879. *Reactivities of Aromatic Hydrocarbons. Part I. Bromination.*

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Reaction of molecular bromine in 85% acetic acid at 25° with benzene, diphenyl, and naphthalene is shown to be nearly of the third order. Under the same conditions that of phenanthrene is nearly of the second order, owing to the predominance of addition over substitution. The relative reactivities of benzene, diphenyl, and naphthalene, which cover a range of $>10^5$, are proportional to the atom localisation energies of the most reactive positions in these molecules, the correlation giving an apparent β value of -29 kcal./mole for bromination. The significance of the β values for a number of aromatic substitutions is discussed in relation to a limiting β value derived from the relative ionisation constants of the aromatic hydrocarbons.

It has been shown that the free energies of activation ($\Delta G^\ddagger$) for electrophilic [1,2] and free-radical [1,3] substitution in a series of aromatic hydrocarbons are linearly proportional to the atom localisation energies ($E_L\beta^{-1}$) of the most reactive position in the hydrocarbon, and that the relative free energies of substitution in the various positions of a polycyclic aromatic nucleus give a similar correlation with the $E_L\beta^{-1}$ values of these positions.[1] The atom localisation energy of a given position in an aromatic hydrocarbon, which is the difference in π-electron energy between the hydrocarbon (*e.g.*, benzene) and the corresponding Wheland intermediate [4] (*e.g.*, I), is obtained [5] in terms of the empirical carbon–carbon resonance integral (β), which, from the resonance energies of the aromatic hydrocarbons, has the value of about -20 kcal./mole in the Hückel approximation.[6] From the gradients of the correlations between $\Delta G^\ddagger$ and $E_L\beta^{-1}$ in a series of hydrocarbons apparent β values for a number of substitution reactions have been derived.[1-3] In a number of cases the apparent β values are smaller than the Hückel value, from which it has been inferred [1] that

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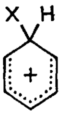
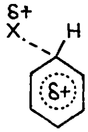
[1] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[2] Dewar and Mole, *J.*, 1957, 342.
[3] Coulson, *J.*, 1955, 1435.
[4] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.
[5] Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.
[6] Coulson, " Valence," Oxford University Press, 1952, p. 240.

the Wheland intermediate (*e.g.*, I) is only partly formed (*e.g.*, II) in the transition state for aromatic substitution. The linear relations between $\Delta G^\ddagger$ and $E_L\beta^{-1}$, and the different apparent β values, are then accounted for if it is assumed that the degree to which the intermediate is formed in the transition state is constant in a series of hydrocarbons for a given reaction, but varies from one substituting reagent to another.


(I)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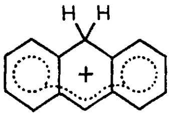
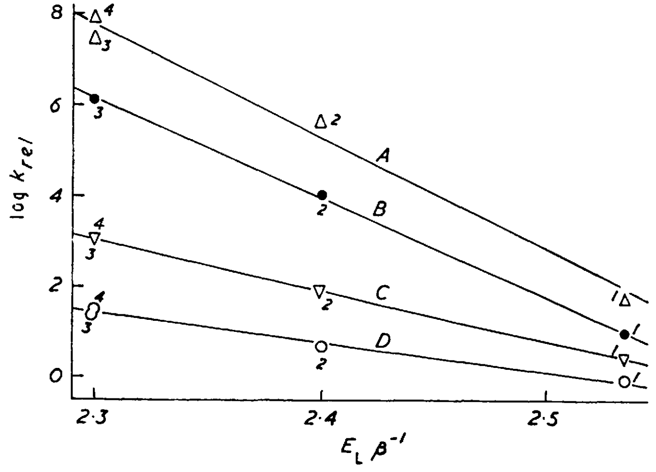

(III)

The apparent β values for the various reaction-series increase with the selectivity of the attacking reagent for substitution at the most reactive position in a given aromatic compound,[1,2] from which it may be supposed that the transition state for substitution more nearly resembles the intermediate the greater the selectivity of the attacking reagent. On the basis of Hückel localisation energies,[5] some apparent β values are —7 kcal./mole for the attack of methyl radicals,[3] —16 kcal./mole for the attack of trichloromethyl radicals,[7] nitration,[1] and hydrogen–deuterium exchange,[8] and, for chlorination,[2] —28 and —36 kcal./mole for substitution in acetic acid and in 3 : 1 carbon tetrachloride–acetic acid the relative reactivities of benzene, diphenyl, naphthalene, and phenanthrene towards molecular bromine in 85% acetic acid have now been measured. The kinetics of the reaction between molecular bromine and aromatic hydrocarbons are complex,[17,18] but the relative reactivities of a number of benzene derivatives with bromine in acetic acid have been obtained from the time required to achieve a given percentage of reaction under a standardised set of conditions.[16,17,19,20] This method was employed in the present study, the conditions adopted being given by the following considerations. In glacial acetic acid the reaction between bromine and benzene is very slow at 25°, whilst naphthalene in the same circumstances gives reaction kinetics nearly of the fourth order.[17,18] In 85% acetic acid, however, the rate of reaction between bromine and benzene at 25° becomes measurable, the kinetics given by a number of benzene derivatives being approximately of the third order,[16,17] and there were indications that naphthalene under the same conditions would give third-order kinetics over a certain concentration range.[17,18]

The relations between the atom localisation energy ($E_L\beta^{-1}$) and the logarithms of (A) the relative ionisation constants,[10] *(B) the relative rates of bromination, (C) the relative rates of nitration,*[1] *and (D) the relative rates of reaction with methyl radicals*[3] *of* (1) *benzene,* (2) *diphenyl,* (3) *naphthalene, and* (4) *phenanthrene.*



At the concentrations studied, and under the above conditions, it is found (Table) that benzene, diphenyl, and naphthalene react approximately according to a third-order kinetic law. The reaction of phenanthrene is, however, very nearly of the second order (Table), probably owing to the predominance of the 9 : 10-addition of bromine over nuclear substitution, so that little or no hydrobromic acid is formed to remove bromine as the tribromide ion or hydrogen tribromide and thus to increase the order with respect to bromine.[21] Only the relative reactivities of benzene, diphenyl, and naphthalene, based on the times required for 5 and 10% reaction, are, therefore, comparable. The relative reactivities cover a range of greater than 10^5 (Table), and the relative free energies of activation are found to increase with the atom localisation energies of the most reactive

[redacted]

completely formed in the transition states for these reactions. It has been argued [22] that the absence of an isotope effect in aromatic nitration and bromination [23] demonstrates that the transition state in electrophilic substitution cannot resemble the Wheland intermediate, since there should be a marked fall in zero-point energy when the C–H bond of the carbon atom under attack changes from sp^2 to sp^3 hybridisation. Although the stretching frequency of a C–H bond falls with such a change of hybridisation, the deformation frequencies rise, and the overall energy change is small, the calculated zero-point energies being 2400 and 2367 cm.$^{-1}$ for sp^2 and sp^3 C–H bonds respectively.[23]

The times required for 5% and 10% reaction between benzene, diphenyl, naphthalene, and phenanthrene with bromine in 85% acetic acid at 25°. The orders of the reaction (n), the relative reactivities (R) of the hydrocarbons, and the atom localisation energies of the most reactive position in the hydrocarbon ($E_L\beta^{-1}$).

Hydrocarbon	[ArH] (molar)	[Br$_2$] (molar)	T (5%) (min.)	T (10%) (min.)	n	R	$E_L\beta^{-1}$ [b]
Benzene	0·45	0·0425	—	77,000 [a]	~3	1	2·536
	0·60	0·06	19,000	44,000			
Diphenyl	0·10	0·01	610	1350	3·05	$1\cdot1 \times 10^3$	2·400
	0·167	0·0167	215	460			
Naphthalene	0·04	0·005	23·5	51	2·95	$1\cdot4 \times 10^5$	2·299
	0·08	0·01	6·0	13·5			
Phenanthrene	0·01	0·002	9·0	21	2·12	—	2·299
	0·02	0·004	20	47			

[a] Quoted from ref. 16. [b] Quoted from Part II (to follow).

The absence of an isotope effect in bromination and nitration is consistent with the theory of aromatic substitution presented above, but there are other aspects of the theory which are less satisfactory. In electrophilic substitution with molecular halogens the reactants are neutral species,[21] and the formation of a transition state resembling the Wheland intermediate requires the separation of charge. The apparent β values for chlorination suggest that the transition state more nearly resembles the intermediate in 3 : 1 carbon tetrachloride–acetic acid than in acetic acid solution, which leads to the unsatisfactory conclusion that the separation of charge in the transition state is larger in the solvent of lower ionising power. Again, bromination in aqueous acetic acid and chlorination in glacial acetic acid give nearly the same apparent β values, though bromine is the more selective reagent and aqueous acetic acid the solvent of higher ionising power.

For substitutions of a series of aromatic hydrocarbons it is probable that there are major variables other than the atom localisation energy of the position attacked, notably, the solvation energy of the transition state. For electrophilic substitution the Wheland intermediate is an odd alternant carbonium ion with the positive charge dispersed over the starred atoms. The spread of the charge varies in a determinate manner from one intermediate to another, and the solvation energy of the intermediate, particularly that due to the charging process,[24] should vary likewise in a series of aromatic hydrocarbons. The influences of the atom localisation energy and the solvation energy of the transition state upon the course of electrophilic substitution may be distinguished in principle, as the former is an internal-energy and the latter a free-energy term. The temperature gradient of the solvation energy should, therefore, give rise to a difference in the entropy of activation between one hydrocarbon and another in a reaction with a given reagent. The differences should be most marked with a reaction in which the Wheland intermediate is the most completely formed in the transition state, namely, in a reaction with a reagent of high orientational selectivity. Although molecular bromine is the most selective reagent for substitution, the kinetic complexities of bromination do not allow the entropies of

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[22] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
[23] Melander, *Arkiv Kemi, Min., Geol.*, 1950, **2**, 211.
[24] Mason, *J.*, 1958, 808.

activation to be measured at all readily, and the supervention of addition limits the range of hydrocarbons which may be studied. Accordingly, chlorination in acetic acid was chosen for the investigation of the entropies of activation in aromatic substitution, which it is hoped to describe subsequently.

EXPERIMENTAL

Acetic acid was treated by standard methods [17-20] and had m. p. 16·5°. "AnalaR" bromine was used without further purification. "AnalaR" benzene was dried (Na) and fractionated, the middle portion, b. p. 80°, being collected. Naphthalene was of an analytical grade, and phenanthrene was purified by treatment with maleic anhydride.[2] After recrystallisation, diphenyl had m. p. 70°, and phenanthrene m. p. 100°.

Rate Measurements.—These were carried out by standard methods,[16, 20] sealed tubes being used, in conjunction with controls, in the case of benzene, and brown bottles for the polycyclic hydrocarbons. To avoid losses by evaporation, the bottles were filled and not more than three samples were taken from any one bottle. The reactions were followed by pipetting 5—10 c.c. samples into excess of 5% potassium iodide solution and titrating these mixtures against 0·05—0·002N-sodium thiosulphate. The percentage of reaction was plotted against time, and the 5% and the 10% intercept were noted.

THE UNIVERSITY, EXETER. [*Received, June 20th*, 1958.]