CHEMISTRY

Effect of Hybridization Changes on the Bond Energies of Carbon—Carbon Single Bonds

It has previously been suggested[1] that the energy of a bond is related to the overlap integral of the two atomic orbitals which are thought to form the bond. To try to provide a quantitative expression of this idea we have assumed that the bond energy is directly proportional to the overlap integral of the bond orbitals. The proportionality constant can be evaluated by using the bond energy of the C_{sp}^3 — C_{sp}^3 single bond obtained from experimental values of the heats of formation of saturated long-chain hydrocarbons[2]. The bond energies of the five other types of carbon–carbon single bonds may then be calculated by using tables of overlap integrals[3] and the appropriate bond lengths[4] (Table 1). Then by using the C_{sp}^2–H bond energy, obtained from the same set of data as the tetrahedral carbon–carbon bond energy, and the observed[2] heats of formation of ethylene, propylene, acetylene and propyne, the bond energies for the carbon–carbon double and triple bonds and the C_{sp}^2H and C_{sp}–H bonds can be calculated (Table 1). This table of 'standard' bond energies can then be used to predict the heats of formation and heats of hydrogenation of any unsaturated hydrocarbon for which steric effects are small (Table 2). It is seen that the predicted values are quite close to the experimental ones even in cases where there is usually considered to be considerable resonance or hyperconjungative stabilization; in fact, most of the results show a small destabilization energy probably due to the simplifying assumption of neglecting polar effects and non-bonding interactions.

This conclusion that resonance and hyperconjugative effects are small in comparison with changes in hybridization for non-aromatic compounds is in accordance with the recent views[5] that compounds may be classified into two types : (1) those for which two or more classical structures of equal energy can be written, for example, benzene, for which the resonance stabilization is considerable ; (2) those for which only one low-energy classical structure may be written, for example, butadiene, cyclopentadiene.

Recent examination of the experimental observations originally put forward as evidence for the predominance of resonance or delocalization effects in governing bond lengths[6], dipole moments[7], force constants[8], chemical reactions[9] and electronic spectra [10] support the view that in type (2) molecules, at least, these effects are small compared with other factors previously ignored.

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Table 1. CALCULATED BOND ENERGIES*

Bond type	Bond distance (A.)	Overlap integral	Bond energy (kcal./mole)
C_{sp}^3 — C_{sp}^3	1·543	0·647	(82·76)
C_{sp}^3 — C_{sp}^2	1·530	0·668	85·48
C_{sp}^3 — C_{sp}	1·460	0·715	91·42
C_{sp}^2 — C_{sp}^2	1·470	0·716	91·58
C_{sp}^2 — C_{sp}	1·420	0·754	96·48
C_{sp} — C_{sp}	1·380	0·800	103·60
C_{sp}^3 — H			(98·67)
C_{sp}^2 — H			98·69
C_{sp} — H			102·38
C = C			143·10
C ≡ C			187·23

* Using L_{C-C} = 171 kcal. ; $D(H_2)$ = 104·18 kcal.

Table 2. HEATS OF HYDROGENATION (REF. 2) IN KCAL./MOLE

Substance	Observed ($-\triangle H$)	Calculated ($-\triangle H$)	Stabilization energy
Ethylene	(32·82)		
Propylene	(30·12)		
Acetylene	(75·06)		
Propyne	(69·70)		
2-Butene (trans)	27·62	27·42	−0·20
1 : 3-Butadiene (trans)	57·07	55·50	−1·57
1-Methyl-1 : 3-butadiene	54·11	52·80	−1·31
Styrene*	28·20	26·72	−1·48
Stilbene (trans)*	20·10	20·82	+0·72
1 : 4-Diphenyl-1 : 3-butadiene (trans-trans)*†	44·00	44·62	+0·62
2-Butyne*	65·12	64·73	−0·39
Diphenylethyne*	63·34	59·85	−3·49
Diphenylbutadyne*	126·99	124·67	−2·32
Cyclooctatetraene	98·00	95·84	−2·16
Cyclopentene	26·92	27·38	+0·46
1 : 3-Cyclopentadiene	50·90	51·38	+0·48
Heptafulvene	92·63	96·00	+3·37

* Refers to hydrogenation of aliphathic multiple bonds only.
† Coops, J. et al., Rec. trav. chim., 72, 781 (1953).

Quantitative Paper Chromatography based on the Sub-Micro Titration of Derivatives containing Nitro Groups

An extensive literature on the quantitative paper chromatography of a large variety of organic compounds already exists. Most of these methods are based on : (a) measurement of the optical density of a coloured spot produced on the paper chromatogram by spraying with a suitable reagent ; or (b) measurement of the optical density (in ultra-violet or visible light) of an extract of the component considered, after separation from other components by paper chromatography.

A very simple and rapid method has been developed by us for the quantitative determination of different carbonyl compounds in complex mixtures.

The carbonyl compounds are converted to their dinitrophenyl-hydrazones. The mixture of these derivatives is separated on paper using a modification of the method of Matthias[1]. The bands are cut out, concentrated on a small surface if necessary and put into a small titration vessel containing oxygen-free acetic acid. After addition of a suitable amount of sodium acetate excess 0·003 N titanous chloride solution is added (~0·5 ml.) and the mixture stirred for 5–10 minutes (if necessary at about 50°C.). After acidification with hydrochloric acid the excess is back titrated with 0·03 N ferric chloride, delivered from a micrometer syringe, using rhodanide as an indicator.