188. *Relations between Internuclear Distance, Force Constant, and Energy of Dissociation for Carbon-to-Carbon Linkages.*

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Combining a relation $D = k_e r_e^2/mn$, derived from a general potential function given by Sutherland, with $k_e r_e^5 = \text{const.}$, it is shown that $D r_e^3 = \text{const.}$ for carbon-to-carbon linkages. When the ratio U/D is plotted against r/r_e a form of curve is obtained which applies to all such linkages.

In a recent paper (J., 1938, 2106) we gave an outline of the relation between r_e, the internuclear distance, k_e, the force constant, and D, the energy of dissociation of a carbon–carbon linkage. It is possible to extend this, since Sutherland (*Proc. Indian Acad. Sci.*, 1938, *A*, **8**, 341) pointed out that for diatomic molecules a simple potential function of the form

$$U = \alpha/r^m - \beta/r^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α, β, m, and n are constants, and r is the internuclear distance, leads to the important result that $D = k_e r_e^2/mn$. He showed that the product mn did not vary much for a number of diatomic molecules; and we have applied this relation to carbon-to-carbon linkages with the following results :

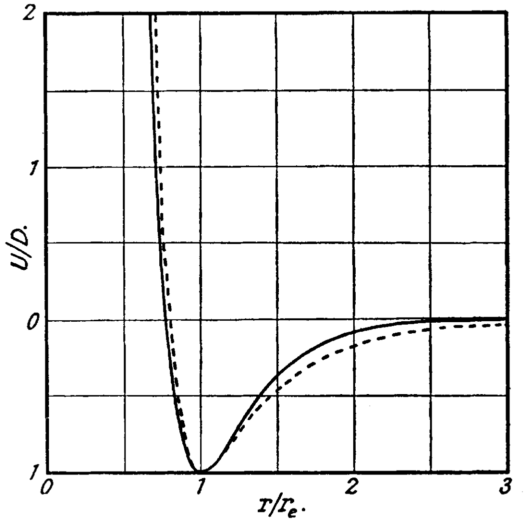
Linkage	C≡C	C═C	$C_{ar.}$—$C_{ar.}$	C—C (hydrocarbons)
k_e (10^5 dynes/cm.)	15·6	9·8	7·6	4·4
r_e (obs.), A.	1·204	1·33	1·40	1·555
D (kg.-cals./g.-mol.)	161	125·1	105·3	71·8
$k_e r_e^2/D = mn$	20·5	20·2	20·6	21·6

In this evaluation of mn, it is necessary to multiply D (cals.) by $4{\cdot}185 \times 10^7/6{\cdot}097 \times 10^{23}$ in order to convert it into ergs per link; mn is seen to be constant within the limits of the accuracy of the data.

Some time ago we found that, although a Morse–Clark relation, of the form $k_e r_e^6 =$ constant, gave very fair results for the C–C linkages, yet the results were even better if we used the fifth power instead of the sixth, as shown below :

Linkage	$C\equiv C$	$C=C$	$C_{ar.}—C_{ar.}$	$C—C$
k_e (10^5 dynes/cm.)	15·6	9·8	7·6	4·4
r_e (calc. from $13{\cdot}2/k_e^{1/6}$), A.	1·226	1·324	1·382	1·514
r_e (calc. from $20{\cdot}93/k_e^{1/5}$), A.	1·208	1·326	1·395	1·556
r_e (obs.), A.	1·204	1·33	1·40	1·555

For C–C linkages, therefore, we have the relations $k_e r_e^2/D =$ constant and $k_e r_e^5 =$ constant, and by eliminating k_e, $r_e^3 D =$ constant. This relation fits the curve connecting r_e and D, which we have previously given (*loc. cit.*; which see also for the origin of the data used here), and Douglas Clark has informed us in a private communication that, working along different lines, he has obtained the same result. Thus, if k_e only is known for a C–C linkage, the corresponding value of D can be found by eliminating r_e between the above equations, whereupon D will be found to vary as $k_e^{\frac{3}{5}}$, and not directly as k_e, as is sometimes assumed.



Full curve from equation (4) (*Morse type*).
Broken curve from equation (5).

Equation (1) can be put in the form

$$U = D\left(\frac{n}{m-n}\right)\left[\left(\frac{r_e}{r}\right)^m - \frac{m}{n}\left(\frac{r_e}{r}\right)^n\right] \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

and this may be compared with the Morse potential function

$$U = D\ [e^{-2ax} - 2e^{-ax}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where $x = r - r_e$, and a is a constant for *each* linkage. If x is small compared with r_e, we can expand (2) and (3), and neglecting powers of x higher than x^2, we have from (2)

$$U = D\ [-1 + mnx^2/2r_e^2]$$

and from (3) $$U = D\ [-1 + a^2x^2]$$

These are Hooke's-law potential functions and are identical provided that $a^2 =$

$mn/2r_e^2$, and since we have seen that for carbon-to-carbon linkages mn is constant, with mean value 20·7, it follows that $a = 3{\cdot}22/r_e$. The Morse function can then be written

$$U/D = [e^{-6{\cdot}44(r/r_e-1)} - 2\,e^{-3{\cdot}22(r/r_e-1)}] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If now U/D is plotted against r/r_e a type of Morse curve is obtained which applies to *all* carbon-to-carbon linkages. The relation $a^2 = mn/2r_e^2$ ensures that both potential functions (2) and (3) are the same in the *immediate* neighbourhood of the equilibrium position ($r = r_e$), but agreement elsewhere can only be approximate, and depends on the values chosen for m and n (mn being fixed). We find that, to obtain the best agreement, m and n must approach equality, and the following calculations are made on this basis :

Put $m - n = \delta$, then from (2) we have

$$\frac{U}{D} = \frac{n}{\delta}\left(\frac{r_e}{r}\right)^m\left[1 - \frac{m}{n}\left(\frac{r}{r_e}\right)^{\delta}\right]$$

and on expansion we have

$$\left(\frac{r}{r_e}\right)^{\delta} = 1 + \delta\ln\frac{r}{r_e} + \frac{\delta^2}{2!}\left(\ln\frac{r}{r_e}\right)^2 + \quad . \quad . \quad .$$

Since δ is here small compared with unity,

$$\begin{aligned}\frac{U}{D} &= \frac{n}{\delta}\left(\frac{r_e}{r}\right)^m\left[1 - \left(1 + \frac{\delta}{n}\right)\left(1 + \delta\ln\frac{r}{r_e}\right)\right]\\ &= -\frac{n}{\delta}\left(\frac{r_e}{r}\right)^m\left[\frac{\delta}{n} + \delta\ln\frac{r}{r_e}\right]\\ &= \left(\frac{r_e}{r}\right)^m\left[m\ln\frac{r_e}{r} - 1\right]\end{aligned}$$

for m is very close to n.

For carbon-to-carbon linkages $mn = 20{\cdot}7$, so that this potential function may be written

$$\frac{U}{D} = \left(\frac{r_e}{r}\right)^{4{\cdot}55}\left[4{\cdot}55\ln\frac{r_e}{r} - 1\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The figure shows the comparison between the curve plotted from this function and a Morse-type curve (equation 4).

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