437. *Theoretical Investigation of Reactivities of Conjugated Bonds. Part II.* The Significance of Some Theoretical Quantities.*

By R. D. Brown.

The significance of the various theoretical quantities which have been suggested as criteria of bond reactivity is studied in detail. It is shown that the bond-localization energy represents an attempt, subject to some approximations, to compute the heat of activation of a bond reaction. Other theoretical quantities such as mobile-bond order and free valence are shown to be related to the first terms of Taylor series for the bond-localization energy. Their successful correlation with experimental reactivities depends upon empirical relations of a statistical nature existing between bond-localization energy and successive terms of its Taylor expansion.

Some additional advantages of discussing bond reactivities in terms of bond-localization energies are indicated.

In Part I * it was shown that the localization theory provides a very satisfactory interpretation of the relative reactivities of conjugated bonds towards reagents such as osmium tetroxide. A series of notes has recently appeared discussing the relative reactivities of the three dinaphthylethylenes in terms of various theoretical quantities (Badger, *Nature*, 1950, **165**, 647; Coulson, *J.*, 1950, 2252; Daudel, *Compt. rend.*, 1950, **231**, 908; Berthier, Berthod, Mayot, and Pullman, *ibid.*, p. 1149) and it would seem desirable to assess the relative merits of these quantities as criteria of reactivity.

The thermodynamic treatment of reaction rates (Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," 1941, p. 195) leads to the equation

$$k = \frac{\boldsymbol{k}T}{\boldsymbol{h}} \,.\, \exp\,(\Delta S^{\ddagger}/\boldsymbol{R}) \,.\, \exp\,(-\Delta H^{\ddagger}/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and ideally we should discuss the relative rate constants in terms of the entropy of activation, $\Delta S^{\ddagger}$, and the heat of activation, $\Delta H^{\ddagger}$. Molecules which react readily with osmium tetroxide are for the most part of such complexity that it is not feasible to calculate $\Delta S^{\ddagger}$ by means of the appropriate partition functions, so the assumption has to be made that the entropies of activation are the same for the reactions of two different bonds, either in the same or in different

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* Part I, *J.*, 1950, 3249.

molecules, with osmium tetroxide. This of course requires $\boldsymbol{R}T \log (k_a/k_b)$ to be independent of temperature, where k_a and k_b are the rate constants for reaction of the two bonds considered at the same temperature. Although rates of reaction of a number of hydrocarbons have been measured (Badger, *J.*, 1949, 456; 1950, 1809; Badger and Lynn, *J.*, 1950, 1726) their temperature dependence has not, so this assumption has not been tested directly so far. However, the approximate quantitative success of the localization theory (Part I) suggests that the assumption is reasonable.

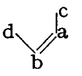
The discussion of relative rates is thus reduced to a discussion of the relative values of $\Delta H^{\ddagger}$. Dewar (*Trans. Faraday Soc.*, 1946, **42**, 767) has in effect shown that the simple molecular-orbital approximation, using an appropriate value for the parameter γ, provides a reliable estimate of the contribution to the molecular *heat content* due to the π-electrons. The environments of reactive bonds in polycyclic hydrocarbons are so similar that differences in heats of activation for such bonds will in good approximation be due to differences in the contributions made by the π-electrons. Again this is borne out indirectly by the approximate quantitative success of the localization theory. The formation of the activated complex will be accompanied by a partial localization of the π-electrons, so the contribution of the latter to the heat of activation may be termed the *heat of localization.* This quantity will provide a relatively sound basis for discussion of relative reactivities of conjugated bonds.

The various theoretical quantities which have been correlated with bond reactivities are, of course, concerned only with the π-electrons, so it is to be expected that the relative merits of these quantities are determined by their degree of correlation with the heat of localization, $\Delta H^{\ddagger}_{\pi}$. The ultimate requirement for reaction of a bond with a molecule of osmium tetroxide is that the former must supply two π-electrons to bind the osmium tetroxide to the carbon atoms at each end of the bond. The π-electron heat of reaction, ΔH_{π}, will consequently be the difference in π-electron heat content of the conjugated system left after reaction (the residual molecule) and of the original conjugated system (apart from some constant amount arising from the π-electrons which form the σ-bonds with the OsO_4 molecule).

The bond-localization energy, B, represents the molecular orbital approximation to ΔH_{π} and the use of this as a criterion of bond reactivity supposes that $\Delta H^{\ddagger}_{\pi}$ is proportional to ΔH_{π}. The rough quantitative success of the localization theory suggests that if an appropriate value of γ is employed, B is in fact a good approximation to $\Delta H^{\ddagger}_{\pi}$. We conclude then that the bond-localization energy is a very good criterion of bond reactivity.

Next we may consider the mechanism of the formation of the activated complex. If it is supposed that the approach of the osmium tetroxide to a particular bond occasions an alteration in the magnitude of the coulomb integrals of the atoms at either end of the bond under consideration, then the change in π-electron heat content may be expanded as a Taylor series :

$$\delta H_{\pi} = (\partial H_{\pi}/\partial\alpha_a)\delta\alpha_a + (\partial H_{\pi}/\partial\alpha_b)\delta\alpha_b + \tfrac{1}{2}\{(\partial^2 H_{\pi}/\partial\alpha_a^2)(\delta\alpha_a)^2 + 2(\partial^2 H_{\pi}/\partial\alpha_a\partial\alpha_b)\delta\alpha_a\delta\alpha_b + (\partial^2 H_{\pi}/\partial\alpha_b^2)(\delta\alpha_b)^2\} + \quad \dots\dots \quad (2)$$



(I.)

α_a, α_b, being the coulomb integrals of atoms a and b at either end of the bond (I). If it is supposed that both coulomb integrals are perturbed by the same amount, *i.e.*

$$\delta\alpha_a = \delta\alpha_b = X\beta \text{ (say)},$$

where β is the resonance integral of a benzene bond, and the differential coefficients in equation (2) are identified with the electron densities, q, and the mutual polarizabilities, π (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, *A*, 1947, **191**, 39), then equation (2) becomes :

$$\delta H_{\pi} = (q_a + q_b)X\beta + \tfrac{1}{2}(\pi_{a,a} + 2\pi_{a,b} + \pi_{b,b})X^2\beta^2 + \quad \dots\dots \quad (3)$$

Now the polarizabilities are computed in units of $1/\beta$, so it is convenient to write :

$$S = \beta(\pi_{a,a} + 2\pi_{a,b} + \pi_{b,b}) \quad \dots\dots\dots \quad (4)$$

and furthermore all hydrocarbons so far studied experimentally are alternant hydrocarbons, for which $q_a = q_b = 1$, so we finally have :

$$\delta H_{\pi} = (2X + \tfrac{1}{2}SX^2 + \dots)\beta \quad \dots\dots\dots \quad (5)$$

It seems reasonable to assume that the magnitude of the perturbation, X, is determined only by the nature of the attacking molecule and its distance from the bond undergoing addition. Then, since the C–O bond lengths in activated complexes of the most reactive bonds of polycyclic hydrocarbons must surely be very similar, the relative changes in H_{π} for the different bonds considered will be determined by the relative values of the sum of polarizabilities, S, *provided* *that the higher terms in the expansion* (5) *can be neglected.* The latter will be the case if X is sufficiently small, but unfortunately there is at present no way of determining the value of X appropriate to the activated complex, and even its sign is not certain because bond reagents are neither electrophilic nor nucleophilic. We cannot therefore decide whether the values of S for various bonds will give a qualitative indication of H_π except by comparison with, say, the corresponding bond-localization energies. We have given some values for the two quantities in Table I.

TABLE I.*

Hydrocarbon.	Bond.	*S.*	*B*(-*β*).	Hydrocarbon.	Bond.	*S.*	*B*(-*β*).
Benzene	—	0·481	1·528	Ethylene	—	0	0
Naphthalene	1 : 2	0·422	1·259	Butadiene	1 : 2	0·224	0·472
	2 : 3	0·590	1·729		2 : 3	0·714	2·472
Anthracene	1 : 2	0·404	1·204	Hexatriene	1 : 2	0·322	0·516
	2 : 3	0·590	1·786		2 : 3	0·791	2·298
					3 : 4	0·332	0·988
Phenanthrene	1 : 2	0·455	1·319				
	2 : 3	0·563	1·655				
	3 : 4	0·458	1·338				
	9 : 10	0·345	1·065				

* Polarizability data taken from Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, *A*, 1947, **192**, 16; *J.*, 1949, 971.

The correlation of S with B is reasonably good (for the cyclic hydrocarbons the points all lie close to a straight line passing through the origin), but unfortunately in the wrong sense. As S is a positive number, and β a negative energy quantity, the smallest activation energy would correspond to the *greatest* value of S, and to the *smallest* value of B. It will be noticed that the reactive bonds correspond to the smallest values of S however. We are forced to the conclusion that the higher terms in the expansion (5) are important or that *the attacking molecule gives rise to other more important perturbations.*

The next possibility is that the osmium tetroxide produces a change in the resonance integral, β_{ab}, between the atoms a and b. Proceeding in the same way we write

$$\delta H_\pi = (\mathrm{d}H_\pi/\mathrm{d}\beta_{ab})\delta\beta_{ab} + (\mathrm{d}^2H_\pi/\mathrm{d}\beta_{ab}^2)(\delta\beta_{ab})^2/2\,! + \;.\;.\;.\;.\;. \quad (6)$$

$$= 2p_{ab}\delta\beta_{ab} + \tfrac{1}{2}\pi_{ab,\,ab}(\delta\beta_{ab})^2 + \;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (7)$$

and, if it is assumed that $\delta\beta_{ab}$ has the same value for all activated complexes, the relative values of δH_π will be determined by the mobile bond orders, p_{ab}, of the various bonds considered, provided that the second and higher terms are negligible. Again this will depend upon the magnitude of $\delta\beta_{ab}$. It would be expected that $\delta\beta$ is negative,† so that if p_{ab}, the mobile order of bond ab, does determine the π-electron heat of activation, then the most reactive bond would be that of highest mobile order. The fact that mobile-bond order has been widely used as an index of bond reactivity (*e.g.*, Badger, *J.*, 1950, 1809), together with the very high degree of

TABLE II.

Hydrocarbon.	*B*(-*β*).	*p.*	*T.*	Σ*F.*
Pentaphene	1·006	0·790	1·936	0·812
1 : 2-Benzanthracene	1·030	0·783	1·974	0·807
1 : 2-7 : 8-Dibenzanthracene	1·041	0·780	1·992	0·804
1 : 2-5 : 6-Dibenzanthracene	1·045	0·778	2·000	0·804
Pyrene	1·057	0·777	2·012	0·800
Phenanthrene	1·065	0·775	2·024	0·798
3 : 4-Benzophenanthrene	1·102	0·762	2·082	0·795
Picene	1·108	0·758	2·098	0·795
Chrysene	1·121	0·754	2·118	0·793
Pentacene	1·183	0·742	2·216	0·768
Naphthacene	1·188	0·741	2·222	0·767
Anthracene	1·204	0·738	2·242	0·763
1 : 2-3 : 4-Dibenzanthracene	1·241	0·727	2·292	0·760
Naphthalene	1·259	0·725	2·316	0·752
Triphenylene	1·383	0·690	2·480	0·740
Benzene	1·528	0·667	2·667	0·693

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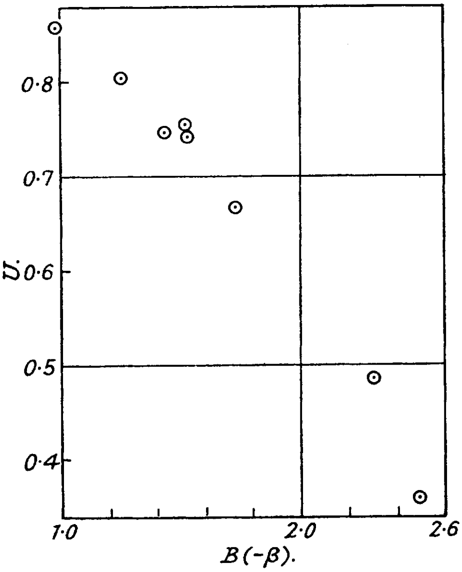
† This supposes that the mechanism of addition consists first in increasing the mobile order of the bond ab to a value approaching that of ethylene, followed by addition to this perturbed bond. One could, however, imagine mechanisms which would require $\delta\beta$ to be positive. The correlation of these p_{ab} values with B_{ab} indicates that these latter mechanisms must be rejected.

correlation of p with bond-localization energy of the most reactive bond for a considerable number of polycyclic hydrocarbons (Table II), suggests that $\delta\beta$ is relatively small. Some idea of the changes involved can be gained as follows. It has been found empirically (Brown, unpublished work) that

$$\mathrm{d}p_{\mathrm{ab}}/\mathrm{d}\beta_{\mathrm{ab}} = \pi_{\mathrm{ab,\,ab}} \simeq 3(1 - p_{\mathrm{ab}})/4\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

for various bonds in isolated molecules. If we suppose that this approximation also holds for a small change in the resonance integral of a given bond, then we may integrate expression (8) to derive $\delta\beta_{\mathrm{ab}}$ from δp_{ab}. Suppose that p_{ab} is increased from 0·8 to 0·9; a simple calculation shows that this corresponds to $\delta\beta_{\mathrm{ab}} = \beta\,\frac{4}{3}\log 2 \simeq 0{\cdot}9\beta$. Such an estimate of $\delta\beta$ cannot be regarded as quantitatively reliable but it serves to show that the value of $\delta\beta$ corresponding to formation of the activated complex is not likely to be so small that the second and higher terms in equation (7) can be neglected (for bonds of mobile order around 0·7 to 0·8, $\pi_{\mathrm{ab,\,ab}}/2$ is of the order of $0{\cdot}1/\beta$).



It would seem that the success of the correlation of, say, p_{ab} with B_{ab} is due in part to the additional linear relation (8) between $\pi_{\mathrm{ab,\,ab}}$ and p_{ab}, and hence between $\pi_{\mathrm{ab,\,ab}}$ and B_{ab}. It is quite possible that higher terms are similarly related to B, but they have not so far been investigated.

It is of interest to put $\delta\beta_{\mathrm{ab}} = X\beta$ in expression (7) and to substitute (8) for $\pi_{\mathrm{ab,\,ab}}$. The result is

$$\delta H_\pi = [3X + (16 - 3X)p + \ldots]X\beta/8 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

so that, provided that the effect of higher terms can be neglected, one would obtain an inverse correlation of p with δH_π unless X is smaller than 16/3; such a huge perturbation to β_{ab} would not be physically reasonable, but equation (9) brings out the opposing tendencies of p and π on δH_π.

Neither of the localization mechanisms so far considered corresponds to localization of the bond under consideration; their effect is to build up the electron density in the bond or at the atoms at either end of it. Localization of the bond is achieved, however, if the resonance integrals of all adjoining bonds are reduced in magnitude. Again the heat content change may be expanded as

$$\begin{aligned}\delta H_\pi &= (\partial H_\pi/\partial\beta_{\mathrm{ca}})\delta\beta_{\mathrm{ca}} + (\partial H_\pi/\partial\beta_{\mathrm{bd}})\delta\beta_{\mathrm{bd}} \\ &\quad + [(\partial^2 H_\pi/\partial\beta^2_{\mathrm{ca}})(\delta\beta_{\mathrm{ca}})^2 + 2(\partial^2 H_\pi/\partial\beta_{\mathrm{ca}}\partial\beta_{\mathrm{bd}})\delta\beta_{\mathrm{ca}}\delta\beta_{\mathrm{bd}} \\ &\qquad + (\partial^2 \mathrm{H}_\pi/\partial\beta^2_{\mathrm{bd}})(\delta\beta_{\mathrm{bd}})^2]/2 + \ldots\ldots \\ &= 2(p_{\mathrm{ca}} + p_{\mathrm{bd}})X\beta + (\pi_{\mathrm{ca,\,ca}} + 2\pi_{\mathrm{ca,\,bd}} + \pi_{\mathrm{td,\,bd}})X^2\beta^2 + \quad . \quad . \quad . \qquad (10)\end{aligned}$$

assuming the resonance integral perturbations to bonds ca and bd (I) to be both equal to $X\beta$. For complete localization the corresponding value of X is of course -1, so in this case we can be fairly sure that higher terms become rapidly less important when we use the value of X corresponding to the activated complex. We can write equation (10) as

$$\delta H_\pi = (TX + UX^2 + \ldots\ldots)\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The values of the coefficient T are listed in Table II. These show at least as good a correlation with B as does p, and indeed it would be better to use the sum of the mobile orders of bonds adjoining a given bond as a criterion of its reactivity than to use its own mobile order. Clearly, as X is now negative, if the reactivity is determined by T, then the *smaller* T the more reactive the bond. The justification for using T in this way will depend upon the magnitude of the sum of polarizabilities, as well as of X, and so far we have established only that the latter is less than unity. Some values of U for bonds in butadiene, hexatriene, benzene, naphthalene, and styrene whose environments are similar to (I) in that they all have just two neighbouring bonds, are shown plotted against B in the accompanying figure. The values of U were computed from the polarizability data of Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, *A*, 1948, **193**, 447). It is seen that the two are related approximately by a smooth curve which is nearly linear. This does not hold, however, when there is other than one adjoining bond at either end of the one in question; for example, U for ethylene is zero and for the αβ-bond of styrene is 0·338, and discrepancies are also found for the 9 : 10- and 1 : 9-bonds of naphthalene.

This relationship between U and B might be the cause of the correlation between T and B because U is by no means negligible compared with T. It is quite possible that similar relationships between B and higher coefficients are to be found; indeed correlations between apparently unrelated molecular-orbital quantities seem to be the rule rather than the exception.

It would seem from the above discussion that the value of T for a bond is a sounder criterion of reactivity than p, because it is only in the case of the former that we can determine the relative importance of higher terms in the energy expansion, since we know that the magnitude of X must be less than unity. In both cases the successful correlation with reactivity must in part be due to the approximate monotonic relationships mentioned above between both p and T and their higher terms in the expansions (7) and (11).

Another quantity which has been widely used in the discussion of chemical reactivity is free valence. The free valence of atom a of a conjugated system is defined by :

$$F_a = N_{\text{max.}} - \Sigma_i p_{ai} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the summation is over all atoms i adjacent to a. It is easily seen that $F_a + F_b$ is a linear combination of p_{ab} and T_{ab}. The latter both bear approximate linear relationships to B_{ab}, so the same must be true of the sum of the two free valences, $F_a + F_b$. Values of ΣF for the most reactive bonds of a number of polycyclic hydrocarbons are listed in Table II. The correlation with B is as good as those involving p and T, so ΣF is another quantity which could be used as a criterion of bond reactivity. It is to be emphasised, however, that the use of ΣF in this connection is as empirical as the use of p or T. The bond localization energy, B, is more fundamentally related to the heat of activation, and hence to the chemical reactivity, of a bond than is p, T, or ΣF. Nevertheless this state of affairs would be resolved if the mathematical structure of the molecular-orbital theory could be shown to imply the various statistical relations which have been found between the various theoretically defined quantities.

It has also been proposed (Badger, *J.*, 1950, 1809) to use the oxidation–reduction potential of the *o*-quinone as an index of the reactivity of a bond. The assumption here is that the transition state has a quinonoid electronic structure. However, there is no evidence on which to base this hypothesis. The correlation which Badger notes between oxidation–reduction potential and mobile-bond order is a necessary consequence of the empirical relation between p and B. The correlation with oxidation–reduction potential follows because B represents the increase in H_π in going from the original hydrocarbon to the *o*-quinone, assuming that the $C{=}O$ bonds in the latter do not form a part of the conjugated system and also that the carbonyl groups do not cause any perturbations to coulomb or resonance integrals. Oxidation–reduction potentials have been discussed in terms of quantities equivalent to B (Evans, *Trans. Faraday Soc.*, 1946, **42**, 113; Diatkina and Syrkin, *Acta Physicochim.*, 1946, **21**, 921) and linear relations found between the two.

Evidently the oxidation–reduction potential is to be regarded as an empirical criterion of bond reactivity with rather less justification than p, T, and ΣF.

Finally it is to be noted that the bond-localization energy involves only energy quantities, and that improved values of B could be obtained by refining the energy calculations. The same is not true of p, T, ΣF, and the oxidation–reduction potential. The first three are not observables, they are mathematical conveniences of the molecular-orbital theory, and there is no way of improving their calculation if the values at present used are found unsatisfactory. The other advantage of the bond-localization energy is that it is a linear function of the heat of activation and so can be employed to estimate relative reaction rate constants. This feature is particuarly useful when comparing the reactivities of a pair of hydrocarbons such as 1 : 2-benzanthracene and 1 : 2-7 : 8-dibenzanthracene. The former has one bond very much more reactive than all the others while the latter, from its symmetry, has two equivalent bonds of high reactivity. The values of B, p, T, and ΣF (Table II) all indicate that the benzanthracene bond is more reactive than the dibenzanthracene bond, but the question arises whether the presence of two such bonds in dibenzanthracene will be sufficient to increase the total reactivity to more than the benzanthracene value. If we employ the values of B, then by converting them into relative rate constants and summing over all bonds in the two molecules we obtain the total reactivities of the two hydrocarbons. It is then found (Part I, Table II) that in fact the total reactivity of dibenzanthracene is greater than of benzanthracene although the most reactive bond of the latter is more reactive than the most reactive bond of the former. Clearly such a result could not have been obtained from considerations of values of p, T, or ΣF because it is not clear how the individual values are to be combined to obtain the total molecular reactivity. However, the various empirical relations with B offer a possible method of doing this when the bond localization energies have not been directly computed.

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