Tetrahedron, 1960, Vol. 9, pp. 65 to 66. Pergamon Press Ltd. Printed in Northern Ireland

CARBON-CARBON BOND ENERGIES

J. C. Earl
Thurlton, Norwich

(*Received* 23 *October* 1959)

Abstract—Although it is difficult to arrive at entirely reliable and precise values for bond energies of the various types of carbon–carbon bonds, it is possible to estimate probable relative values. This is done in the following discussion without involving the heats of sublimation of diamond or graphite, but the requirement still outstanding is an unequivocal value for any one bond of known order.

We have in diamond a precise standard for the length of the single C–C bond, but data for the energy of the bond are less certain. The heat of sublimation of diamond (124·3 kcal) however precisely it may have been observed experimentally must be interpreted in terms of bond energy with some caution. If it is assumed that it is identical with the heat of dissociation into single carbon atoms, it follows that 62·15 kcal must be the energy of the single C–C bond. There must, however remain some doubt whether dissociation to single carbon atoms is complete and whether other energy-consuming processes are involved.

The heat of sublimation of graphite as a standard in the determination of bond energies is even less satisfactory. Wheland[1] uses the energy equation $a\text{C (graphite)} \rightarrow a\text{C (gas)} - 171{\cdot}7$ kcal in replacement of the earlier[2] $a\text{C (diamond)} \rightarrow a\text{C (gas)} - 124{\cdot}3$ kcal when calculating the energy of C–C and C–H bonds. In consequence, the value of 58·6 kcal arrived at first for single C–C bonds is replaced by the very different value 83·6 kcal. The element of confusion introduced by this change of presumed fundamental standards makes it difficult to assess the significance of such calculations. It is, therefore, proposed to by-pass them as far as possible, in the following discussion.

When diamond is burnt to carbon dioxide it can be assumed that two processes—breakdown of the molecule to atoms and combustion of atomic carbon—are superimposed. For every carbon set free, two single bonds are broken. The net energy release is the heat of combustion of diamond, which has been determined as 94·505 kcal. Therefore, if a be the energy of the single C–C bond and c the energy involved in the formation of carbon dioxide from atomic carbon and molecular oxygen

$$2a = 94{\cdot}505 + c \qquad (1)$$

No certain value can be assigned to either a or c, but the expression is of use for determining the properties of the C–C bonds in the higher paraffins. The heats of combustion of many of the normal paraffins have been determined with accuracy under comparable conditions. For the lower members of the series the increase in heat of combustion with the number of carbon atoms is irregular, but above pentane there is almost complete regularity. For a hydrocarbon C_nH_{2n+2} the processes

---

[1] G. W. Wheland, *Resonance in Organic Chemistry* p. 115. John Wiley, New York (1955).
[2] G. W. Wheland, *The Theory of Resonance and its Application to Organic Chemistry.* p. 75. John Wiley, New York (1944).

concerned in its combustion to carbon dioxide and water are:

(i) the breaking of $(n-1)$ C–C bonds $\rightarrow a_1(n-1)$ kcal
(ii) the breaking of $(2n+2)$ C–H bonds $\rightarrow b(2n+2)$ kcal
(iii) the conversion of n atoms of C into carbon dioxide $\rightarrow nc$ kcal
(iv) the conversion of $(2n+2)$ atoms of H into water $\rightarrow d(2n+2)$ kcal

Applying this to heptane and nonane we get the two equations:

$$6a_1 + 16b = 1160{\cdot}01 + 7c + 16d \text{ kcal}$$

$$8a_1 + 20b = 1474{\cdot}90 + 9c + 20d \text{ kcal}$$

From these equations b and d can be eliminated giving

$$2a_1 = 99{\cdot}55 + c \qquad (2)$$

From the two expressions (1) and (2) it follows that a_1 is greater than a by 2·52 kcal, a piece of information which is of considerable interest and would be more so if a precise value could be assigned to either a_1 or a.

Pauling's scale of empirical bond energies can be correlated with the order of C–C bonds by means of the equation[3]

$$E = 130{\cdot}9 - 8(4 - N)^2$$

where E is the energy and N the order of the bond. This equation does not, however, fit the case where $N = 0$; one must assume that E would then be zero also, whereas the equation would give it a value of 2·9 kcal. If it is assumed that the general form of the equation is correct, it can be written as $E = x - y(4 - N)^2$. When $N = 0$, $E = 0$ and $x = 16y$. This cuts out one of the constants, leaving $E = y[16 - (4 - N)^2]$. Substituting in this equation various values for N, say, 1, 2, 3, 1·55 (graphite), 1·67 (benzene), a series of relative values for E are obtained, namely, $7y$, $12y$, $15y$, $10y$, $10{\cdot}57y$. A precise figure for the energy of any one C–C bond of known order would then enable a self-consistent scale to be established for all C–C bonds. Although this requirement cannot yet be met, interesting results are obtained by assuming that 58·6 kcal, the value judged by Pauling to approximate to the energy of a single bond, is actually the true value. Then y becomes 8·37 and the relative energies given above 58·6, 100·4, 125·5, 83·7 and 88·5 respectively. In this way a means is provided for assigning an energy value to any C–C bond whose length can be measured, since the order and the length are connected by the equation

$$N = \frac{3R_1^2}{R_x^2} - 2$$

(R_1 being the length of a single C–C bond and R_x the length of the bond being investigated: $3R_1^2$ is numerically 7·155).

A test of the validity of the above arguments is furnished by a calculation based on the energy of the C–C bonds in the higher normal paraffins. As has been shown earlier, this is 2·52 kcal greater than that of the true single bond which we have taken to be 58·6 kcal. By applying the equations given above in reverse, the order (1·050) and the length (1·532 Å) of the paraffin C–C bonds can be calculated. The lengths of the C–C bonds in n-pentane, n-hexane and n-heptane have recently been measured by an electron diffraction method and found to be 1·531, 1·533 and 1·534 Å respectively.[4]

---

[3] J. C. Earl, *Tetrahedron* **3**, 355 (1958).

[4] R. A. Bonham, L. S. Bartell and D. A. Kohl *J. Amer. Chem. Soc.* **81**, 4765 (1959).