

633. *Theoretical Investigation of Reactivities of Conjugated Bonds.*

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The relative reactivities of aromatic hydrocarbons with bond reagents such as osmium tetroxide and ozone are investigated by the localisation theory. Theoretical results for all aromatic hydrocarbons containing up to five rings are presented. It is shown that quantities termed "bond localisation energies" may be employed to derive reaction-rate constants with unexpected precision. The consequences of this precision and the mechanism of bond reactions are discussed.

THE relative reactivities of hydrocarbons towards reagents such as osmium tetroxide, ozone, and diazoacetic ester have usually been considered as characterising the mobile orders of the bonds attacked (Badger, *J.*, 1949, 456; *J. Proc. Roy. Aust. Chem. Inst.*, 1950, 17, 14). In a discussion of the ozonolysis of naphthalene, Kooyman and Ketelaar (*Rec. Trav. chim.*, 1946, 65, 859) used experimental resonance energies to calculate the energy required to convert a conjugated bond into a double bond. The latter energy has been termed the "bond localisation energy" by the author, who showed that it was closely related to bond order when both quantities are calculated by the molecular-orbital method (*Aust. J. Sci. Res., A*, 1949, 2, 564). In the present paper complete tabulations of bond localisation energies, calculated by the LCAO approximation and denoted by B or B' according as overlap is neglected or included (for nomenclature see Brown, *Trans. Faraday Soc.*, 1950, 46, 146), are given for all aromatic hydrocarbons containing five or less rings. In addition, a more complete correlation with chemical properties will be given.

Method of Calculation.—The bond localisation energy, B , is defined as the difference in resonance energy of the original molecule, R , and of the molecule left after removal of the atoms at each end of the bond under consideration, R_r . The latter molecule (or molecules) is termed the residual molecule and it is easy to show that the quantity B so defined is the energy required to convert the bond into a double bond (Brown, *loc. cit.*, 1949). Hence, $B = R - R_r$. The

problem is then to calculate R and R_p . The various methods of obtaining these by the LCAO approximation have been summarised by Brown (*loc. cit.*); the extension to larger conjugated systems has been facilitated by the discovery of an empirical method of deducing the resonance energy from the resonance energies of two smaller systems (Brown, *Trans. Faraday Soc.*, in the press). The resonance energies of many of the residual molecules have been estimated by using some empirical relationships for deriving conjugation energies (*idem, loc. cit.*, 1949; further results in course of publication). The resultant bond localisation energies are listed in the tables. The values of B' have been converted into kcal./mole by using the conversion factor $\gamma = -33.6$ kcal.

Mechanism of Bond Reactions.—These reactions are characterised by the property that reaction occurs very readily with ethylenic bonds, saturated compounds do not enter into reaction, and aromatic bonds are of intermediate reactivity. It seems likely that these reactions may be regarded as additions to a particular bond, the hydrocarbon being required to furnish two of its π -electrons to form two new σ -bonds between the reagent and the hydrocarbon. In the activated complex the presence of incipient σ -bonds will require at least partial localisation of two of the π -electrons in the bond being attacked, and these partial σ -bonds will be so long that delocalisation of electrons from the attacking reagent over the conjugated system of the hydrocarbon will be precluded even if they possess the requisite symmetry properties.

It is now reasonable to assume that the variable portion of both the energy of activation and the heat of reaction will be due mainly to the varying ease with which the two π -electrons mentioned above can be partly or wholly localised in the bond being attacked. The energy required to achieve complete localisation is just the bond localisation energy, and the assumption will be made that the LCAO approximation to this energy is representative of the relative energies of activation as well as of heats of reaction. It remains to assume constancy of entropy of activation and of reaction (this will generally mean that the most stable products are most rapidly formed), these assumptions being implicit in the qualitative electronic theory widely employed in current organic literature, and being necessary in the present localisation theory in the absence of more detailed information.

On these assumptions it is easy, given the bond-localisation energy, to compute rates of reaction of various hydrocarbons relative to, say, phenanthrene, just as has been done elsewhere (Brown, *J.*, 1950, 691) when discussing the Diels-Alder reaction. In Table I the relative

TABLE I.

(a) *Tricyclic hydrocarbons.*

Bond.	$B(-\beta)$.	B' .		k_p .	Bond.	$B(-\beta)$.	B' .		k_p .
		$(-\gamma)$.	kcal.				$(-\gamma)$.	kcal.	
Anthracene.					Phenanthrene.				
1 : 2	1.204	0.597	20.0	0.001 ₉	1 : 2	1.321	0.712	23.9	—
2 : 3	1.786	1.141	38.3	—	2 : 3	1.655	1.012	34.0	—
					3 : 4	1.338	0.725	24.4	—
					9 : 10	1.065	0.4843	16.2	1.000

(b) *Tetracyclic hydrocarbons.*

Naphthacene.					Chrysene.				
1 : 2	1.188	0.581	19.5	0.0044	1 : 2	1.121	0.540	18.1	0.04 ₃
2 : 3	1.798	1.155	38.8	—	3 : 4	1.303	0.692	23.3	—
					4 : 5	1.712	1.032	34.7	—
					5 : 6	1.318	0.704	23.6	—
1 : 2-Benzanthracene.					3 : 4-Benzphenanthrene.				
1' : 2'	1.358	0.745	25.0	—	1 : 2	1.102	0.525	17.6	0.10
2' : 3'	1.604	0.961	32.3	—	1' : 2'	1.302	0.692	23.3	—
3' : 4'	1.340	0.730	24.5	—	2' : 3'	1.708	1.028	34.5	—
3 : 4	1.030	0.455	15.3	5.1	3' : 4'	1.311	0.698	23.4	—
5 : 6	1.224	0.617	20.3	—					
6 : 7	1.767	1.122	37.7	—					
7 : 8	1.227	0.619	20.8	—					
Pyrene.					Triphenylene.				
1 : 2	1.057	0.476	16.0	1.6	1 : 2	1.383	0.769	25.8	10 ⁻⁷
					2 : 3	1.595	0.955	32.1	—

TABLE I (continued).

(c) *Pentacyclic hydrocarbons.*

Bond.	$B(-\beta)$.	B' .		k_p .	Bond.	$B(-\beta)$.	B' .		k_p .
		$(-\gamma)$.	kcal.				$(-\gamma)$.	kcal.	
Pentacene.					2 : 3-5 : 6-Dibenzphenanthrene.				
1 : 2	1.183	0.577	19.4	0.005 _s	1' : 2'	1.219	0.613	20.6	—
2 : 3	1.803	1.160	39.0	—	2' : 3'	1.779	1.135	38.2	—
1 : 2-Benznaphthacene.					3' : 4'	1.223	0.615	20.7	—
1' : 2'	1.357	0.744	25.0	—	1'' : 2''	1.306	0.694	23.3	—
2' : 3'	1.562	0.919	30.9	—	2'' : 3''	1.712	1.066	35.8	—
3' : 4'	1.339	0.729	24.5	—	3'' : 4''	1.298	0.687	23.1	—
3 : 4	1.014	0.447	15.0	8.0	7 : 8	1.117	0.540	18.1	0.04 ₃
7 : 8	1.187	0.580	19.5	—	9 : 10	1.065	0.490	18.5	0.72
8 : 9	1.788	1.143	38.4	—	5 : 6-Benzchrysenes.				
9 : 10	1.187	0.580	19.5	—	1 : 2	1.166	0.586	19.7	0.0033
Pentaphene.					3 : 4	1.089	0.511	17.2	0.22
1 : 2	1.236	0.627	21.1	—	1' : 2'	1.308	0.698	23.4	—
2 : 3	1.757	1.111	37.3	—	2' : 3'	1.673	1.031	34.6	—
3 : 4	1.232	0.625	21.0	—	3' : 4'	1.316	0.705	23.7	—
6 : 7	1.006	0.432	14.5	18	7 : 8	1.100	0.520	17.5	0.13
1 : 2-3 : 4-Dibenzanthracene.					9 : 10	1.308	0.699	23.5	—
1' : 2'	1.40	0.78	26	—	10 : 11	1.677	1.035	34.8	—
2' : 3'	1.568	0.921	30.9	—	11 : 12	1.324	0.711	23.9	—
3' : 4'	1.40	0.78	26	—	1 : 2-5 : 6-Dibenzanthracene.				
5 : 6	1.241	0.633	21.3	0.0002 _s	1' : 2'	1.349	0.736	24.8	—
6 : 7	1.737	1.094	36.8	—	2' : 3'	1.626	0.984	33.1	—
4 : 5-Benzchrysenes.					3' : 4'	1.331	0.721	24.2	—
1 : 2	1.084	0.504	16.9	0.33	3 : 4	1.045	0.468	15.7	2.4
1' : 2'	1.219	0.612	20.6	—	1 : 2-7 : 8-Dibenzanthracene.				
2' : 3'	1.779	1.134	38.1	—	1' : 2'	1.348	0.735	24.7	—
3' : 4'	1.223	0.614	20.6	—	2' : 3'	1.625	0.983	33.0	—
7 : 8	1.137	0.564	18.9	0.011	3' : 4'	1.330	0.720	24.2	—
9 : 10	1.292	0.682	22.9	—	3 : 4	1.041	0.465	15.6	2.9
10 : 11	1.716	1.069	35.9	—	3 : 4-Benzpyrene.				
11 : 12	1.314	0.699	23.5	—	1 : 2	1.110	0.525	17.6	0.1 ₀
1 : 2-Benzchrysenes.					6 : 7	1.019	0.440	14.8	12
1' : 2'	1.37	0.75	25	—	1 : 2-Benzpyrene.				
2' : 3'	1.627	0.980	32.9	—	6 : 7	1.0 _s	0.5 ₀	17	<1
3' : 4'	1.37	0.75	25	—	Picene.				
3 : 4	1.37	0.76	26	—	1 : 2	1.309	0.700	23.5	—
4 : 5	1.631	0.984	33.0	—	2 : 3	1.678	1.036	34.8	—
5 : 6	1.37	0.76	26	—	3 : 4	1.235	0.712	23.9	—
7 : 8	1.151	0.569	19.1	0.008 _s	5 : 6	1.186	0.602	20.2	—
9 : 10	1.288	0.678	22.8	—	11 : 12	1.108	0.527	17.7	0.09
10 : 11	1.718	1.071	36.0	—	3 : 4-5 : 6-Dibenzphenanthrene.				
11 : 12	1.296	0.685	23.0	—	1 : 2	1.090	0.513	17.2	0.2
					1' : 2'	1.309	0.700	23.5	—
					2' : 3'	1.674	1.033	34.7	—
					3' : 4'	1.317	0.707	23.7	—
					9 : 10	1.147	0.571	19.2	0.008

reactivity of the bond under consideration compared with the 9 : 10-bond of phenanthrene is listed as k_p , the values applying to room temperature (*i.e.*, $RT = 0.6$ kcal.). Thus, expressing B' in units of $-\gamma$, we have

$$k_p = \exp[56(0.484 - B')]$$

The experimental rate of reaction of course corresponds to the sum of the k_p over all bonds, the summation being simplified owing to the very great spread of values of k_p for the various bonds of a given molecule (many bonds are not considered in the Tables because it is clear qualitatively that the corresponding residual molecules are so unstable that k_p would be insignificantly small).

In Table II, which lists the hydrocarbons in order of predicted reactivity, these summations are listed relative to the summation for phenanthrene in the column headed Σk_p . In almost every case any difference between Σk_p and k_p for the most reactive bond is due to the latter's being repeated in the molecule from the molecular symmetry. The number of equivalent bonds of highest k_p value is also listed in the column of Table II headed "Stat. factor" (statistical factor).

Discussion of Results.—Considering, first, the smaller hydrocarbons, it will be noticed that for naphthalene the most reactive bond is predicted (Table II) to be the $\alpha\beta$ -bond, and comparison with the value of k_p for a benzene bond indicates that naphthalene will be more reactive than the latter in bond reactions (bond-localisation energies for bonds of naphthalene other than the $\alpha\beta$ -bond are given by Brown, *loc. cit.*, 1949). This is confirmed by the observation that naphthalene reacts with osmium tetroxide in concentrated solution whereas benzene is unreactive (Badger, *loc. cit.*, 1950). Addition to the $\alpha\beta$ -bond of naphthalene leaves styrene as the residual molecule, which explains the observed formation of a di-adduct (Badger, *loc. cit.*) as due to the very small bond localisation energy of the styrene $\alpha\beta$ -bond (Brown, *loc. cit.*). Ozonolysis experiments confirm the superior reactivity of the $\alpha\beta$ -bond in naphthalene (Wibaut and van Dijk, *Rec. Trav. chim.*, 1946, **65**, 413; Kooyman, *ibid.*, 1947, **66**, 201).

The bond localisation energies indicate that anthracene similarly will be more reactive than benzene and naphthalene. Addition to the 1 : 2-bond leaves β -vinylnaphthalene, the exocyclic bond of which has a very low bond localisation energy, so that di-addition is to be expected. This again agrees with the formation of a di-adduct with osmium tetroxide found experimentally (Badger, *loc. cit.*).

The bond localisation energy of the 9 : 10-bond of phenanthrene is considerably smaller than any of the values for the preceding three hydrocarbons, this being confirmed experimentally by the osmium tetroxide reaction, which proceeds more readily than for the above compounds, attack occurring at the 9 : 10-bond (Cook and Schoental, *J.*, 1948, 170; *Nature*, 1948, **161**, 237; Badger and Reed, *ibid.*, p. 238). The superior reactivity of the 9 : 10-bond is also demonstrated by its reaction with diazoacetic ester (Drake and Sweeney, *J. Org. Chem.*, 1946, **11**, 67), and probably by ozonolysis experiments (Harries and Weiss, *Annalen*, 1905, **343**, 369).

TABLE II.

Idealised relative reaction rates of hydrocarbons.

Hydrocarbon.	Bond.	Stat. factor.	$B(-\beta)$.	$B'(-\gamma)$.	Σk_p .
Pentaphene	6 : 7	1	1.01	0.43	18
3 : 4-Benzpyrene	6 : 7	1	1.02	0.44	12
1 : 2-Benznaphthacene	3 : 4	1	1.01	0.45	8
1 : 2-7 : 8-Dibenzanthracene	3 : 4	2	1.04	0.47	6
1 : 2-Benzanthracene	3 : 4	1	1.03	0.46	5
1 : 2-5 : 6-Dibenzanthracene	3 : 4	2	1.05	0.47	5
Pyrene	1 : 2	2	1.06	0.48	3
Phenanthrene	9 : 10	1	1.07	0.48	1
2 : 3-5 : 6-Dibenzphenanthrene	9 : 10	1	1.07	0.49	0.8
5 : 6-Benzchrysene	3 : 4	1	1.09	0.51	0.4
3 : 4-5 : 6-Dibenzphenanthrene	1 : 2	2	1.09	0.51	0.4
4 : 5-Benzchrysene	1 : 2	1	1.08	0.50	0.3
1 : 2-Benzpyrene	6 : 7	1	1.08	0.50	< 1
3 : 4-Benzphenanthrene	1 : 2	2	1.10	0.53	0.2
Picene	11 : 12	2	1.11	0.53	0.2
Chrysene	1 : 2	2	1.12	0.54	0.09
Pentacene	1 : 2	4	1.18	0.58	0.02
Naphthacene	1 : 2	4	1.12	0.58	0.02
1 : 2-Benzchrysene	7 : 8	1	1.15	0.57	0.009
Anthracene	1 : 2	4	1.20	0.60	0.007
1 : 2-3 : 4-Dibenzanthracene	5 : 6	2	1.24	0.63	0.0005
Naphthalene	1 : 2	4	1.26	0.65	—
Triphenylene	1 : 2	6	1.38	0.77	—
Benzene	—	6	1.53	0.89	—

TABLE III.

Predicted and observed rate constants for addition of osmium tetroxide.

Hydrocarbon.	Predicted.	Observed.	Hydrocarbon.	Predicted.	Observed.
Benzanthracene	(1)	(1)	Phenanthrene	0.2	0.1
3 : 4-Benzpyrene	2	2.0	5 : 6-Benzchrysene	0.06	slow
1 : 2-5 : 6-Dibenzanthracene	1	1.3			

Coming now to the four-ring hydrocarbons we notice that for naphthacene the most reactive bond is the 1 : 2-bond, its reactivity lying intermediate between those of anthracene and phenanthrene, but closer to the former; di-addition again would be expected. However, no experimental data are available for this compound.

In the case of 1 : 2-benzanthracene the 3 : 4-bond has easily the smallest bond localisation energy, smaller than for the 9 : 10-phenanthrene bond. Again, experimental observation confirms this as the site of attack by osmium tetroxide (Cook and Schoental, *loc. cit.*), which, occurs more rapidly than for phenanthrene (Badger and Reed, *loc. cit.*). Indeed, the bond localisation energies indicate that benzanthracene will be the most reactive of all polycyclic hydrocarbons containing four or fewer rings. It is interesting to compare the valence-bond results for bond indices, which indicate that benzanthracene will be less reactive than phenanthrene (Pullman, *Ann. Chim.*, 1947, 2, 5; Pullman and Pullman, *Experientia*, 1946, 2, 364).

Chrysene and 3 : 4-benzphenanthrene have k_p values such that they should be rather more reactive than anthracene and naphthacene, but not nearly as reactive as phenanthrene and benzanthracene. In the case of the former compound the 1 : 2-bond will be the most reactive, and this has been observed for the reaction with osmium tetroxide (Cook and Schoental, *loc. cit.*); no investigation has been made for benzphenanthrene.

The 1 : 2-bond of pyrene should also be very reactive, as judged by its k_p value, its reactivity being exceeded only by that of benzanthracene among the tetracyclic hydrocarbons. This bond has been found to add osmium tetroxide (Cook and Schoental, *loc. cit.*), and it seems likely that the mono-adduct so formed would react with another mole of osmium tetroxide because it contains the phenanthrene system of bonds. Cook and Schoental used equimolar quantities of hydrocarbon and tetroxide, so this point does not seem to have been tested experimentally [phenanthrene is less reactive than pyrene (Table II) so the second stage would take place more slowly than the first, in contrast to naphthalene and anthracene]. A similar double attack occurs in the reaction of pyrene with ozone (Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, 531, 1).

The remaining tetracyclic hydrocarbon, triphenylene, is less reactive than any of the hydrocarbons considered above with the exception of benzene. It is so much less reactive than naphthalene, as judged from its k_p value, that it could not be expected to react with osmium tetroxide at all. The 1 : 2-bond is presumably the more reactive, and it may prove possible to demonstrate this by ozonolysis experiments.

We now consider the pentacyclic hydrocarbons which have been investigated experimentally. Complete theoretical data for all pentacyclic hydrocarbons (apart from perylene, see below) are given in Table I(c).

The reactivity of 1 : 2-5 : 6-dibenzanthracene is very similar to that of 1 : 2-benzanthracene, as judged from the respective values of Σk_p . This is borne out quite well by rate measurements for the osmium tetroxide addition (Badger, *J.*, 1949, 456), attack being presumably at the 3 : 4-bond.

5 : 6-Benzchrysene (1 : 2-5 : 6-dibenzphenanthrene) is less reactive than phenanthrene, which, in turn, is less reactive than benzanthracene; this also is in good agreement with Badger and Reed's rate measurements (see below). Again, the site of attack does not seem to have been established, but from the present theory is doubtless the 3 : 4-bond.

As a final crucial test of the present calculations (and their implied mechanism for bond reactions, as discussed above), the predicted relative rates may be compared with some directly measured rates for the bimolecular reaction of osmium tetroxide with the hydrocarbons in chloroform containing pyridine at 20° ($RT = 0.583$ kcal.). For these particular results it is more convenient to report values of k_b , *i.e.*, the rates relative to benzanthracene, and for 20°. The results are shown in Table III, which includes the relative value for phenanthrene reported by Badger and Reed (*loc. cit.*). The agreement is astonishingly good, particularly in view of the simplifying assumptions mentioned above. This means that it is likely that two of the π -electrons are very strongly localised in the activated complex and that the entropy of activation stays sensibly constant, the only portion of the heat of activation varying appreciably from hydrocarbon to hydrocarbon being calculable in good approximation by the LCAO method.

It remains to consider the hydrocarbon perylene. The residual molecules from localisation of the 1 : 2- or the 2 : 3-bonds are both methylene derivatives of benzanthrene and would be expected to be unstable, so that neither bond will be very reactive. In view of this the rather unwieldy secular determinants for these two residual molecules have not been reduced to determine the resonance energies directly, but the following superficial discussion serves to indicate the relative bond reactivities of perylene. The residual molecule (I) for the 2 : 3-bond

will be more stable than that for the 1 : 2-bond (II) because six Kekulé-type structures can be written for the former and only three for the latter; this is borne out by the experimental fact



that the benzanthrone corresponding to the former is quite stable and readily prepared while the benzanthrone corresponding to (II) is unknown ("Elsevier's Encyclopædia of Organic Chemistry," Vol. 14, pp. 459—471). Thus the 2 : 3-bond will be the more reactive. This, of course, could also have been deduced from the mobile bond orders (Baldock, Berthier, and Pullman, *Compt. rend.*, 1949, **228**, 931). From the mobile order of the 2 : 3-bond and the empirical relationship with B' (Brown, *loc. cit.*, 1949) the value of B' for the bond may be deduced to be -0.69γ . This places perylene in the class of hydrocarbons less reactive than naphthalene, *i.e.*, it is not likely to react with osmium tetroxide even under the forcing conditions employed for reaction with naphthalene. The lack of bond reactivity is also illustrated by the fact that attempts to prepare an *o*-quinone have not proved successful (Clar, "Aromatische Kohlenwasserstoffe," p. 230). This is likely only when there is no particularly reactive bond in the molecule [the stability, and so, frequently, the ease of formation, can be shown to be closely related to bond localisation energy in the case of *o*-quinones (Brown, in course of publication)].

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