_8 \qquad -\,11.5\pm1.0 \tag{5}$$

$$3\,C_2H_6 \longrightarrow 2\,CH_4 + (CH_3)_3CH \qquad -\,31.6\pm1.6 \tag{6}$$

$$4\,C_2H_6 \longrightarrow (CH_3)_4C + 3\,CH_4 \qquad -\,56.1\pm2.2 \tag{7}$$

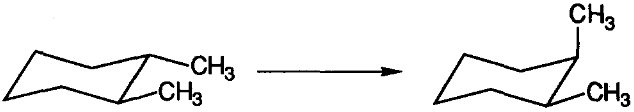
$$(CH_3)_3CH + CH_3CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH_3 + C_2H_6 \qquad 1.4\pm1.4 \tag{8}$$

$$2\,(CH_3)_3CH \longrightarrow C_2H_6 + (CH_3)_2CH\text{-}CH(CH_3)_2 \qquad 6.3\pm1.8 \tag{9}$$



7.9±2.6 (10)

8.1±2.5 (11)



7.8±2.6 (12)

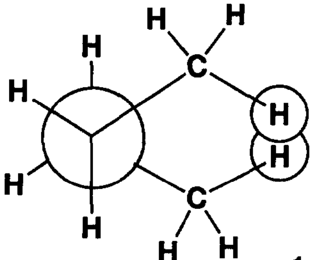
The contribution of a C_{sp3}-H bond (3-H) to $-\Delta H_f$ for an alkane is simply a quarter of ΔH for reaction (1) and has a value of +18.6 ± 0.1. The corresponding intrinsic bond energy, 574.5, is derived from the atomization reaction (2). From the heats of formation and atomization of ethane (reactions 3 and 4) and 3-H, the carbon-carbon contribution to $-\Delta H_f$, 3-3, can be calculated on the assumption of constant intrinsic bond energies for particular types of bond as -27.8 ± 0.7.

These two atom contributions 3-H and 3-3 do not account accurately for the heats of formation of higher alkanes. For example, in reaction 5, both reactants and products contain two 3-3 and twelve 3-H bonds. However, the reaction is exothermic by 11.5 ± 1.0 kJ mol^{-1}. This energy, significantly bonding, is defined as the three atom contribution 3-3-3. If 3-H, 3-3 and 3-3-3 contributions are sufficient to account for ΔH_f of n-alkanes, the effect of lengthening an alkane by one CH_2 unit should be to reduce ΔH_f by 3-3 + 2(3-H) + 3-3-3 = 20.9 in accord with known differences heats of formation of the alkanes (-20.7 from ethane to decane).

What is responsible for the three atom contribution? Since hydrogen and carbon have different electronegativities and are using different orbitals for bonding, it is possible that there may be small hybridization differences in the carbon atoms of different alkanes, giving, perhaps, stronger C-C bonds in propane than in ethane. However, the following argument points to van der Waals interactions as the main cause of the three bond contributions. The isodesmic[7] reaction (6), exothermic by 31.6 involves the creation of three 3-3-3 interactions at a single carbon atom, or 10.5 ± 0.5 per interaction; within the limits of error, this is the same as that found in reaction (5). Likewise reaction (7) involves the creation of six 3-3-3 interactions at the central carbon atom, rating each interaction at 9.35 ± 0.4. If the increase of hydrocarbon stability on branching were due to hybridization differences, it would be likely that the progression in exothermicity from reactions (5) → (6) → (7) would be linear, or that (6) → (7) would be less than (5) → (6). However, the near constancy of the interaction term is well explained by van der Waals interactions. The C-C-C angle in propane[8] is 112.4 + 0.2°, slightly larger than the tetrahedral angle. This implies that the positions for the carbon and hydrogen atoms in the two methyl groups are most favourable for van der Waals interactions if the C-C-C angle is splayed slightly: a small angle change is not very costly in energy terms, but van der Waals interactions are very sensitive to changes in distance. In 2-methylpropane, maintenance of the C-C-C angle at the isobutane value would result in a significant decrease in the C-C-H angle: in fact, the C-C-C angle[9] is 111.15 + 0.1°, which results in a slight decrease in the derived 3-3-3 term (although the interactions computed for propane and isobutane are not significantly different). However, on introduction of the fourth methyl group to the central carbon atom, the C-C-C angles are forced back to the tetrahedral angle, reducing the values of the van der Waals interactions by a significant amount.

The constancy of the 3-3-3 term for alkanes where alkyl groups are involved as the terminal C atoms rather than methyl groups can be understood on the basis that alkyl groups tend to adopt the staggered conformation, leaving the carbon substituent directed away from the interacting carbon atoms, and therefore not involved significantly in van der Waals interactions.

The other interaction important in moderately unhindered alkanes is the gauche interaction. The homodesmotic[10] reactions (9) to (12) all involve the creation of two gauche interactions in systems where the gauche strain cannot be relieved by a change in dihedral angle away from the staggered position. The mean of these results gives 3.8 ± 0.6 kJ mol^{-1} as the unfavourable contribution to heat of formation for this type of interaction. Reaction (8) involves the creation of just one gauche interaction, with a contribution of + 1.4 ± 1.4 to the heat of formation. This smaller value may reflect the fact that in this situation, the gauche repulsion may be made smaller by an increase in the gauche dihedral angle above 60°.



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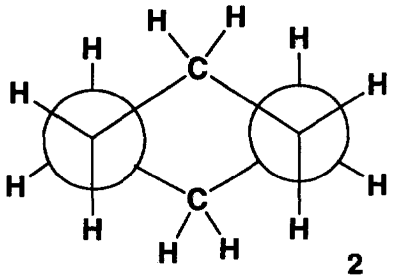

2

The gauche interaction in butane could arise from repulsion of the C-C bonding electrons in the two bonds involved, or from unfavourable van der Waals interactions between the terminal methyl groups. That the latter effect is dominant is suggested by the fact that cyclohexane has virtually no gauche strain: its heat of formation

(-20.6 ± 0.1 kJ mol^{-1} per CH_2) is within experimental error the same as the incremental value per CH_2 group of -20.7 for (staggered) alkanes. The unfavourable H-H interaction in gauche butane (**I**) is not present in cyclohexane (**2**): the two carbon atoms that would have been involved are covalently bonded.

HEATS OF FORMATION OF ALKENES AND ALKYL RADICALS

Alkenes and alkyl radicals involve further thermochemical complications: sp^2 hybridization has to be considered, as well as double bonds, conjugated or non-conjugated. We assume that contributions from C_{sp2}-H (2-H) will be different from 3-H, that 3-3, 3-2 and 2-2 will be different, and that the total energy of a double bond (2=2) will be the sum of 2-2 and a π-bond energy denoted 2·2. Three atom terms will also be needed.

	ΔH	
$CH_3^{\cdot} \longrightarrow C(s) + 1.5\ H_2$	-146.0±1.0	(13)
$CH_3^{\cdot} \longrightarrow C + 3\ H^{\cdot}$	1878.9	(14)
$C_2H_6 + CH_3CH{=}CH_2 \longrightarrow CH_4 + CH_3CH_2CH{=}CH_2$	-10.5±1.4	(15)
trans-$CH_3CH{=}CHCH_3 \longrightarrow (CH_3)_2C{=}CH_2$	-5.5±1.3	(16)
$C_2H_6 + CH_2{=}CH_2 \longrightarrow CH_4 + CH_3CH{=}CH_2$	-23.1±1.1	(17)
$CH_3^{\cdot} + C_2H_6 \longrightarrow CH_4 + CH_3CH_2^{\cdot}$	-18.1±2.1	(18)
$CH_3CH_2^{\cdot} + CH_2{=}CH_2 \longrightarrow CH_3^{\cdot} + CH_3CH{=}CH_2$	-5.0±2.2	(19)
$CH_3CH_2^{\cdot} + C_2H_6 \longrightarrow CH_4 + (CH_3)_2CH^{\cdot}$	-21.2±3.5	(20)
$(CH_3)_2CH^{\cdot} + C_2H_6 \longrightarrow CH_4 + (CH_3)_3C^{\cdot}$	-29.9±3.5	(21)

We assume that there is no special stabilization of the methyl radical, which is planar and hence will show sp^2 hybridization. On this basis, 2-H is calculated from equation (13) to be -48.7 ± 0.3. Ethene (ΔH = + 52.5 ± 0.4) is comprised of four 2-H and 2=2, the latter contribution therefore has a value of 142.2 ± 1.4. A kinetic study[11] of the isomerization of *trans*-1,2-dideuterioethene to its *cis* isomer gives the barrier to rotation and hence 2·2 as 272.0 ± 5.0. Thus 2-2 is -129.8 ± 5.2. We can now use this data to estimate the heat of formation of 1,3-butadiene: -[6 x (2-H) + 2 x (2=2) + (2-2)] or (to obtain a better error estimate) 2 x $\Delta H_f(C_2H_4)$ + 2 x (2-H) - (2-2) = 137.5 ± 5.3. The experimental value for ΔH_f is 110.0 ± 1.1, giving a difference of 27.5 ± 5.4, presumably due to the conjugation energy not allowed for in the two-atom contributions. The experimental barrier† for rotation round the central bond in butadiene[12,13] is 26.7, in remarkable agreement with the calculated figure, and supporting the validity of the thermochemical approach.

The three atom interactions 3-3-2 and 3-2-3 can be assessed from equations (15) and (16) to be 10.5 ± 1.4 and 5.5 ± 1.3 respectively. The good agreement of the observed and calculated heat of formation for butadiene implies that 2-2-2 is small.

We are now in a position to assess the importance of hybridization effects and radical stabilization, using reactions (17-19). The exothermicity of equation 17 is attributed to a change in hybridization of a carbon-carbon bond from sp^3-sp^3 to sp^3-sp^2, accompanied by a change of hybridization of a carbon-hydrogen bond from sp^2-s to sp^3-s, denoted in shorthand by $3 \rightarrow 2$ [≡(3-2) - (3-3) + (3-H) - (2-H)], along with the interaction 3-2-2.‡ Reaction (18) involves $3 \rightarrow 2$ plus the extra stabilization of the ethyl radical over the methyl radical 'Et' (if any). Reaction (19) involves 3-2-2 minus 'Et'. The ethyl radical is unlikely to be destabilized (since there is some delocalization of spin density on to the CH_3 protons) which puts a lower limit of 5.0 on 3-2-2. This is likely also to be close to the upper limit: any increase in 3-2-2 must be accompanied by a decrease in $3 \rightarrow 2$. However, the (maximum) value of 18.1 for 3-2 corresponds to an sp^3-sp^2 C-C bond only slightly stronger (by 1.8 kJ mol-l) than the mean of 2-2 and 3-3: a value of 16.3 would correspond to 2-3 at the arithmetic mean of 2-2 and 3-3. It is most unusual for bonds between X and Y to be weaker than the mean of X-X and Y-Y: there is normally an increase related to the difference in electronegativities, in this case estimated as 7.0 kJ mol^{-1} from Huheey's data[14], although lower values for the electronegativity difference have been computed, based on appearance potentials and ionization energies of methyl and vinyl.[15]

Thus 3-2 is likely to lie within the range of -77.0 to -78.8, 'Et' between 0.0 and 1.8, and 3-2-2 between 5.0 and 6.8. Mean values of these three quantities have been entered in the table§. Hence the predominant reason for the 'stabilization' of ethyl compared with methyl (reaction 18) is the re-hybridization of the carbon-carbon and carbon-hydrogen bonds, accounting for approximately 17 kJ mol^{-l} of the exothermicity, leaving only 1 kJ mol^{-l} for the extra delocalization in the ethyl radical. The strengthening of the C-C bond on going from sp^3-sp^3 to sp^3-sp^2 hybrid-

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† The barrier for the interconversion of *cis*- to *trans*- 1,3-butadiene is taken from reference 12, the corresponding energy difference from reference 13.

‡ The 3-2-2 interaction includes any stabilization due to the hyperconjugative interaction of the methyl group with the double bond as well as the van der Waals interactions.

§ If the correlation between benzylic and allylic stabilization with the α-CH_2 coupling constant observed by Nicholas and Arnold[16] can be applied to alkyl substituents on methyl[17], a value of 2.9 kJ mol^{-1} for 'Et' is obtained.

Table

Contributions to heats of formation and atomization energies of alkanes, alkenes, and alkyl radicals.

Interaction	Reaction	Contribution to $-\Delta H_f$	Contribution to atomization energy
3-H	1	18.6±0.1	574.5
2-H	13	-48.7±0.3	626.6
3-3	1,3	-27.8±0.7	648.0
3-2	a	-77.9	717.3
2-2	a	-129.8±5.2	784.7
2ˉ2	a	272.0±5.0	272.0
2=2	a	142.2±1.4	1056.7
3-3-3	5	11.5±1.0	
3-3-2	15	10.5±1.4	
3-2-3	16	5.5±1.3	
3-2-2	a	5.9	
2-2-2	a	~0	
gauche[b]	9-12	-3.8±0.6	
ethyl delocalization	a	0.9	

a See text

b In cases where torsion angle cannot be increased above 60°, see text.

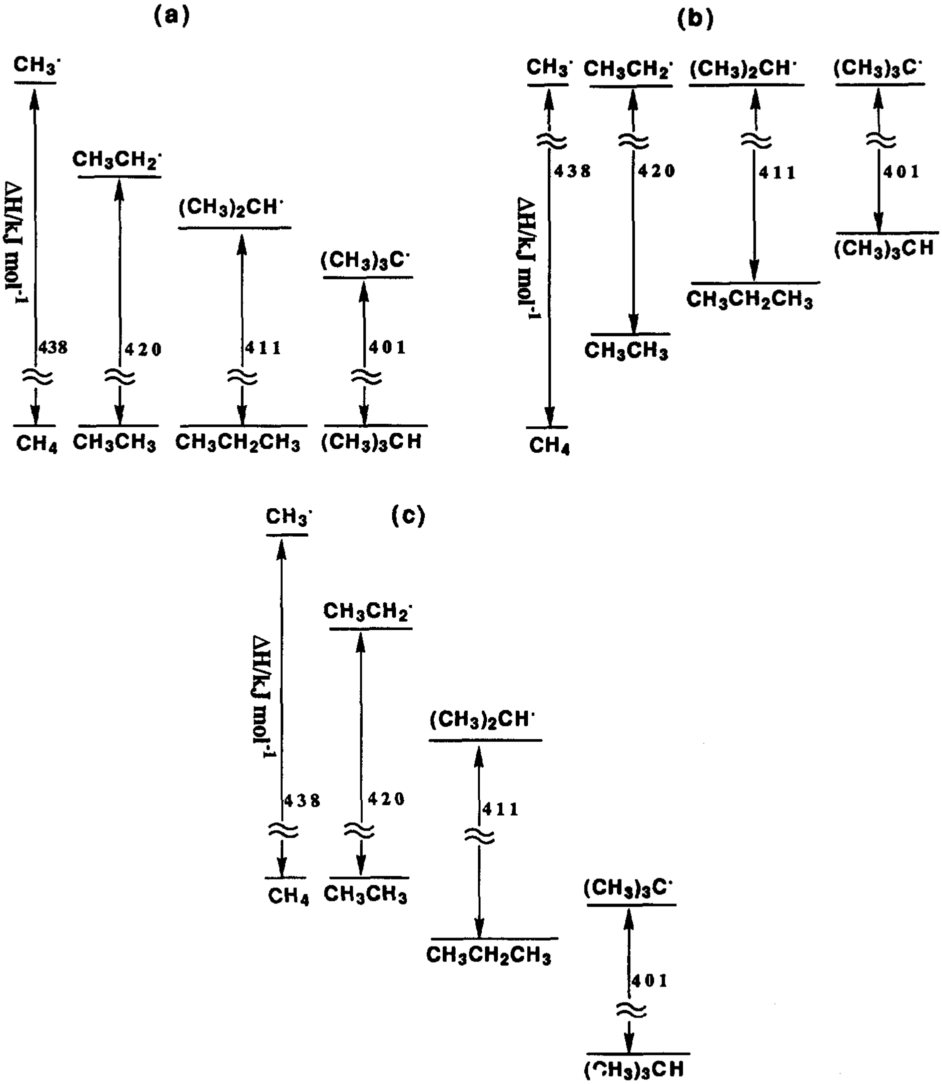
ization (69.3) more than compensates for the decrease in bond strength on changing from C_{sp^2}-H to C_{sp^3}-H (52.1 kJ mol^{-1}).

Reactions (20) and (21) relate to the production of isopropyl and t-butyl‡ respectively. Correction for the introduction of a 3-2-3 interaction in (20) and for two such interactions in (21) gives -15.7 ± 3.7 for (20) and -18.9 ± 4.4 for (21), values that can now be compared directly with the value of -18.1 ± 2.1 for (18), giving agreement with the value for 3→2. Since we have argued in favour of a small value for ethyl stabilization, these results suggest a similar small increase in stabilization on going from ethyl to isopropyl and from isopropyl to t-butyl.

‡ No correction has been made for the non-planarity of t-butyl, which has an inversion barrier[18] of ca. 2 kJ mol^{-1}.

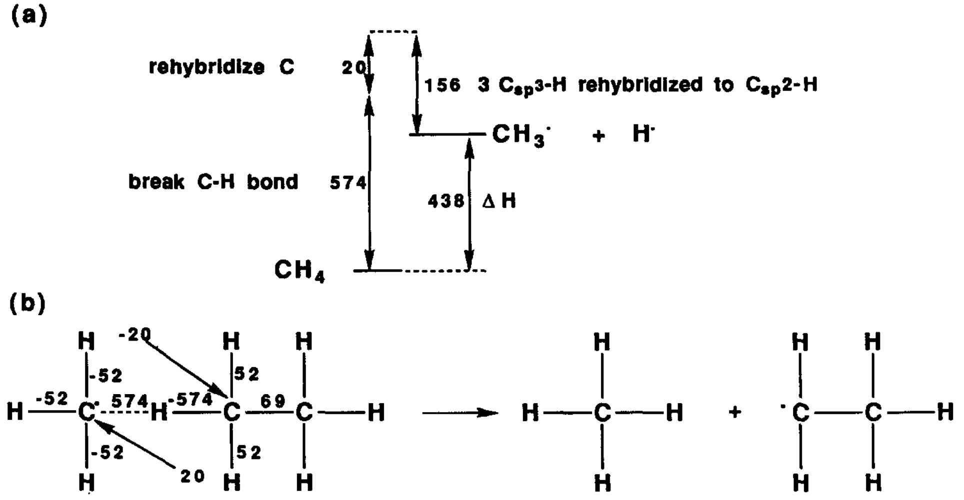
Figure 1

$$R\text{-}H \longrightarrow R^{\cdot} + H^{\cdot}$$



Dissociation energies of C-H bonds in alkanes. (a) 'Usual' interpretation. (b) Interpretation based on destabilization of higher alkanes. (c) Interpretation of this paper: datum line is for alkanes with only C-C and C-H intrinsic energies considered. (a) and (b) are adapted from reference 1.

Figure 2



Contributions to ΔH for (a) dissociation of CH_4 to $CH_3\cdot$ and H· and (b) the metathetical reaction of $CH_3\cdot$ with C_2H_6 to give CH_4 and $C_2H_5\cdot$ Changes in bond strengths and promotion energies on going from left to right in the reaction: (+) more stable in products; (-) less stable in products. Ethyl delocalization energy (ca. 1 kJ mol^{-1}) has not been included.

COMPUTATIONAL DETAILS

Heats of formation of organic molecules with associated error estimates are taken from reference 19, and all refer to the gaseous state and 25°C. Values for organic free radicals are from reference 2. Inorganic values are from reference 20. In computing atomization energies, allowance has been made for the rehybridization of carbon atoms in the valence state.[21] Error estimates of derived thermochemical quantities have been made on the assumption that published error estimates represent standard deviations: variances obtained by squaring these have been summed to give variances of the derived quantity, the square root of the variance giving the standard deviation.

CONCLUSION

Although there is a small stabilization effect due to delocalization in ethyl compared with methyl because the electron is significantly delocalized on to the CH_3 group, this effect is energetically unimportant compared with the rehybridization of carbon-carbon and carbon-hydrogen bonds. Reverting to Rüchardt's hypothesis[1] that changes in bond dissociation energy along a related series of compounds could reflect either stabilization in the radical [Fig. 1(a)] or destabilization in the corresponding hydrocarbon [Fig. 1(b)], we now see that these effects are due to a stabilization in the branched alkanes, which is more than compensated for by the increased stabilization of the tertiary compared with secondary and primary radicals [Fig. 1(c)]. The smaller changes in D(R-H) between ethyl and isopropyl and between isopropyl and t-butyl, compared with that between methyl and ethyl can be seen as due to 3-atom terms in the more highly substituted compounds: these are more stabilizing in the alkanes than in the corresponding radicals. The slight deviation from planarity shown by the t-butyl radical[18] accords with this picture. Substantial and partially compensating changes in bond and atom properties occur on homolytic breakage of covalent bonds [Fig. 2(a)] and metathesis reactions [Fig. 2(b)]; these contributions can now be individually assessed.

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