

244. *Reactivities of Aromatic Hydrocarbons. Part II.*¹ *Chlorination.*

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The second-order rate constants for the reaction of molecular chlorine with benzene, diphenyl, naphthalene, and phenanthrene in acetic acid have been measured at 15, 20, 25, and 30° c, and the energies of activation and the frequency factors have been determined. The frequency factors decrease as the reactivity of the hydrocarbon increases, suggesting, from a consideration of the solvation entropy, that the Wheland intermediate is formed more completely in the transition state for a given reaction the more reactive the hydrocarbon. The effects of the atom localisation, electron interaction, and solvation energies of the transition state upon the course of aromatic substitution are discussed.

In connection with the theory of aromatic substitution,¹ the frequency factors for the reaction of a series of aromatic hydrocarbons with an electrophilic reagent of high orientational selectivity were required. The molecular halogens are highly selective reagents,² and although the kinetics of aromatic bromination are complex,³ the reactions of chlorine with aromatic compounds have been found generally⁴⁻⁹ to be of the simple kinetic form $-d[\text{Cl}_2]/dt = k_2[\text{ArH}][\text{Cl}_2]$. The rates of chlorination of benzene, diphenyl, naphthalene, and phenanthrene in acetic acid at 15, 20, 25, and 30° have now been measured, and the energies of activation and the frequency factors have been calculated from the experimental data (Table 1). In the chlorination of the polycyclic hydrocarbons, catalysis by hydrogen chloride generated in the course of the reaction was observed, in agreement with some previous investigations.^{6,9} Accordingly, the quoted rate constants are averages calculated from the first half-life of the reaction, though the kinetic runs were taken to the third or fourth half-life.

TABLE 1. *The second-order rate constants at 15, 20, 25, and 30 ± 0.05° c for the reaction of benzene, diphenyl, naphthalene, and phenanthrene with chlorine in acetic acid; the energies of activation (E_a) and the logarithms of the frequency factors (log PZ).*

Hydrocarbon	[Ar] (M)	[Cl ₂] (M)	K_{15} (l. mole ⁻¹ sec. ⁻¹)	K_{20} (l. mole ⁻¹ sec. ⁻¹)	K_{25}^b	K_{30}	E_a (kcal./mole)	log PZ
Benzene	0.5	0.04	3.8×10^{-7}	6.8×10^{-7}	1.2×10^{-6c}	2.2×10^{-6}	20	9
Diphenyl	{ 0.2 0.1	{ 0.04 0.02	3.32×10^{-4}	5.19×10^{-4}	8.62×10^{-4}	1.25×10^{-3}	14.8	7.8
Naphthalene	0.04	0.004	3.72×10^{-2a}	5.21×10^{-2}	7.30×10^{-2d}	1.03×10^{-1}	11.5	7.3
Phenanthrene	{ 0.01 0.005	{ 0.002 0.002	3.10×10^{-1}	4.55×10^{-1}	—	—	—	—
			3.24×10^{-1}	4.45×10^{-1}	5.91×10^{-1}	7.94×10^{-1}	10.5	7.4

^a Compare 7.0×10^{-2} at 15.3°, ref. 6. ^b The results of refs. 5 and 8 are not comparable with the present data, the former owing to the volatilisation of chlorine,⁶ and the latter because only pseudo-first-order rate constants are given. ^c Compare 1.48×10^{-6} at 24°, ref. 6; 1.54×10^{-6} , ref. 9; and 1.1×10^{-6} , ref. 12. ^d Compare 10.5×10^{-2} at 24°, ref. 6.

The results show (Table 1) that the energies of activation increase as the reactivities of the aromatic hydrocarbons towards chlorine fall, and that the frequency factors, although showing less variation, tend to larger values as the reactivities of the hydrocarbons decrease. Since the free energies of activation in a series of aromatic hydrocarbons increase with the atom localisation energy ($E_L\beta^{-1}$) of the most reactive position in a variety of substitution

¹ Part I, *J.*, 1958, 4329.

² Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421.

³ Robertson, de la Mare, and Johnston, *J.*, 1943, 276.

⁴ Orton and King, *J.*, 1911, 1369.

⁵ Lauer and Oda, *Ber.*, 1936, **69**, 1061.

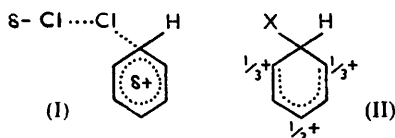
⁶ de la Mare and Robertson, *J.*, 1943, 279.

⁷ Robertson, *J.*, 1954, 1267.

⁸ Dewar and Mole, *J.*, 1957, 342.

⁹ Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.

reactions,^{1,8,10} it is probable that the transition state for aromatic substitution (*e.g.*, I) lies on a potential energy curve connecting the reactants with the Wheland intermediate¹¹ (*e.g.*, II; X = Cl). There are indications^{1,8,10} that the intermediate is formed the more



completely in the transition state the greater the orientational selectivity of the attacking reagent, the degree of formation being substantial in aromatic substitution with molecular halogens. The effect of electrolytes on the rates of aromatic chlorination indicates^{9,12} that the electrophilic reagent is molecular chlorine, so that the formation of the transition state involves the separation of charge, resulting in an increase in the free energy of solvation. For electrophilic substitution the Wheland intermediate is an odd alternant carbonium ion with the positive charge delocalised over the starred atoms [*e.g.*, one-third of the charge at the *ortho*- and *para*-positions in (II), according to the Hückel approximation], and in a series of aromatic hydrocarbons the charge in the corresponding intermediates is dispersed to differing degrees. The free energy of solvation, particularly that due to the Born charging process,¹³ accordingly varies from one transition state to another. For the fully formed intermediate the charging energy (ΔG_s) is given by the equation

$$\Delta G_s = -\sum_r \sum_s q_r q_s (1 - 1/D) / 2R_{rs} \quad . \quad . \quad . \quad (1)$$

where q_r , q_s , are the fractional positive charges on atoms r and s , separated by the distance R_{rs} , and D is the dielectric constant of the solvent. If the intermediate (*e.g.*, II) is formed to a degree, d in the transition state (*e.g.*, I), and the fractional positive charge, $d+$, is delocalised over the starred atoms in the transition state, as in the intermediate, eqn. (1) becomes, by considering only the more important one-centre terms,

$$\Delta G_s^\ddagger = -\sum_r q_r^2 d^2 (1 - 1/D) / 2R \quad . \quad . \quad . \quad (2)$$

where R is the effective radius of a positively charged carbon atom. The derivative of the free energy of solvation (ΔG_s^\ddagger) with respect to temperature then gives the entropy of the solvation of the transition state due to the charging process (ΔS_s^\ddagger), namely,

$$\Delta S_s^\ddagger = \sum_r q_r^2 d^2 (d \ln D / dT) / 2RD \quad . \quad . \quad . \quad (3)$$

If, for a given substitution, the degree of formation of the intermediate in the transition state (d) is constant in the series of aromatic hydrocarbons, the frequency factor for the reaction should increase, by eqn. (3), as the summed squares of the charges ($\sum_r q_r^2$) fall, since the temperature coefficient of the dielectric constant is a negative quantity for liquids, apart from a few cases, including acetic acid,¹⁴ where the coefficient is positive at temperatures close to the freezing point. If variable in the series of aromatic hydrocarbons for a given reaction, the degree of formation of the intermediate in the transition state should increase as the atom localisation energy falls, as, in any given case, the path of lowest activation energy should pass closer to the intermediate the lower the energy required to form the latter (Fig.). Since the separation of charge in the transition state is larger the more completely the intermediate is formed, the frequency factor should then

¹⁰ Dewar, Mole, and Warford, *J.*, 1956, 3581.

¹¹ Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

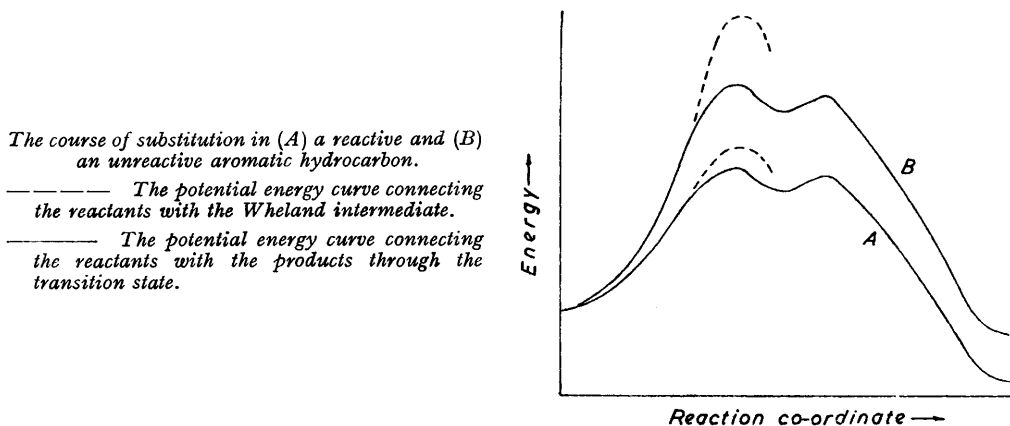
¹² de la Mare and Hassan, *J.*, 1958, 1519.

¹³ Hush and Blackledge, *J. Chem. Phys.*, 1955, **23**, 514; Hoijtink, de Boer, van de Meij, and Weijland, *Rec. Trav. chim.*, 1956, **75**, 487.

¹⁴ Philippe and Piette, *Bull. Soc. Chim. Belges*, 1955, **64**, 600.

fall with the atom localisation energy. The frequency factors for the chlorination of the aromatic hydrocarbons studied are of the order 10^7 — 10^9 (Table 1), suggesting that the transition states are more polar than the reactants, and the trend of the factors in the series indicates that the separation of charge in the transition state is larger the more reactive the hydrocarbon.

These conclusions are unaffected by the assumption of a Hückel distribution of positive charge in the transition state. Given a uniform degree of formation of the Wheland intermediate in the transition state, any mode of charge dispersion would require the larger hydrocarbons to have the higher frequency factors. Steric factors could account for the observed trend in the frequency factors, namely, *peri*-hindrance to substitution in naphthalene and phenanthrene, and *ortho-ortho'*-interference in diphenyl, but if the



transition state resembles the Wheland intermediate steric effects are not to be expected, as the carbon atom under attack assumes a near tetrahedral configuration with the entering and leaving groups out of the plane of the nucleus.

The dielectric constant of acetic acid over part (16—20°) of the temperature range studied has a positive temperature coefficient,¹⁴ probably due to an extensive breakdown in the structure of the liquid for a small temperature rise above the freezing point. Curved Arrhenius plots for reactions involving a separation of charge in the transition state might be expected in solvents of this nature for a temperature range near to the freezing point (eqn. 3). The Arrhenius plots obtained for the chlorination of the aromatic hydrocarbons were all reasonably linear, the kinetic effect of the positive temperature coefficient of the dielectric constant being probably rather small. In order to allow for the breakdown of the solvent structure by the reactant solutes, as manifest in the depression of the freezing point, a number of kinetic runs were made below the melting point of the pure solvent, at 15°. The more dilute solutions, *e.g.*, phenanthrene at 0.005M, were slightly supercooled at this temperature, but no crystallisation of the solvent was observed during the brief kinetic run (half-life of ~10 min.).

The observed variation of the frequency factors for chlorination of the series of aromatic hydrocarbons studied has a bearing on the interpretation of the linear relations which have been found between the free energy of activation and the atom localisation energy in a number of aromatic substitutions.^{1,8,10} The variation of the frequency factors suggests that, for a given reaction, the Wheland intermediate is formed in the transition state to a degree (d) which is approximately proportional to the reactivity of the hydrocarbon. The observed relations between ΔG^\ddagger and $E_L\beta^{-1}$ require that any variations in d should be of this form, as otherwise those relations would not be linear. Thus, the reaction co-ordinate leaves the potential energy curve connecting the reactants with the Wheland intermediate at an earlier stage the larger the atom localisation energy (*e.g.*, cases A and B,

Fig.). The apparent β value obtained from the correlation between ΔG^\ddagger and $E_L\beta^{-1}$ for a given reaction is a composite quantity, therefore, expressing not only an average degree of formation of the Wheland intermediate in the transition state for a series of hydrocarbons, but also a range of variation of d in the series and a variable solvation energy of the transition state.

The solvation of the transition state, whilst affecting the entropy of activation for electrophilic aromatic substitution (eqn. 3), may not have a great influence upon the energy of activation, as a more detailed treatment suggests that π -electron energy terms, not considered in the simple Hückel theory, partly compensate the variations in the solvation energy of the transition state in the substitutions of a series of aromatic hydrocarbons. By using a simplified self-consistent field method,¹⁵ with the Hückel molecular orbitals as a base, the π -electron energy difference (E_π) between an aromatic hydrocarbon (*e.g.*, benzene) and the corresponding Wheland intermediate (*e.g.*, II) is given¹⁵ by the expression

$$E_\pi = E_L + E_B \pm E_C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

E_C being negative for the carbonium ion and positive for the radical intermediate. E_L , the atom localisation energy of the Hückel theory, arises from the delocalisation of π -electrons over a σ -core field which is less extensive in the intermediate than in the hydrocarbon

$$E_L = 2[\sum'_{r>s} P_{rs}(\text{Int}) - \sum'_{r>s} P_{rs}(\Delta r\text{H})]\beta \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The bond repulsion energy, E_B , is due to the smaller probability that pairs of electrons shall be found on neighbouring atoms in the intermediate than in the hydrocarbon

$$E_B = 1/2[\sum_r^{st} \sum_s^{un} P_{rs}^2(\gamma_{12} - \gamma_{rs})_{\text{Int}} - \sum_{r>s} P_{rs}^2(\gamma_{12} - \gamma_{rs})_{\Delta r\text{H}}] \quad . \quad . \quad . \quad . \quad (6)$$

where P_{rs} refers to the mobile bond order between the atoms r and s , the sums \sum^{st} , \sum^{un} , and \sum' being taken over the starred, the unstarred, and neighbouring atoms, respectively, and γ_{rs} is the electron repulsion integral between the atoms r and s , ArH referring to the hydrocarbon and Int to the corresponding Wheland intermediate. The charge dispersal energy, E_C , arises from the lower probability that a pair of electrons shall be situated on a given atom in the delocalised than in the fixed bond state of the intermediate

$$E_C = 1/2 \sum_{r>t}^{st} C_{or}^2 C_{ot}^2 (\gamma_{11} - \gamma_{rt}) \quad . \quad . \quad . \quad . \quad (7)$$

where C_{or} is the coefficient of the atom r in the non-bonding molecular orbital on the intermediate. Values of the various π -electron energy terms for a number of Wheland intermediates in aromatic substitution are given in Table 2.

In electrophilic substitution the transformation of an aromatic hydrocarbon into a transition state resembling a partly formed Wheland intermediate involves a change in π -electron delocalisation energy proportional to the degree of formation of the intermediate, d , but changes in electron interaction and solvation energy proportional to d^2 . Thus the variation in the free energy of activation in a series of aromatic hydrocarbons for a given reaction should be given by the equation

$$\Delta G^\ddagger = dE_L + d^2(\Delta G_s + E_B - E_C) + \text{Constant} \quad . \quad . \quad . \quad (8)$$

The charge-dispersal energy (E_C) has the form of a charging energy. It may be considered (eqn. 7) as the difference between the charging energy of two charges, C_{or}^2 and C_{ot}^2 , when on a common centre and when on their proper centres, the atoms r and t , summed over all pairs of charges. The charge-dispersal energy and the solvation energy due to the charging process (eqns. 1 and 2) are, therefore, related. In the series of aromatic hydrocarbons E_C increases as $\sum q_r^2$ falls (Table 2), and the changes in the charge-dispersal and the solvation

¹⁵ Brickstock and Pople, *Trans. Faraday Soc.*, 1954, **50**, 901.

TABLE 2. The atom-localisation ($E_L\beta^{-1}$), charge-dispersal (E_O), and bond-interaction (E_B) energies, and the summed squares of the positive charges ($\sum q_r^2$), calculated according to the Hückel approximation, of some Wheland intermediates in aromatic substitution. The hyperconjugation energies of the cations ($E_{HO}\beta^{-1}$), and the delocalisation energies of the corresponding aryl methyl systems ($E_D\beta^{-1}$).

Hydrocarbon	Position	$E_L \beta^{-1}$	E_B^a (kcal./mole)	E_O^b (kcal./mole)	$\sum q_r^2$	$E_{HO}\beta^{-1}^c$	$E_D\beta^{-1}$
Benzene		-2.536	-6.7	19.5	0.333	0.75	0.722
Diphenyl	{ 2	-2.400	-8.9	26.2	0.227	—	0.767
	{ 4	-2.447	-10.4	26.2	0.227	—	0.756
Naphthalene ...	{ 1	-2.299	-10.6	23.3	0.289	0.67	0.812
	{ 2	-2.480	-8.6	22.3	0.313	—	0.744
Phenanthrene ...	{ 1	-2.318	-13.6	26.5	0.296	—	0.802
	{ 9	-2.299	-12.0	23.1	0.319	0.66	0.812
Anthracene ...	9	-2.013	-18.3	27.1	0.220	0.58	0.951

^a Calculated from eqn. (5) with $\gamma_{12} = 168.3$, $\gamma_{14} = 113.0$ kcal./mole, and the point-charge approximation for larger distances. ^b Calculated from eqn. (6) with $\gamma_{11} = 242.7$, $\gamma_{13} = 125.9$ kcal./mole, and the point-charge approximation for larger distances. ^c Quoted from ref. 16.

energies, in part, are mutually compensating irrespective of the degree of formation of the intermediate.

Attention has been drawn recently¹⁶ to another π -electron energy term which partly compensates for the changes of solvation energy in a series of Wheland carbonium-ion intermediates, namely, the Coulombic stabilisation due to the movement of the π -electrons in the field of the carbon atoms carrying a positive charge. If the intermediate is formed to a degree, d , in the transition state, the Coulombic stabilisation energy of the latter, E_E , is given by

$$E_E = m(d - \sum q_r^2 d^2)\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where q_r , the net positive charge on atom r , is equal to C_{or}^2 , and m is a constant which has been given the values^{17,18} of unity and 1.4. The Coulombic stabilisation energy of the transition state increases (eqn. 9) in proportion as the solvation energy falls (eqn. 2). The overall effect of the charge dispersal, Coulombic, and solvation energies of the transition state upon the relative reaction rates of a series of hydrocarbons may be small, therefore, though the solvation energy is manifest, because it is a free-energy term, in the relative frequency factors.

The linear relations between the free energy of activation and the atom localisation energy in a series of hydrocarbons observed in a number of substitution reactions^{1,8,10} can be accounted for if, as the relative frequency factors suggest (Table 1), the degree of formation of the Wheland intermediate in the transition state is approximately proportional to the reactivity of the hydrocarbon. The partial compensation between the solvation energy and the charge dispersal and Coulombic energies of the transition state has the effect that the atom localisation energy remains the most important single variable governing the relative reactivities of a series of hydrocarbons for a given substitution, the bond repulsion energy becoming important also when the average degree of formation of the intermediate in the transition state is large (eqn. 8). The bond repulsion energy (E_B) tends to larger values as the atom localisation energy ($E_L\beta^{-1}$) falls (Table 2), and so the former should not lead to marked irregularities in the correlations between ΔG^\ddagger and $E_L\beta^{-1}$. However, the values of E_B available account for an otherwise anomalous relative reactivity. Naphthalene and phenanthrene have the same atom localisation energies for the most reactive positions, but the reduction of electron repulsion (E_B) on change from the hydrocarbon to the intermediate is larger in the latter than in the former (Table 2), in accord with the greater reactivity of phenanthrene.

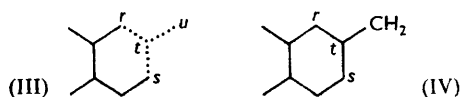
¹⁶ Mackor, Hofstra, and van der Waals, *ibid.*, 1958, **54**, 66.

¹⁷ Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264.

¹⁸ Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4770.

The apparent β values obtained from the slopes of the relations between ΔG^\ddagger and $E_L\beta^{-1}$ in a series of aromatic hydrocarbons for the various substitution reactions are less satisfactorily explained. An empirical upper limit of -35 kcal./mole for such apparent β values is provided by the relation between the ionisation constants¹⁶ of a series of aromatic hydrocarbons in anhydrous hydrofluoric acid and $E_L\beta^{-1}$, since the cations formed probably have the structures of the corresponding Wheland intermediates.¹⁶ The apparent β values derived from rate studies should be smaller, as the intermediate is incompletely formed in the transition state and the degree of formation in a series of hydrocarbons would appear to be proportional to the reactivity of the hydrocarbon. However, the apparent β value obtained¹ from the reaction of a series of hydrocarbons with chlorine in 3 : 1 carbon tetrachloride-acetic acid⁸ is -36 kcal./mole. Further, the relative enthalpies of activation for the reaction with chlorine in acetic acid, which are given by the relative energies of activation (Table 1), as each hydrocarbon was investigated between the same temperature limits, correlate with the atom localisation energies (Table 2) to give an apparent β value of -48 kcal./mole, whilst the enthalpies of ionisation, like the free energies, give a value of -35 kcal./mole, since no differential entropy of ionisation was observed in the series of hydrocarbons studied.¹⁹

Two factors may account for the large apparent β values obtained from the aromatic halogenation series. First, the cations of the hydrocarbons are stabilised by hyperconjugation between the $>CH_2$ group and the π -electron system of the ion¹⁸ (*e.g.*, II; X = H), whilst the transition state in the substitution reaction is less stabilised by hyperconjugation as the entering group is a halogen and not a hydrogen atom. The calculated hyperconjugation energies¹⁶ of the cations of the aromatic hydrocarbons increase with the atom localisation energy (Table 2), so that these two energy terms mutually compensate to some degree in the hydrocarbons. Thus, if hyperconjugation is not explicitly considered in the correlations, the free energies of ionisation of the hydrocarbons appear to be less strongly dependent upon the atom localisation energies than the free energies of activation for a substitution with a transition state in which the Wheland intermediate is largely formed. Secondly, in the product of an aromatic halogenation the halogen atom conjugates more strongly with the nucleus the more reactive is the position substituted. An approximate measure of the conjugating power of a nuclear position for a given substituent is afforded by the delocalisation energy ($E_D\beta^{-1}$) of the corresponding arylmethyl radical or ion (*e.g.*, benzyl) additional to that of the nucleus (*e.g.*, benzene), an energy term which increases in proportion as the atom localisation energy falls (Table 2). In an aromatic halogenation the energy of the partly formed carbon-halogen bond should lower the energy of the transition state, and the more reactive the position substituted, the stronger the conjugation across the partial bond, and the more stable should be the transition state. The effects of both hyperconjugation in the transition state and the conjugation of the partly bonded substituent are to accentuate the dependence of the relative reactivities of a series of hydrocarbons on the atom localisation energy, and they both help to account for the large apparent β values derived from the aromatic halogenations.



The interdependence of the atom localisation energy (E_L) of a given position in an aromatic hydrocarbon, the hyperconjugation energy of the corresponding cation (E_{HO}), and the extra delocalisation energy of the corresponding arylmethyl system (E_D), may be accounted for by the perturbation method of Dewar.²⁰ The localisation energy of the atom t in the hydrocarbon (III) is given²⁰ by

$$E_L = 2(C_r + C_s)\beta \dots \dots \dots (10)$$

¹⁹ Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 186.

²⁰ Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

where C_r and C_s are the coefficients of the non-bonding molecular orbital in the corresponding Wheland intermediate at the atoms r and s adjacent to t . If the H_2 pseudo-atom of the corresponding cation is the atom u in (III), and if, for the purposes of illustration, all Coulomb integrals and all resonance integrals are taken to be equal, the hyperconjugation energy of the cation is

$$E_{\text{HC}} = 2(1 + C_r + C_s)\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The extra delocalisation energy of the corresponding arylmethyl system (IV) is given, similarly, by

$$E_{\text{D}} = 2(1 - C_r' - C_s')\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where C_r' , C_s' , are the values C_r and C_s assume after the renormalisation of the non-bonding molecular orbital to include the coefficient of the orbital at the exocyclic atom. Thus E_{L} , E_{HC} , and E_{D} are interrelated (equations 10—12) through the coefficients C_r and C_s . These connections indicate that a correlation between the reactivities of a series of hydrocarbons and their atom localisation energies does not necessarily imply that the transition state resembles the Wheland intermediate. If the product of an aromatic substitution contains a highly conjugated substituent, and if the transition state resembles the product, an accidental correlation between relative reactivity and the atom localisation energy might be found, owing to the connection between E_{L} and E_{D} (eqns. 10 and 12).

The apparent β values obtained from the slopes of the relations between ΔG^\ddagger and $E_{\text{L}}\beta^{-1}$ in a series of aromatic hydrocarbons, in general, become smaller the less selective the attacking reagent,^{1,8,10} suggesting that the transition state more resembles the reactants the more reactive the substituting agent.^{8,10} The present results indicate that the transition state more nearly resembles the Wheland intermediate the more reactive the hydrocarbon, which, at first sight, is surprising, since there is no distinction in principle between the reactants, the hydrocarbon, and the substituting reagent. However, the lower the atom localisation energy of an aromatic hydrocarbon the more nearly the intermediate resembles the hydrocarbon itself in regard to the important variable determining the course of reaction, *i.e.*, energy, so that in this respect the present conclusions do not require the non-equivalence of the reactants in aromatic substitution.

EXPERIMENTAL

Materials and Rate Measurements.—These were as in Part I. The formula $k_2 = 2.303 \{ \log_{10} b(a-x)/a(b-x) \} / t(a-b)$ was used to calculate second-order rate constants, where a and b are the molarities of aromatic hydrocarbon and of chlorine, respectively, and x is the molarity of chlorine consumed after a time t . The following is an example of a typical run, illustrating the catalytic effect of hydrogen chloride generated during the course of the reaction and the reproducibility of rate constants calculated from the first half-life (about ± 7 units in the last significant figure for a standard set of reaction conditions). Naphthalene (0.04M) and chlorine (0.00437M) reacted at 20°; samples (10 ml.) were titrated against 0.001N-sodium thiosulphate.

Time (sec.)	0	83	200	330	440	520	660	780
Titre (ml.)	43.7	33.8	26.5	20.7	16.2	12.7	9.8	7.8
$10^2 k_2$ (l. mole ⁻¹ sec. ⁻¹)	—	5.15	5.28	5.18	5.38	5.48	5.67	5.60

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