

Estimation of Bond Dissociation Energies, including $DH^\circ(\text{RSCH}_2\text{-H})$, from Barriers to Internal Rotation

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A linear correlation between C-H bond dissociation energies in molecules of the type $\text{RCH}_2\text{-H}$ and the corresponding barriers to rotation about the $\cdot\text{CH}_2\text{-R}$ bonds is established and used to derive the $\text{C}_\alpha\text{-H}$ bond dissociation energy of sulphides.

In recent years the barriers to internal rotation about the $\cdot\text{CH}_2\text{-R}$ bonds in several free radicals of the type $\cdot\text{CH}_2\text{-R}$ have been determined in hydrocarbon solutions by e.s.r. spectroscopic techniques such as exchange line broadening¹⁻⁵ and steady state of kinetic measurements.⁶⁻⁸ The barriers, V_o , are strongly influenced by the extent of electron delocalisation, which roughly determines the double bond character in the C-R bond, and by inductive-hyperconjugative effects.⁹ The same factors are important in controlling the C-H bond dissociation energies, $DH^\circ(\text{RCH}_2\text{-H})$, so that a relationship between V_o and $DH^\circ(\text{RCH}_2\text{-H})$ is expected. In Table 1 we list the barriers and bond dissociation energies for all the primary species $\text{RCH}_2\cdot$ for which both parameters are now available. The V_o values mostly have confidence limits better than ± 1 kcal mol⁻¹,[†] but the bond dissociation energies, which have been taken from the recent compilation of McMillen and Golden¹⁰ are rather less reliable (see Table 1).

There is a good linear correlation ($r = 0.993$) between the two sets of data (excluding the acetylmethyl results) which may be represented by equation (1). Figure 1 illustrates that

$$DH^\circ(\text{RCH}_2\text{-H})/\text{kcal mol}^{-1} = (97.7 \pm 0.7) - (0.75 \pm 0.04)V_o \quad (1)$$

the DH° values can be calculated to within the experimental error using this relationship for all the compounds except MeCOMe. When more data become available it may well be found that the correlation holds for only a restricted range of

Table 1. Barriers to rotation in $\text{R-CH}_2\cdot$ radicals and $\text{RCH}_2\text{-H}$ bond dissociation energies.

$\text{RCH}_2\text{-H}$	$V_o(\text{R-CH}_2\cdot)/$ kcal mol ⁻¹	$DH^\circ(\text{RCH}_2\text{-H})/$ kcal mol ⁻¹	Keys
MeCH ₂ -H	0.0 ^a	98.2 ± 1	1
EtCH ₂ -H	0.42 ^a	97.9 ± 1	2
HOCH ₂ -H	4.0 ^a	94 ± 2	3
MeOCH ₂ -H	5.3 ^b	93 ± 1	4
MeCOCH ₂ -H	9.4 ^{c,a}	98	5
PhCH ₂ -H	13 ^d	88.0 ± 1	6
CH ₂ =CHCH ₂ -H	15.7 ^e	86.3 ± 1.5	7

^a Ref. 3. ^b Ref. 1, 11. ^c Ref. 12. ^d Ref. 5. ^e Ref. 13. ^f Ref. 10. ^g Key to numbers in Figure 1.

[†] 1 kcal = 4.18 kJ.

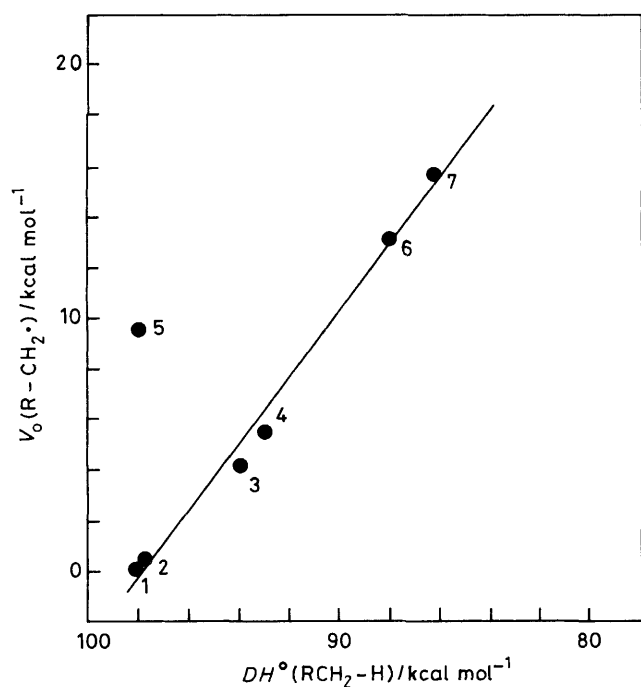


Figure 1

compounds, particularly when steric effects are important, but at present compounds which give planar or non-planar radicals (such as $ROCH_2-H$) fit equally well.

The data for MeCOMe deviate very markedly from the correlation line. The recommended value of 98 kcal mol⁻¹ for $DH^0(\text{MeCOCH}_2-H)$ was derived from studies of the iodination¹⁴ and bromination¹⁵ of acetone, but this result would suggest that there is zero electron delocalisation in acetyl-methyl radicals. However, e.s.r. studies of acetylmethyl and related radicals show significant electron delocalisation onto the carbonyl oxygen;^{3,11} in particular, the ¹⁷O hyperfine splitting in cyclohexanonyl radicals indicates ca. 20% spin density on oxygen.¹⁶ The relatively high rotational barriers suggest approximately 30% allylic character.³ Doubts about the thermochemically measured bond dissociation energy are underlined by a recent e.s.r. study of α -(alkoxycarbonyl)alkyl radicals, $\cdot\text{CH}_2\text{CO}_2\text{R}$, which show that in these radicals there is also partial π -delocalisation onto the carbonyl oxygen and that the barriers to rotation about the $\cdot\text{CH}_2\text{-CO}_2\text{R}$ bond are substantial (ca. 9 kcal mol⁻¹).¹⁷ An earlier study of hydrogen abstraction from acetone by NF_2 radicals led, via the Evans-Polanyi correlation, to a value of 93 kcal mol⁻¹ for $DH^0(\text{MeCOCH}_2-H)$;¹⁸ this would bring the acetylmethyl point to within range of the correlation. It would obviously be advantageous to have a reinvestigation of the thermochemistry of acetylmethyl and related radicals.

This simple empirical correlation will be useful for evaluating thermochemical bond dissociation energies and radical heats of formation. It opens up the possibility of utilising solution phase e.s.r. data, which are relatively easily obtained,

to obtain fundamental thermochemical quantities. For example, we recently found barriers to rotation in $\text{Bu}^t\text{S-CH}_2\cdot$ and 1-adamantyl-S- $\text{CH}_2\cdot$ radicals of 6.1 ± 0.5 and 6.3 ± 0.2 kcal mol⁻¹ respectively, using the e.s.r. exchange broadening technique.¹⁹ Use of the above correlation gives $DH^0(\text{RSCH}_2-H) = 93$ kcal mol⁻¹. Carbon-hydrogen bond dissociation energies have not previously been determined for sulphides by thermochemical methods^{10,20} or otherwise. This result predicts the C-H bonds in sulphides to be 2 kcal mol⁻¹ weaker than those of ethers, which is in agreement with the suggestion that sulphur is more effective at delocalising unpaired spin than oxygen.^{1,19} α -Thioalkoxy groups have a much greater accelerating effect than α -alkoxy groups on the rate of decomposition of substituted azoalkanes $\text{XCMe}_2\text{N=NCMe}_2\text{X}$ again suggesting that sulphur is more effective at delocalising unpaired spin than oxygen.²¹ Our result provides a quantitative measure of this influence.

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