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Abstract

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THE ENERGY OF RUPTURE OF C–H BONDS IN HYDROCARBONS

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Deviations from additivity in the heats of formation of molecules of paraffin hydrocarbons are small. This indicates that the comparatively strong dependence of the rupture energies of C—H bonds on the structure of the molecules cannot be explained by the interaction of atoms within the molecule itself. Indeed, on going from methane to the higher members of the series, the average bond energies change by approximately 1 kcal, whereas the bond-rupture energies change by approximately 8 kcal.

It is known that in diatomic molecules the rupture energy of the single bond is exactly equal to the average energy. Upon dissociation of diatomic molecules only atoms are formed. The decomposition of a complex molecule proceeds into two radicals, or into a radical and an atom. It is natural to suppose that it is precisely the radicals formed in decomposition that are responsible for those changes in bond-rupture energies which are observed experimentally. This question has been analyzed most thoroughly by N. N. Semenov (^1).

Pointing out that the cause of the comparatively large variations in bond-rupture energies must be sought not in the properties of the molecules RX, but in the properties of the radicals R and X formed as a result of dissociation of the molecule, N. N. Semenov arrives at a formula which, for the case of rupture of C—H bonds in hydrocarbon molecules, will have the form

$$D(\mathrm{R}-\mathrm{H}) = D^0_{\mathrm{H}} - V(\mathrm{R}), \tag{1}$$

where $V(\mathrm{R})$ is the stabilization energy of the radical R; D^0_{H} is a certain constant quantity.

The gain in energy as a result of stabilization of the radical is caused by the interaction of the free valence with the remaining bonds in the radical. Naturally, the energetic effect of such an interaction will depend both on the state of the free valence itself (π- or σ-state) and on the type of bond with which this free valence interacts. In addition, the degree of this interaction should apparently vary with distance.

Let us assume that the interaction of the free valence with saturated bonds in the radical decreases with distance according to an exponential law. The energy of interaction of the free valence with one bond has the form

$$V_n = \alpha_j e^{-\beta n}, \tag{2}$$

where α_j and β are coefficients characterizing the interaction; n is the number of the carbon atom at which the bond of type j, with which the free valence interacts, is located. For a carbon atom bearing a free–

zero valence, $n = 0$. Summing over all bonds in the radical R, we obtain

$$V(\mathrm{R}) = \sum_{j,n} j\alpha_j e^{-\beta n}, \tag{3}$$

$$D(\mathrm{R-H}) = D^0_{\mathrm{H}} - \sum_{j,n} j\alpha_j e^{-\beta n}, \tag{4}$$

where j is the number of bonds of the j-th type at the n-th carbon atom. Allowing for distance by the number of carbon atoms is, of course, a rough approximation. Comparison of the calculation results obtained from the formula with experimental data will show the degree of reasonableness of this assumption.

Table 1

Energies of rupture of C–H bonds (in kcal)

Bond broken	Pyrolysis of iodides	Electron impact	Photobromination
CH_3—H	102	102	101
C_2H_5—H	97	98	98
n-C_3H_7—H	95	100	–
n-C_4H_9—H	94	101	–
sec-C_3H_7—H	89	97	–
tert-C_4H_9—H	86	89	89

It can be shown that in calculating $V(\mathrm{R})$ the interaction of the free valence with single C–C bonds need not be taken into account, since it is automatically allowed for in the coefficients of interaction of the free valence with other bonds in the radical R.

Table 1 gives experimental data on the energies of rupture of C–H bonds in molecules of paraffin hydrocarbons, obtained by various methods*. The values $D(n\text{-}C_3H_7\text{—H}) = 95$ kcal and $D(n\text{-}C_4H_9\text{—H}) = 94$ kcal are the most reliable of all the values of D(C—H) obtained from data on the pyrolysis of iodides ([3]),

whereas the values of the rupture energies of these same bonds obtained by the electron-impact method are, apparently, greatly overestimated ([4]). If the values of D(C—H) in the methyl groups of propane and butane obtained from data on the pyrolysis of iodides are taken as more correct, then the experimental values of the bond-rupture energies given in Table 1 are satisfactorily described by formula (4) for coefficient values

$$D_{\mathrm{H}}^{0} \simeq 161 \text{ kcal};$$
$$e^{-\beta} \simeq 0.4;$$
$$\alpha_j = \alpha_{\mathrm{CH}} \simeq 20 \text{ kcal}.$$

The formula for calculating the energies of rupture of C–H bonds in molecules of paraffin hydrocarbons will have the form

$$D(\mathrm{C—H}) \simeq 161 - 20 \sum j(0.4)^{n**}. \tag{5}$$

To proceed to the calculation of D(R—H) in unsaturated hydrocarbons, let us calculate α_π, i.e., the coefficient α_j for the interaction of the free valence with a π-bond. In addition, if the free valence located

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* Here and below, experimental values of bond-rupture energies are taken from works ([2,3]).

** From formula (5) one can easily obtain the formula of V. V. Voevodsky ([5]):

$$Q_{\mathrm{CH}} = 78 + 8.0 \sum (0.40)_i^n,$$

whose validity was confirmed on a number of examples.

in the "π-state," is located in the α-position to a π-bond, a conjugation energy of approximately 19-20 kcal is released. ([6,7]). Let us take $E_{\mathrm{conj}} \simeq 20$ kcal. To calculate α_π we shall use the value of the energy of abstraction of an H atom from the methyl group of propylene, equal to 77 kcal. The calculation gives for α_π a value $\simeq 24$ kcal. To calculate the energies of rupture of C–H bonds in molecules containing systems of conjugated π-bonds, let us consider the benzene molecule. We shall denote the coefficient α_j, taking into account the interaction of the free valence with C–C bonds in benzene, by α_{B}. Taking $D(\mathrm{C_6H_5—H}) \simeq 102$ kcal, we obtain $\alpha_{\mathrm{B}} \simeq 11.5$ kcal.

If the benzene molecule is represented as a system with alternating single and double bonds, then the coefficient α_π for the double bonds in benzene will be equal to $2\alpha_{\mathrm{B}} \simeq 23$ kcal, i.e., very close to the value $\alpha_\pi \simeq 24$ kcal found for the interaction of a free valence with an isolated π-bond.

This allows one to suppose that, in calculating D(C—H) in molecules of the type, for example, of butadiene, one may proceed from the usual ideas of alternating single and double bonds.

Having a set of coefficients α_j for the interaction of the free valence with C–H bonds, isolated π-bonds, C–C bonds of the benzene type, and also knowing the numerical values D^0_{H}, $e^{-\rho}$, and E_{conj}, one can use formula (4) to calculate the rupture energies of C–H bonds in hydrocarbon molecules of the most diverse structure. The results of such a calculation and the corresponding experimental data are given in Table 2.

Table 2

Bond broken	D(C—H)$_{\mathrm{calc.}}$, kcal	D(C—H)$_{\mathrm{exp.}}$, kcal	Bond broken	D(C—H)$_{\mathrm{calc.}}$, kcal	D(C—H)$_{\mathrm{exp.}}$, kcal
CH_3—H	101	101–102	$C_6H_5 \cdot C(CH_3)_2$—H	69.4	~ 71
C_2H_5—H	97	96–98	n-$CH_3 \cdot C_6H_4 \cdot CH(CH_3)$—H	73.3	74
n-C_3H_7—H	95.4	~ 95	[[structural formula: fused aromatic ring]]CH_2—H	75.7	76
n-C_4H_9—H	94.7	~ 94	[[structural formula: fused aromatic ring]]CH_2—H	76.6	76
sec-C_3H_7—H	93	89–93	C_6H_5—H	102	102
tert-C_4H_9—H	89	86–89	$CH_2 : CH$—H	101	96–122
cyclo-C_6H_{11}—H	90	~ 92			
$CH_2 : CH \cdot CH_2$—H	77	77			
$CH_2 : C(CH_3) \cdot CH_2$—H	75.4	~ 76			
$C_6H_5 \cdot CH_2$—H	77.4	77.5			
o-$CH_3 \cdot C_6H_4 \cdot CH_2$—H	76.7	~ 75			
m-$CH_3 \cdot C_6H_4 \cdot CH_2$—H	77.2	~ 77			
n-$CH_3 \cdot C_6H_4 \cdot CH_2$—H	77.3	~ 76			
$C_6H_5 \cdot CH(CH_3)$—H	73.4	~ 74			

With the aid of formula (4) it is possible to calculate the rupture energies of C–H bonds in molecules of various X-substituted hydrocarbons, where X may be a halogen atom or some other substituent. For this it is necessary, from at least one experimental value, to calculate α_x, i.e., the coefficient α_j for the interaction of the free valence with the C–X bond.

The proposed method for calculating the dissociation energies of C–H bonds is, of course, very approximate, but it makes it possible to estimate comparatively quickly and simply the strengths of C–H bonds in hydrocarbon molecules of the most varied structures.

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Note: Figure translations are in progress. See original paper for figures.