401. *The Relation between the Force Constant, Internuclear Distance, and the Heat of Rupture of a Linkage.*

By JOHN JACOB FOX and ALBERT EDWARD MARTIN.

Values of the heats of rupture of C–H and C–C linkages are calculated on the assumption that all C–H linkages have very nearly the same heat of rupture. This assumption is justified by force-constant data obtained from spectroscopic observations.

It is shown that a smooth curve is obtained by plotting heat of rupture and internuclear distance for various C–C linkages, and in some simple cases thermochemical data may be used to determine internuclear distances.

INVESTIGATIONS of infra-red absorption spectra of organic substances in the region of 3 μ (cf. Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257) have furnished values for force constants of various C–H and C–C linkages with some accuracy. It is of interest to apply these data to the determination of other molecular constants, such as the heat of rupture of a linkage, and the internuclear separation of the atoms concerned. Force constants for various linkages have been obtained from Raman and infra-red data by many workers. A detailed analysis of the molecular vibrations is necessary, such as that given by Thompson and Linnett (J., 1937, 1376) or by Glockler and Wall (*J. Chem. Physics*, 1937, **5**, 813).

Relation between Force Constant and the Heat of Rupture of a Linkage.—If the distance between two atoms is increased from the equilibrium value r_e to some other distance r, the restoring force, F_e, will be proportional to $r - r_e$ for very small displacements, so that $F_e = k\,(r - r_e)$, where k is the force constant. The energy, U, required for this extension is $\frac{1}{2}F_e(r - r_e) = \frac{1}{2}k(r - r_e)^2$. For large displacements this relation does not hold, but U will be some function of r, say $f(r)$, such that $f(r_e) = 0$ and $f(\infty)$ is the energy of dissociation of the linkage. The energy required to increase the distance from r to $r + dr$ is $dU = f'(r)dr = F.dr$, where F is the force tending to pull the atoms together. Now suppose that this restoring force F at the distance r is balanced by an applied force F; then the two atoms will be in equilibrium under these conditions, and if the distance r is again increased to $r + dr$ an extra restoring force, dF, will come into play and will be equal to $k.dr$, where k is the force constant appropriate to the distance r as already defined. This gives the relation $k = dF/dr = d^2U/dr^2$.

This equation indicates the intimate connexion between force constant and energy of stretching of a linkage, and some calculations we have made show that it is possible to make at least approximate estimates of heats of rupture from the appropriate force constants. The values obtained for C–C linkages from thermal data depend on the value taken for the heat of atomisation of carbon, about which there is much discussion (cf. Kistiakowsky, *J. Physical Chem.*, 1937, **41**, 175; Herzberg, Herzfeld, and Teller, *ibid.*, p. 325; Goldfinger and Jeunehomme, *Trans. Faraday Soc.*, 1936, **32**, 1591; Berriman and Clark, *Proc. Leeds Phil. Soc.*, 1938, **3**, 465), but the energies calculated from the force constants do not require any knowledge of this quantity, so that the agreement between the heats of rupture calculated from force constants and from thermal data depends on the exact value chosen for the heat of atomisation. For the present purpose it is sufficient to take from the literature any available value for the heat of atomisation of carbon, say 150 kg.-cals. per g.-atom, for which Sidgwick has calculated a considerable amount of data ("The Covalent Link in Chemistry," 1933). We can obtain the corresponding values for the heats of rupture of the various C–C linkages, but to do this it is of course necessary to know the values for different C–H linkages, and our calculations indicate that the differences are sufficiently small to be neglected. For example, the maximum difference in length for various C–H bonds, so far as they are known, is about 0·04 A., while the force constant varies from $5{\cdot}88 \times 10^5$ (for C_2H_2) to $4{\cdot}52 \times 10^5$ dynes per cm. (for $>CH_2$) (Fox and Martin, *loc. cit.*). If we imagine the C–H linkage in acetylene to be stretched until the internuclear distance is that found in compounds containing the $>CH_2$ group, but in such a way that the force constant always has the value appropriate to the internuclear separation at every point, then, taking an average force constant of $5{\cdot}2 \times 10^5$ dynes per cm., we have for the energy difference $\frac{1}{2}k(r_2 - r_1)^2$, r_1 and r_2 being the C–H distances for the two linkages. This expression is equal to $\frac{1}{2} \times 5{\cdot}2 \times 10^5 \times (0{\cdot}04)^2 \times 10^{-16} = 0{\cdot}004 \times 10^{-11}$ ergs $\simeq 600$ cals. per g.-mol., and should represent a large part of the energy difference between these two C–H linkages. This difference in comparison with the total heat of rupture of a C–H linkage (~ 94 kg.-cals.) can for the present purpose be ignored.

In Table I we give the values obtained for C–H and various C–C linkages. The C–H and the C–C single bond energies have been chosen to give as good agreement as possible with observations for the saturated paraffins, while the C–C bond energy for diamond is half the value taken for the heat of atomisation of diamond, since the energy to remove one carbon atom from the lattice is equal to the energy of rupture of 2 C–C linkages. The C=C and C≡C energies are obtained from ethylene and acetylene respectively. For $C_{ar.}$–$C_{ar.}$ the mean value found from a few simple aromatic compounds is given. From Table I the heats of rupture can also easily be modified for any value of the heat of atomisation of carbon different from 150 kg.-cals. To show that these calculated values are of general application a few typical heats of formation are given in Table II. The observed values are from Sidgwick (*op. cit.*) and are for hydrocarbons with normal interatomic distances. The importance of this proviso is seen from Fig. 1, in which the bond energy for various C–C bonds is plotted against the internuclear distance. Graphite provides a point on this curve, since the energy to free a carbon atom from the graphite lattice is $\frac{3}{2}C_{gr.}$–$C_{gr.}$, where $C_{gr.}$–$C_{gr.}$ is the C–C bond energy of graphite, instead of 2

C–C in diamond; $\frac{3}{2}C_{gr.}$–$C_{gr.}$ must equal 2 C–C since the heats of combustion of diamond and graphite are the same within experimental error, and so $C_{gr.}$–$C_{gr.} = \frac{4}{3}$C–C = 100 kg.-cals. The internuclear distance in graphite is taken as 1·42 A. (cf. Finch and Wilman, *Proc. Roy. Soc.*, 1936, *A*, **155**, 345). The other C–C distances (in A.) are as follows: acetylene, 1·204, Herzberg, Patat, and Spinks, *Z. Physik*, 1934, **92**, 87; ethylene, 1·33, Penney, *Proc. Roy. Soc.*, 1937, *A*, **158**, 306, from infra-red data of Badger, *Physical Rev.*, 1934, **45**, 648; benzene, 1·40, Pauling and Brockway, *J. Chem. Physics*, 1934, **2**, 867, and Robertson (tetramethylbenzene), *Proc. Roy. Soc.*, 1933, *A*, **142**, 659; diamond, 1·54, calculated directly from density.

TABLE I.

Linkage.	Heat of rupture on assumption that heat of atomisation of carbon is: 150 kg.-cals.	150 ± *x* kg.-cals.
C–C (hydrocarbons)	71·8	71·8 ± $\frac{1}{2}x$
C–C (diamond)	75	75 ± $\frac{1}{2}x$
$C_{ar.}$–$C_{ar.}$ (benzene rings)	105·3	105·3 ± $\frac{3}{4}x$
C=C (olefins)	125·1	125·1 ± x
C≡C (acetylenes)	161	161 ± 1·5x
C–H (all hydrocarbons)	93·6	93·6 ± $\frac{1}{4}x$

TABLE II.

Substance.		Heat of formation (kg.-cals.). Calculated.		Observed.
Ethane	6 C–H	561·6	633·4	634·5
	C–C	71·8		
Benzene	6 C–H	561·6	1193·4	1193·2
	6 $C_{ar.}$–$C_{ar.}$	631·8		
Toluene	8 C–H	748·8	1452·4	1451·0
	1 C–C	71·8		
	6 $C_{ar.}$–$C_{ar.}$	631·8		
p-Xylene	10 C–H	936·0	1711·4	1712·7
	2 C–C	143·6		
	6 $C_{ar.}$–$C_{ar.}$	631·8		
Mesitylene	12 C–H	1123·2	1970·4	1975·3
	3 C–C	215·4		
	6 $C_{ar.}$–$C_{ar.}$	631·8		

FIG. 1.

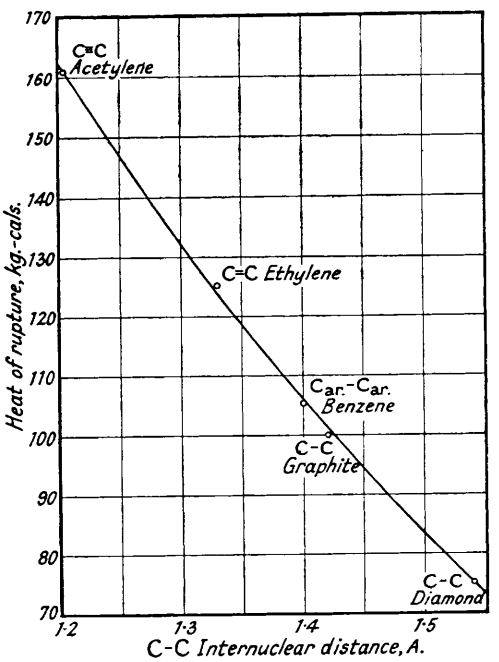
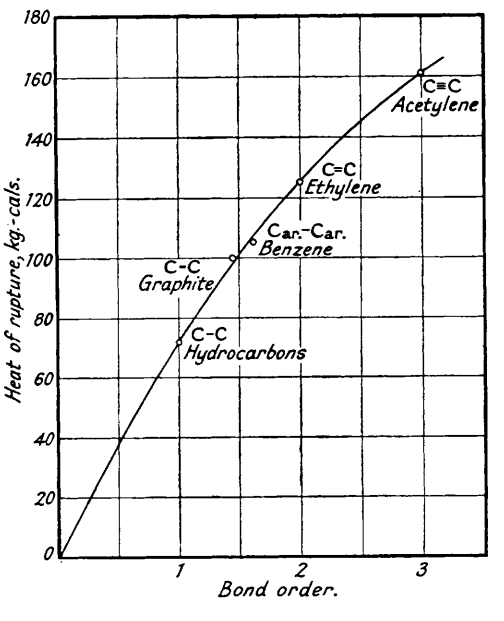


FIG. 2.



It should be noted that the general nature of our results in no way depends on the value chosen for the heat of atomisation of carbon, but of course absolute values are so dependent.

Calculation of Internuclear Distances from Heats of Formation.—Where certain bonds in a molecule may be abnormal, it is not always safe to make calculations similar to those given above, but one can proceed differently in some simple cases and find the bond energy of the abnormal bond or bonds, and then from Fig. 1 find the internuclear distance for the bond. Examples are given below :

Heat of formation of naphthalene	1881·5	Diff. 1132·7
Heat of formation of 8 C–H	748·8	

This energy is required to break the 11 C–C bonds of naphthalene, so that the average energy per C–C bond is 103·0 kg.-cals., and from Fig. 1 this corresponds to an average internuclear distance of 1·41 A., in agreement with the *X*-ray measurement (cf. Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 674).

Heat of formation of *cyclo*hexane	1548·4	Diff. 425·2
Heat of formation of 12 C–H	1123·2	

The energy per C–C linkage is 70·9, and this corresponds to a C–C distance of about 1·56 A., slightly greater than the C–C distance in diamond (1·54 A.).

Relation between Heat of Rupture of a Linkage and Bond Order.—In Fig. 2 we have plotted the heat of rupture for various C–C linkages against the bond order (1 for single bond, 2 for double bond, and 3 for triple bond). It will be seen that we obtain a smooth curve passing through the origin, *i.e.*, zero bond order corresponds with a linkage of zero energy. With regard to graphite and benzene, the bond order to be assigned to the C–C linkages is not so obvious as for the single, double, and triple bonds. If, for example, in graphite we imagine the four valencies of carbon to be divided among the three bonds attached to each carbon atom in the hexagonal molecular sheet, then ignoring forces between the sheets we have a bond order of $\frac{4}{3}$, and similarly for benzene the value $\frac{3}{2}$, but these values do not fit the curve very well. The reason is that for both graphite and benzene there is resonance between several bond structures leading to an increase of stability of the molecule and an enhancement of the bond order. Penney (*Proc. Roy. Soc.*, 1937, *A*, **158**, 306) has used the methods of quantum mechanics to calculate bond orders in molecules of this type and gives 1·45 for graphite and 1·62 for benzene. These are almost exactly the values which one obtains from Fig. 2.

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE, LONDON, W.C. 2.

[*Received, October 25th,* 1938.]