691. *Electrophilic Substitution. Part VI.* The Nitration of Aromatic Hydrocarbons; Partial Rate Factors and their Interpretation.*

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The work on aromatic nitration described in the five preceding papers of this series is reviewed, and partial rate factors are shown to correspond closely to the predictions of the molecular-orbital theory. The relative reactivities of hydrocarbons also run parallel to those for methylation and trichloromethylation by radicals. The nature of the transition state in aromatic substitution and its correlation with reactant structure are discussed.

For reasons outlined in the first paper [1] of this series, aromatic substitution is a suitable reaction for testing theories of chemical reactivity; a preliminary survey indicated that useful data could be obtained from a study of the nitration of hydrocarbons by nitric acid in acetic anhydride.

In Part V [5] we described a study of the relative reactivities of a number of such hydrocarbons by the competitive method, and in the other Parts [1-4] we reported the proportions of isomers found by the nitration of individual hydrocarbons under standard conditions. From these data we have calculated the partial rate factors, shown in the Table, for nitration at various positions in the different hydrocarbons.

Hydrocarbon	Position [a]	Partial rate factor [b]	Reactivity number [c]
Benzene	—	1	2·31
Diphenyl	2	30	2·07
Diphenyl	4	18	2·07
Naphthalene	1	470	1·81
Naphthalene	2	50	2·12
Phenanthrene	1	360	1·86
Phenanthrene	2	92	2·18
Phenanthrene	3	300	2·04
Phenanthrene	4	79	1·96
Phenanthrene	9	490	1·80
Pyrene	1	17,000	1·51
Triphenylene (1, 9)	1	600	2·00
Triphenylene	2	600	2·12
Chrysene	2	3500	1·67
Perylene	3	77,000	1·34
Benzo[*a*]pyrene	6	108,000	1·15
Coronene	—	1150	1·80
Anthanthrene	6(?)	156,000	1·03

[a] " Ring Index " numbering. [b] Allowance is made for the number of positions of each type. [c] The reactivity numbers were found by the method described previously (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*) and agree, with two minor exceptions, with the values listed there.

A commonly accepted theory of aromatic substitution is that first proposed by Wheland.[6] He assumed that the annular carbon atom, i, undergoing attack changes its hydridisation, becoming tetrahedral in the transition state and so being removed from conjugation with the remainder of the aromatic system. In the transition state both the reagent, X, and the hydrogen atom being replaced are attached to this carbon atom by normal σ-bonds. If entropy effects can be neglected, the velocity constant, k_i, is given by the equation:

$$\log k_{\mathrm{i}} = A_{\mathrm{X}} - (\delta E_{\pi})_{\mathrm{i}}/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A_X is a constant characteristic of the reagent, X, and $(\delta E_\pi)_i$ is the change in conjugation energy of the aromatic system when atom i is removed from it.

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* Part V, preceding paper.

[1] Bavin and Dewar, *J.*, 1956, 164.
[2] Dewar and Mole, *J.*, 1956, 1441.
[3] Dewar and Warford, *J.*, 1956, 3570.
[4] Dewar, Mole, Urch, and Warford, *J.*, 1956, 3572.
[5] Dewar, Mole, and Warford, *J.*, 1956, preceding paper.
[6] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

For substitution in an even alternant hydrocarbon, the Wheland transition state is an odd alternant hydrocarbon. For this case it can be shown[7] that we can, as an approximation, re-write equation (1) in the form:

$$\begin{aligned}\log k_i &= A_X + 2\beta(a_{0r} + a_{0s})/\boldsymbol{R}T \\ &= A_X + \beta N_i/\boldsymbol{R}T \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)\end{aligned}$$

where β is the carbon–carbon resonance integral, and a_{0r} and a_{0s} are the coefficients of the atomic orbitals of the atoms r and s, adjacent to atom i in the non-bonding molecular orbital of the transition state. The rate of reaction is therefore determined by the quantity $2(a_{0r} + a_{0s})$ which is termed[1] the reactivity number (N_i) of the atom i.

It follows that

$$\log k_i/k_0 = \beta(N_i - N_0)/\boldsymbol{R}T \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where k_0 and N_0 are the corresponding values for benzene. Fig. 1 shows a plot of $\log_{10} k_i/k_0$, calculated from the data in the Table, against the corresponding reactivity numbers.[7, 8]

FIG. 1. *Plot of* $\log_{10} (k_i/k_0)$ *against* N_i *for nitration of hydrocarbons by nitric acid in acetic anhydride.*

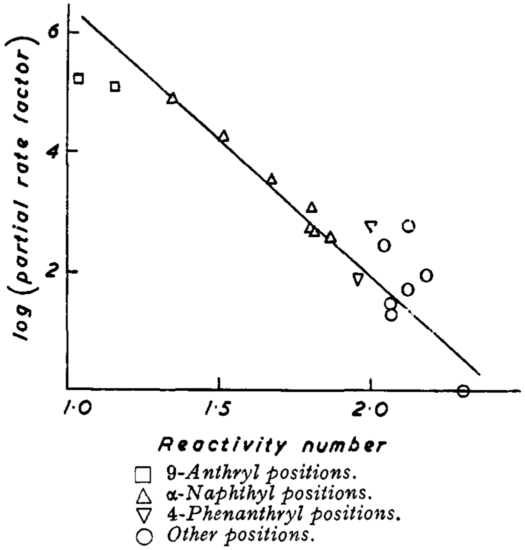
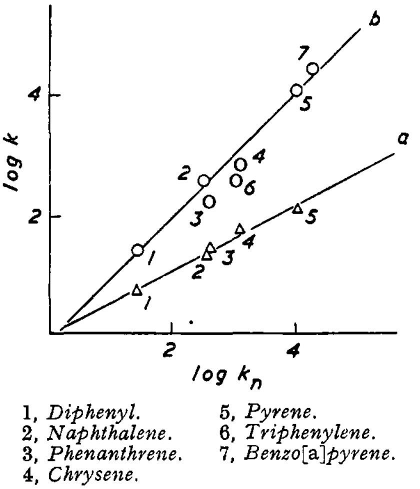


FIG. 2. *Plot of* (*a*) $\log_{10} k_M$ *and* (*b*) $\log_{10} k_T$ *against* $\log_{10} k_N$.



The points lie reasonably well on a straight line. This test of the theory is quite severe since the observed values of k_i cover a range of $10^5 : 1$. Agreement is not perfect; the graph suggests that benzene ought to be four times as reactive as we have found, and that triphenylene is about four times more reactive than it ought to be if equation (3) held accurately. The most serious anomaly is the failure to find any 4-nitropyrene in the nitration of pyrene, since the 4-position has a reactivity number of 1·68.

Differences in steric factors do not appear to influence the partial rate factors for nitration greatly. Reactivities at positions of α-naphthalenic type lie very close to the line in Fig. 1. Those of the more hindered positions of the 9-anthryl type lie consistently below the line and those of the less hindered β-napthalenic positions lie above it, as we would expect. In the nitration of triphenylene approximately equal amounts of 1- and 2-nitrotriphenylene were found.[1, 9] This suggests that a 4-phenanthryl type of position is subject

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[7] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*
[8] Bavin, Ph.D. Thesis, London, 1955.
[9] Barker, Emmerson, and Periam, *J.*, 1955, 4482.

to steric hindrance as compared with a β-naphthalenic type; in this case the steric hindrance is sufficient to affect the ratio of partial rate factors by a factor of 3. The effect seems to be more important for bromination, the only product from triphenylene being its 2-bromo-derivative.[9]

According to the simple molecular orbital treatment, the relative reactivities of even alternant hydrocarbons should be independent of the substituting agent. Partial rate factors should, therefore, be the same for all types of substitution. This prediction cannot be tested directly since no equivalent data are available for other reactions. However, Levy and Szwarc [10] determined the relative reactivities of hydrocarbons towards free methyl radicals, and Kooyman and Farenhorst [11] studied similar reactions with trichloromethyl radicals. Although the products have not been characterised, there seems little doubt [10] that these reactions proceed through intermediates or transition states of the Wheland type. If the reactivity of a given hydrocarbon relative to benzene is k_N, k_M, and k_T for nitration, methylation, and trichloromethylation, respectively, then we should find that $k_N = k_M = k_T$. This, in fact, is not the case, but Fig. 2 shows that there are linear relations between $\log_{10} k_N$ and $\log_{10} k_M$ and between $\log_{10} k_N$ and $\log_{10} k_T$. Levy and Szwarc [10] had already pointed out the correspondence between their results and those of Kooyman and Farenhorst; we have taken the value which they suggest for the rate of reaction of benzene with trichloromethyl radicals.

It is evident from equation (2) that the slope of the line in Fig. 1 is equal to $2{\cdot}3\beta/\boldsymbol{R}T$. Moreover it can be seen that if the values of the parameter β are β_N, β_M, and β_T for the three types of reaction, then the slopes of the lines, *a* and *b*, in Fig. 2 are given by β_M/β_N and β_T/β_N respectively. In this way we find the values:

$$\beta_N = -6{\cdot}0 \text{ kcal./mole}; \quad \beta_M = -3{\cdot}2 \text{ kcal./mole}; \quad \beta_T = -6{\cdot}0 \text{ kcal./mole} \quad . \quad (4)$$

Now β should be a universal constant for these hydrocarbons and its value can be determined by comparing observed and calculated values for their resonance energies. The appropriate value so found [12] is approximately −20 kcal./mole. The values for β_N, β_M, and β_T therefore seem anomalous not only because β_M differs from β_N and β_T, but also because they are numerically too small.

Now it is true that the value of β quoted above was derived from calculated resonance energies of even hydrocarbons. It is possible that a somewhat different value of β might be more appropriate for odd hydrocarbons—such as the Wheland transition state in subsitution—and in that case equation (2) would no longer hold generally. Such an explanation of the anomaly is unacceptable for three reasons. First, one would not expect a linear relation between $\log_{10} k_i$ and N_i. Secondly, it can be shown very simply that equation (2) would still hold for the relative reactivities of different positions in any one hydrocarbon, and, if so, the observed isomerism requires a low value for β. Thirdly, a theoretical treatment analogous to the above has been given for the S_N1 solvolysis of arylmethyl chlorides in moist formic acid, when the even reactant $R{\cdot}CH_2Cl$ gives rise to a transition state containing the odd ion $R{\cdot}CH_2^+$; in this case Dewar and Sampson [13] were able to correlate the observed and calculated rates by using a value for the carbon–carbon resonance integral of $\beta = -30$ kcal./mole, implying that an analogous value of β can be used for both odd and even systems. (In this case a higher numerical value for β would be expected than the one which we quoted earlier, as Dewar and Sampson [13] have shown.)

All the difficulties would be met if, as suggested by Bavin and Dewar,[1] the structure postulated by Wheland is not a transition state but a stable intermediate. The actual transition state would then be one in which the attacking reagent is still comparatively remote from the atom, i, undergoing substitution, and in which the hybridisation of atom i is not sp^3 but intermediate between sp^2 and sp^3. Then the resonance integrals between atom i and atoms r and s in the transition state would not be zero, but would have some

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[10] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.
[11] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.
[12] Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025.
[13] Dewar and Sampson, *J.*, 1956, 2789.

value intermediate between zero and the " normal " value, β. If the degree of hybridisation in the transition state depends mainly on the reagent, being similar for any one reagent for attack on any position in any hydrocarbon, equation (2) becomes

$$\log k_{\mathrm{i}} = A_{\mathrm{X}} + (\beta - \beta_{\mathrm{X}})N_{\mathrm{i}}/\boldsymbol{RT} \tag{5}$$

where β_{X} is the value of the resonance integral between atom i and atoms r and s in the transition state for substitution by X. This can be written in the form

$$\log k_{\mathrm{i}} = A_{\mathrm{X}} + \beta'_{\mathrm{X}}\, N_{\mathrm{i}}/\boldsymbol{RT} \tag{6}$$

where

$$\beta'_{\mathrm{X}} = \beta - \beta_{\mathrm{X}} \tag{7}$$

Consequently equation (2) will appear to hold, but β must be replaced by a numerically smaller parameter β'_{X}, characteristic of the particular reagent, X. Thus the low numerical values of the parameters, β_{N}, β_{M}, and β_{T}, can be explained.

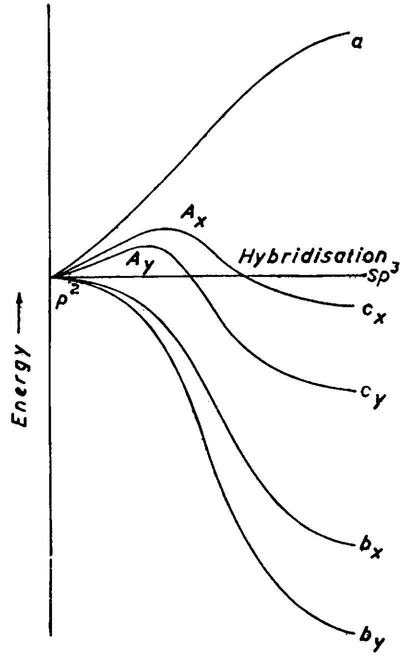

FIG. 3. *Potential energy diagram for substitution by reagents* X *and* Y.

The manner in which β'_{X} should vary with the reagent, X, can also be predicted in a general way, by using a kind of argument first suggested by Bell.[14] Let us plot the energy of the system against a reaction co-ordinate. Since the reaction involves a steady change of hybridisation of the atom, i, from sp^2 to sp^3 we may take hybridisation as a reaction co-ordinate. In Fig. 3, curve (*a*) represents the change in conjugation energy during the reaction and the curve (b_{X}) the changes due to formation of the C–X bond, differential solvation effects, etc. The composite curve (c_{X}) expresses the overall energy of the system, the transition state, A_{X}, corresponding to the value $\beta = \beta_{\mathrm{X}}$.

Consider now a more exothermic substitution reaction by a reagent, Y. Here curve (*a*) remains the same as in the previous case, but the new curve (b_{Y}) lies below (b_{X}), and thus the composite curve (c_{Y}) below (c_{X}). It is obvious from the geometry of the Figure that the more exothermic substitution by Y will in general require less activation energy than substitution by X, and that, since it has a hybridisation of more marked sp^2 character,

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[14] Bell, " Acid–Base Catalysis," Oxford Univ. Press, 1941.

the transition state, A_Y, will correspond to a numerical value of β_Y greater that that of β_X. Then from equation (7),

$$|\beta'_Y| < |\beta'_X| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now considering substitution by X and Y at two hydrocarbon position, *m* and *n*, it follows from equation (5) that

$$\log (k_m/k_n)_X = \beta'_X(N_m - N_n)/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\log (k_m/k_n)_Y = \beta'_Y(N_m - N_n)/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $(k_m/k_n)_X$ and $(k_m/k_n)_Y$ are the ratios of velocity constants for substitution at positions *m* and *n* by X and Y respectively. Suppose that $N_m < N_n$, so that $k_m > k_n$, then from equations (8), (9), and (10) we have:

$$(k_m/k_n)_X > (k_m/k_n)_Y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In other words the ratio of reactivities of the two positions is less for the more reactive reagent. Extension of this argument leads to the rule that the more reactive a substitution agent, X, the lower is the numerical value of β'_X and the less orientational selectivity should the reagent show.

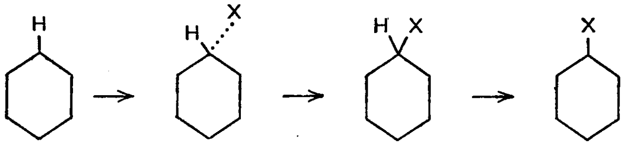
This rule has been deduced empirically by Brown and Nelson [15] for substitution in benzene derivatives. It is a special case of a general phenomenon noted by Dewar.[16] Consider a series of analogous reactions of compound A, in each of which two isomeric products can be formed. Then the greater the ease of reaction, the more nearly equal in general are the amounts of the two products.

The reactions of hydrocarbons with methyl and trichloromethyl radicals confirm this rule. The trichloromethyl radical should be less reactive than the methyl radical, both because of mesomeric stabilisation and because steric repulsion between the chlorine atoms will hinder reactions leading to tetrahedral compound $R{\cdot}CCl_3$ (cf. Brown and Fletcher [17]). In fact $\beta_T > \beta_M$, and the spread of reaction rates is greater for trichloromethylation than for methylation, as Fig. 2 shows. Preliminary experiments suggest that the same is true for bromination as compared with nitration; we are studying this and other reactions in detail in order to obtain further evidence.

The observed values of β'_X are very small ($\frac{1}{4}\beta$). This suggests that the transition state in substitution is much closer to the parent aromatic system than to the Wheland structure. We have, however, to consider one more factor; there must be significant hyperconjugation [18] between the tetrahedral group, $>$CHR, of the Wheland structure and the neighbouring aromatic system. Thus equation (2) should be written

$$\log (k_i/k_o) = (\beta - \beta_h)(N_i - N_o)/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where β_h is the effective value of the C_i–C_r and C_i–C_s resonance integrals in the Wheland structure. Although this effect could hardly be large enough to explain our results completely, it does mean that the transition state for substitution must be closer to the Wheland structure than the low value of β'_X would at first sight suggest.



(I) (II)

We have hitherto assumed that even if the structure (II) postulated by Wheland is not the transition state, substitution nevertheless proceeds by way of it as an intermediate.

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[15] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292; 1955, **77**, 2300 *et seq.*

[16] Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 261.

[17] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1949, **71**, 1845; 1950, **72**, 1223.

[18] Muller, Pickett, and Mulliken, *ibid.*, 1954, **76**, 4770.

Although this idea is very attractive, and probably true, we did not invoke it explicitly in putting forward equation (6), and arguments very similar to those used here would still be applicable if structure (II) were never achieved in the course of the reaction. Our arguments require only the assumption that the transition state is of the type (I), where the C–X bond is comparatively long and weak and the C–H bond is short and strong. Melander [19] has shown that the C–H bond cannot be appreciably stretched in the transition state for the nitration of toluene by the NO_2^+ ion.

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[19] Melander, *Nature*, 1949, **163**, 599.