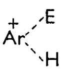
441. *Charge-transfer Complexes and the Mechanism of Aromatic Substitution. Part I. General Theory.*

By R. D. Brown.

A mechanism of aromatic substitution is proposed. It involves unsymmetrical charge-transfer complexes as stable intermediates and accounts for all of the features of electrophilic substitution reactions. The geometry of the unsymmetrical complexes is elucidated from quantum-mechanical considerations using a " configuration-interaction " method. Formulæ for the activation energy are deduced; they include parameters characterising the particular electrophil involved in the reaction and form a basis for a quantitative molecular-orbital treatment of relative reactivities of aromatic compounds and the orientation of substitution in such compounds.

Electrophilic aromatic substitution was until recently believed to proceed by way of a simple transition state (I), the electrophil,* E^+, approaching the aromatic compound ArH somewhat to one side of the conjugated plane, the hydrogen atom on the carbon atom undergoing substitution being synchronously dislodged and moving away on the opposite side of the conjugated plane. The potential energy was imagined to pass through a simple maximum, corresponding to the configuration (I), along the reaction co-ordinate as shown in Fig. 1. This simple picture has recently been modified in an attempt to account for certain features of electrophilic substitution reactions. One school of thought,[1,2,3,4] in order to account for kinetic isotope effects, has suggested that (I) represents an unstable intermediate:

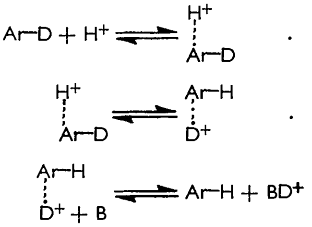


(I)

$$\mathrm{ArH} + \mathrm{E}^+ \rightleftharpoons \mathrm{ArHE}^+$$
$$\mathrm{ArHE}^+ + \mathrm{B} \longrightarrow \mathrm{ArE} + \mathrm{BH}^+ \quad \ldots\ldots\ldots\ldots \quad (1)$$

where B is a base. This formulation was originally proposed by Lapworth [5] and has since been supported by the isolation or detection of intermediates analogous to (I).[6-12] However it will be shown that it does not satisfactorily account for all features of substitution reactions.

The variation of rates of de-deuteration with acidity of the strongly acidic media employed led another group [13,14] to propose a more elaborate mechanism :



$$\mathrm{Ar{-}D} + \mathrm{H}^+ \rightleftharpoons \overset{\mathrm{H}^+}{\underset{\mathrm{Ar{-}D}}{\vdots}} \quad \ldots\ldots\ldots\ldots \quad (2a)$$

$$\overset{\mathrm{H}^+}{\underset{\mathrm{Ar{-}D}}{\vdots}} \rightleftharpoons \overset{\mathrm{Ar{-}H}}{\underset{\mathrm{D}^+}{\vdots}} \quad \ldots\ldots\ldots\ldots \quad (2b)$$

$$\overset{\mathrm{Ar{-}H}}{\underset{\mathrm{D}^+ + \mathrm{B}}{\vdots}} \rightleftharpoons \mathrm{Ar{-}H} + \mathrm{BD}^+ \quad \ldots\ldots\ldots\ldots \quad (2c)$$

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* We initially consider only the most common case of an electrophil having unit positive charge.

[1] Melander, *Arkiv Kemi*, 1950, **2**, 213.
[2] Nelson, *J. Org. Chem.*, 1956, **21**, 145.
[3] Dewar, *Record Chem. Progress*, 1958, **19**, 1.
[4] Zollinger, *Angew. Chem.*, 1958, **70**, 204.
[5] Lapworth, *J.*, 1901, **80**, 1265..
[6] Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 132.
[7] Kohler and Scheibe, *Z. anorg. Chem.*, 1956, **285**, 221.
[8] H. C. Brown and Pearsall, *J. Amer. Chem. Soc.*, 1952, **74**, 192.
[9] H. C. Brown and Brady, *J. Amer. Chem. Soc.*, 1952, **74**, 3570.
[10] Olah, Kuhn, and Olah, *J.*, 1957, 2174.
[11] Chopard-dit-Jean, Heilbronner, Plattner, and Weber, *Helv. Chim. Acta*, 1952, **35**, 1036, 2170.
[12] Cannell, *J. Amer. Chem. Soc.*, 1957, **79**, 2927.
[13] Gold and Satchell, *J.*, 1955, 3609, 3619; 1956, 1635, 2743.
[14] Satchell, *J.*, 1958, 1927.

in which there is a pre-equilibrium (2*a*) involving the formation of an outer complex,[7] *i.e.*, one in which only slight charge transfer to the electrophil occurs. In this mechanism the rate-determining step is (2*b*) in which the transition state corresponds to (I).

Mechanism (2) is also unsatisfactory as a general mechanism of aromatic electrophilic substitution and we suggest a new mechanism, involving unsymmetrical *charge-transfer complexes* (or inner complexes),[15] which appears to embrace all features of the reaction. It will be convenient first to summarise the significant experimental features:

(i) No kinetic hydrogen isotope effect can be detected in the nitration and bromination of aromatic compounds such as nitrobenzene or naphthalene[1] but an isotope effect is observed in the sulphonation of bromobenzene,[16] in the coupling of diazonium compounds with 7-hydroxynaphthalene-1 : 3-disulphonic acid,[4] and in the iodination of phenol.[17]

(ii) The logarithm of the rate of de-deuteration of benzene derivatives varies linearly with Hammett's acidity function H_0.[13,14,18]

(iii) Diazonium coupling of 7-hydroxynaphthalene-1 : 3-disulphonic acid is subject to general base catalysis.[4]

(iv) Electrophilic substitution is observed when the electron affinity of the electrophil is greater than the ionisation potential of the aromatic compound, *i.e.*, when $\Delta = A - I$ is positive, and it is not observed when Δ is negative.[19]

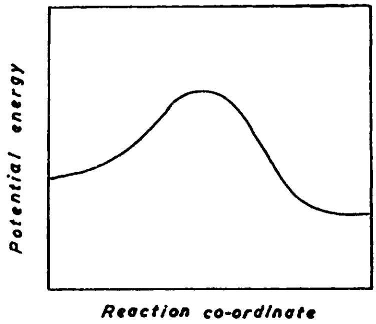


FIG. 1.

(v) Electrophilic substitution and oxidation of aromatic hydrocarbons show strong similarities, especially with respect to orientation of products.[20]

(vi) Intermediates can sometimes be isolated or detected in other ways.

Critique of Previous Mechanisms.—The simplest mechanism, represented by Fig. 1, fails to account for the observations (i), (ii), (iii), and (iv). It therefore calls for no further detailed appraisal.

Mechanism (1) can account for both (i) and (iii), as has been demonstrated by Zollinger.[4] Observation (vi) also fits neatly into this mechanism. However since the second step is a bimolecular reaction with a base it is not possible to account for (ii) because, according to the Zucker–Hammett principle,[21,22] this observation implies that the transition state resembles the conjugate acid of the substrate. It was for this reason that mechanism (2) was proposed.

Mechanism (2) accounts for the observation (ii). No explanation of observations (iv) and (v) emerges but at first sight it does seem possible to account for observations (i) and (iii). Thus if the first step could be rate-determining no kinetic isotope effect would be observed; if (2*c*) could be rate-determining then base catalysis would be understandable. However neither the first nor the third stage of mechanism (2) can become rate-determining because the formation or dissociation of an outer complex requires little activation energy.[15]

The suggestion that a charge-transfer complex is involved in electrophilic substitution was made by Nagakura and Tanaka[19] on the basis of observation (iv) but they did not develop this in the light of the other features of substitution reactions. Others[9,23] have

[15] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

[16] Berglund-Laesson and Melander, *Arkiv Kemi*, 1953, **6**, 219.

[17] Grovenstein and Kilby, *J. Amer. Chem. Soc.*, 1957, **79**, 2973.

[18] Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.

[19] Nagakura and Tanaka, *J. Chem. Phys.*, 1954, **22**, 563.

[20] Waters, *J.*, 1948, 727.

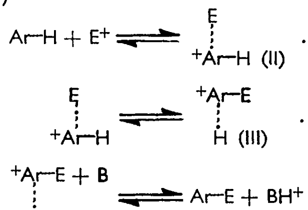
[21] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

[22] Long, *Proc. Chem. Soc.*, 1957, 220.

[23] Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4770.

regarded charge-transfer, or inner, or σ-complexes as intermediates, but with an assumed geometry analogous to (I), and it has just been seen that this simple picture cannot be reconciled with all the observations.

The Charge-transfer Complex Mechanism.—The mechanism now suggested to correlate the observations on electrophilic substitution is the following, differing from mechanism (2) in that unsymmetrical charge-transfer complexes (II) and (III) are invoked in place of the outer complexes formulated in (2):



$$\mathrm{Ar{-}H} + \mathrm{E}^+ \rightleftharpoons \overset{\mathrm{E}}{\vdots}\,{}^+\mathrm{Ar{-}H}\ \text{(II)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3a)$$

$$\overset{\mathrm{E}}{\vdots}\,{}^+\mathrm{Ar{-}H} \rightleftharpoons {}^+\mathrm{Ar{-}E}\ \underset{\mathrm{H}}{\vdots}\ \text{(III)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3b)$$

$${}^+\mathrm{Ar{-}E}\ \underset{\mathrm{H}}{\vdots} + \mathrm{B} \rightleftharpoons \mathrm{Ar{-}E} + \mathrm{BH}^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3c)$$

The first step is the formation of a charge-transfer complex (II) which in the second step isomerises to the charge-transfer complex (III) by way of a transition state analogous to (I). The final step is the base-catalysed loss of a proton from (III). In contrast to mechanism (2), any of the steps of (3) may be rate-determining because, as discussed in detail below, they all involve appreciable activation energies. It is thus possible to account for observations (i), (ii), and (iii). The observation (iv) is readily explained by the proposed mechanism because when Δ is positive a charge-transfer complex will form but not when Δ is negative.* Similarities between electrophilic substitution and oxidation are understandable because the first step (3*a*) is a typical redox reaction.

The possibility that (I) represents a stable intermediate requires that the configurations (II) and (III) are separated by a potential-energy minimum instead of the maximum envisaged here. This possibility is considered more fully later.

Origin of the Potential Barriers.—One important distinction between the proposed mechanism (3) and mechanism (2) is that only for the former can appreciable potential barriers exist for the first and the third step. The origin of these barriers in mechanism (3) must now be considered. The variation in potential energy accompanying the formation of a charge-transfer complex has been discussed by Mulliken,[15] although he has not dealt with the case of interest here, *i.e.*, electrophil with unit positive charge, uncharged nucleophil, and Δ positive. It is convenient to use Mulliken's formulation of the problem—a simple form of configuration-interaction treatment in which the complex is represented as intermediate between the configuration without charge transfer, eigenfunction Ψ_0, and the configuration corresponding to the transfer of one electron from the highest occupied orbital of the nucleophil to the lowest unoccupied orbital of the electrophil, eigenfunction Ψ_1:

$$\Psi = a_0\Psi_0 + a_1\Psi_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

For positive Δ the separated reactants represent an *excited* state of the system because the structure $\mathrm{E}\ldots\mathrm{ArH}^+$ has an energy value lower than that of the structure $\mathrm{E}^+\ldots\mathrm{ArH}$ by an amount Δ. As the reactants approach, the potential energy increases (in the quantum-mechanical picture of the process this is due to increasing mesomerism between Ψ_0 and Ψ_1) until at some stage an electronic transition to the ground state occurs. The process is represented by the full line in Fig. 2. The stage at which an electronic transition to the ground state occurs will depend *inter alia* on the rate at which the reactants approach one another. Eventually a minimum corresponding to (II) is reached. This description applies to reactions in vacuum or in non-polar, non-solvating solvents, conditions under which substitutions involving charged electrophils do not appear to have been observed.

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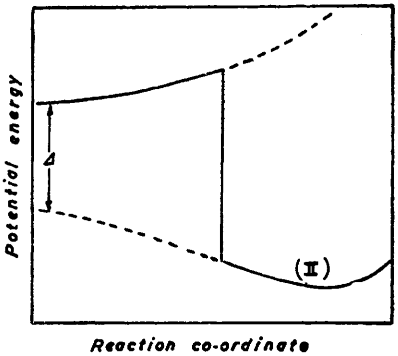
* This criterion needs modification if the electrophil does not carry unit positive charge, or if the substrate is charged.

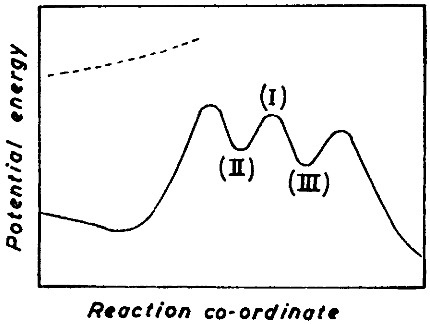
The picture is changed significantly in the presence of a solvating solvent. The electrophil is solvated, often very strongly,* and thus its effective electron affinity is considerably reduced. The potential barrier to formation of the charge-transfer complex (II) arises because in the process the electrophil has to break free from its solvation sheath or at least the sheath has to be considerably distorted to allow a close approach of the electrophil and the aromatic molecule. The activation energy may thus amount to an appreciable fraction of the solvation energy of the electrophil in the particular solvent.† Alternatively the process may be viewed as the bimolecular reaction of the aromatic compound with the charge-transfer complex formed between the electrophil and the solvent nucleophil, *i.e.*, as an electrophil-transfer reaction. It seems likely that the effective electron affinity of the electrophil is reduced in the solvation complex sufficiently to make Δ negative; then the separated reactants represent the ground state of the combined system. As the reactants approach one another an outer complex is formed and, as the electrophil breaks from its solvation sheath, its electron affinity steadily increases until Δ is positive and the complex then is to be regarded as a charge-transfer complex. The variation in potential energy throughout the reaction will be roughly as shown in Fig. 3.

FIG. 2.



Upper curve $E^+ \ldots ArH$.
Lower curve $E \ldots ArH^+$.

FIG. 3.



Upper (broken) curve $E_{solv.} \ldots ArH^+$.
Lower curve $E^+_{solv.} \ldots ArH$.

In certain reactions, such as the Friedel–Crafts reaction, an inert solvent is used and the uncharged electrophil may be considered to be a positively charged electrophil " solvated " by an anion, *e.g.*, $R-AlCl_4$ may be regarded as the carbonium ion " solvated " by the $AlCl_4^-$ ion. A related reaction provides supporting evidence for this proposed mechanism of substitution. Hydrogen chloride and aromatic compounds form unstable complexes in inert solvents at −80°, little or no activation energy being involved.[9] They do not increase the conductivity of the solution and deuterium is not exchanged with the aromatic compound. These must be regarded as outer complexes of the type postulated in mechanism (2). The bare proton has an electron affinity high enough for Δ to be positive in these interactions[19] but it is so strongly " solvated " by the chloride anion that in this combination the effective Δ is negative and the potential barrier to deuterium exchange is prohibitively high. In the presence of aluminium chloride more stable complexes are formed, the solution is an electrical conductor and deuterium is exchanged with the aromatic compound. Furthermore these complexes are observed to form and dissociate slowly. They have been recognised as inner complexes, σ-complexes, or charge-

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* *E.g.*, the solvation energy of a proton in water or similar solvents.

† In the case of polyatomic electrophils non-bonded repulsions between the electrophil and the aromatic compound may sometimes contribute to the activation energy. The rearrangement of the solvation sheath accompanying the formation of the activated complex will also contribute to $\Delta S^\ddagger$; however our primary concern in the present treatment is with the energetics of the mechanism.

transfer complexes.* Consequently it is reasonable to consider any of the steps in mechanism (3) as being the slow step, as is required to account for the observations listed above.

Quantum-mechanical Treatment.—The new mechanism leads to a fresh quantum-mechanical treatment of aromatic substitution. We shall first develop some general results. The eigenfunction of the charge-transfer complex is represented, as in eqn. (4), as a combination of two singlet electronic configurations,† Ψ_0 and Ψ_1, the energy of the ground state of the complex being obtained from the secular equation:

$$\begin{vmatrix} H_{00} - E & H_{01} \\ H_{01} & H_{11} - E \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which for simplicity Ψ_0 and Ψ_1 have been assumed to be orthogonal and the following symbolism has been used:

$$H_{00} = \int \Psi_0 \mathscr{H} \Psi_0 \mathrm{d}\tau ; \; H_{11} = \int \Psi_1 \mathscr{H} \Psi_1 \mathrm{d}\tau ; \; H_{01} = \int \Psi_0 \mathscr{H} \Psi_1 \mathrm{d}\tau \quad . \quad . \quad (6)$$

where $\mathscr{H}$ is the total Hamiltonian for the complex.

The electrostatic energies for the configurations $E^+ \ldots ArH$ and $E \ldots ArH^+$ will be very similar and so ‡ we may write

$$H_{00} - H_{11} = \Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When Δ is positive the solution of (5) of lower energy is

$$E_1 = H_{00} - \{\Delta + (\Delta^2 + 4H_{01}^2)^{\frac{1}{2}}\}/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now except in special cases where Δ happens to be small, the resonance energy H_{01} for interaction of the two configurations will be small compared with Δ. In this case eqn. (8) simplifies to

$$E_1 = H_{00} - \Delta - H_{01}^2/\Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This approximation more clearly reveals the main factors determining the energy of formation of the complex although in the numerical calculations reported in Part II exact formulæ equivalent to (8) have been used.

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* The formation of the charge-transfer complex might be regarded as a bimolecular reaction between the electrophil $AlCl_3$ and the outer complex, the Cl^- nucleophil being transferred to the aluminium chloride to form an anion such as $AlCl_4^-$ and the " desolvated " proton remaining bound to the aromatic compound in a charge-transfer complex. The observed deuterium exchange would occur by isomerization of the complex as in step (3*b*). An alternative interpretation of the charge-transfer complex being formed by a reaction between $HAlCl_4$ and the aromatic compound must be rejected because there is no indication of any compound formation between HCl and $AlCl_3$.[24] The properties of complexes formed by interaction of HBr, $AlBr_3$, and aromatic compounds,[25] and by interaction of HF, BF_3, and aromatic compounds [26] may be interpreted similarly. It is significant that the relative stabilities of these charge-transfer complexes closely parallel the ease of electrophilic substitution in the substrates.[2,9]

† Configurations of the type $E^- \ldots ArH^{++}$ (represented by a configurational function Ψ_d, say), corresponding to a transfer of two electrons, are neglected on the grounds that the electron affinity of E is always much lower than that of E^+ and the ionization potential of ArH^+ is always much higher than that of ArH. Therefore H_{dd} would represent a higher energy than H_{00} and a considerably higher energy value than H_{11} and thus Ψ_d will not make a significant contribution to the total eigenfunction of the complex. In special cases it may happen that Ψ_d and Ψ_0 have comparable energy values so that Ψ_d may make a contribution to the total eigenfunction similar to the small contribution made by Ψ_0 but this aspect has not been explored further in the present study.

‡ The validity of this assumption is confirmed by the success with which calculated relative rates of nitration of polycyclic hydrocarbons, reported in Part II, based on equations (8) and (15), correlate with the observed rates.

[24] Baddeley, *Quart. Rev.*, 1954, **8**, 355.

[25] H. C. Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6268.

[26] McCauley and Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013.

If the energy of the separated reactants is E° and we put $H_{00} - E^\circ = X$ then the energy of formation of the charge-transfer complex from the reactants *in vacuo* is *

$$\Delta E = X - \Delta - H_{01}{}^2/\Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In the presence of a solvent a change in the solvation energy of E^+ accompanying the formation of the complex must be added to the right-hand side of (10). If the energy required to desolvate the electrophil is Y then, in the presence of a solvent:

$$\Delta E = X + Y - \Delta - H_{01}{}^2/\Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

A similar expression will apply for the activation energy for the first step:

$$\Delta E^\ddagger = X^\ddagger + Y^\ddagger - \Delta^\ddagger - H_{01}{}^{\ddagger 2}/\Delta^\ddagger \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which values of the quantities appropriate to the activated complex are indicated by ‡.

One consequence of (12) is that if solvation effects are similar for two different electrophils then the greater the value of $\Delta^\ddagger$, *i.e.*, the greater the electron affinity of the electrophil, the lower will be the first potential barrier. This may account for the fact that in the case of attack by a proton, which has a higher electron affinity than that of other common electrophils, the formation of the charge-transfer complex is not rate-determining whereas when the electrophil is $NO_2{}^+$ or Br^+, of lower electron affinity than H^+, the first step is rate-determining.

For reaction of different aromatic compounds with a given electrophil in a given solvent the greater the value of $\Delta^\ddagger$, and, to a smaller extent, the greater the value of $H_{01}{}^{\ddagger 2}$, the smaller is the activation energy for the first step. Thus when the first step is rate-determining the reaction is faster the lower the ionisation potential of the aromatic compound and the positions preferentially attacked are those for which $H_{01}{}^{\ddagger 2}$ is greatest.

The dependence of the energy of the first transition state upon $H_{01}{}^{\ddagger 2}$ shows that the geometry of the transition state will be that for which $H_{01}{}^{\ddagger 2}$ is as great as possible (limitations by non-bonded repulsions, etc., being borne in mind). According to the principle of maximum overlapping,[27] it will be that for which the lowest-energy vacant orbital of the electrophil most strongly overlaps the highest occupied molecular orbital of the aromatic compound. Every molecular orbital has a local maximum magnitude in the vicinity of each conjugated nucleus (except when this coincides with a node), as is clear when the π-orbitals are successfully represented by linear combinations of atomic $2p\pi$-orbitals. The electrophil will therefore be situated immediately above an atom of the conjugated system to obtain maximum overlap with a $2p\pi$-orbital, as shown in Fig. 4. A series of isomeric charge-transfer complexes may be pictured in which the electrophil is located above each of the conjugated atoms. If the conjugated atom has an attached hydrogen atom then the complex in which the electrophil is located in this atom may isomerise by way of an activated complex (I), E and H changing places, corresponding to the process (3*b*), and leading to a substituted product upon deprotonation. When the formation of (II) is rate-determining the proportions of isomers will be determined by the relative stabilities of the isomeric complexes (II) and so by the relative values of $H_{01}{}^{\ddagger 2}$ for the various positions around the conjugated system. The simple LCAO molecular-orbital theory provides a means of estimating the variation in $H_{01}{}^{\ddagger 2}$ and hence predicting orientations and relative reactivities of positions in aromatic compounds. This aspect is explored in detail in Part II. It may be seen however from (12) that, since the

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* A term representing the increase in energy arising from non-bonded repulsions between the aromatic compound and parts of the electrophil (especially when this is polyatomic) not directly involved in the electron-transfer interaction should strictly be included in equations (10), (11), and (12). Such interactions must be assumed to be constant for a given electrophil, and independent of the aromatic compound and of the position attacked by the electrophil. Although this effect has not been explicitly considered in previous treatments of chemical reactivity, such treatments implicitly involve this assumption.

[27] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.

greater the value of $\Delta^{\ddagger}$ the more rapid is the reaction, for rapid reactions the activation energy is less sensitive to values of $H_{01}{}^{\ddagger 2}$, *i.e.*, the electrophil discriminates less between the various positions of the aromatic system. In fact it will be shown in Part II that quantitative aspects of the selectivity of electrophils noticed by Brown and Nelson [28] may be deduced from eqn. (12).

Quantum-mechanical estimations of the energies of structures of the type (I) have been made by an alternative procedure [23,29,30] in which conjugation of the orbitals of the electrophil and the outgoing hydrogen with the aromatic system is treated by the LCAO molecular-orbital procedure, an antisymmetric combination of the E and H orbitals being regarded as a " pseudo-π-orbital." This type of treatment could equally well be used for the unsymmetrical complexes of type (II) but it suffers from a difficulty, noticed particularly by Fukui *et al.*,[30] that if the pseudo-orbital is assigned a Coulomb parameter greater than that of a carbon orbital, as would be assumed from the known electron affinities of typical electrophils,[19] the final π-electron density in the pseudo-orbital becomes considerably greater than unity. Fukui *et al.* tried to overcome this by incorporating the dependence of Coulomb parameter on π-electron density into the treatment but they did not find this feasible for numerical calculations.

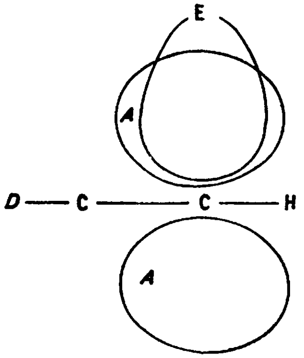

FIG. 4.
A, $2p\pi$ Orbital.
D, Conjugated plane perpendicular to paper.

The present " configuration-interaction " method overcomes this difficulty because we include only configurations with 0 or 1 electron in the electrophil-orbital, so that the electron density in this orbital cannot exceed unity. Furthermore it happens that the " configuration-interaction " treatment is particularly suited to numerical work, it being possible to develop a numerical index of reactivity corresponding to an exact solution of secular equations similar to (5) or (15). The alternative treatments are based either on idealised forms of (I) [31] or on quantities such as " superdelocalisabilities " which come from approximate solutions of secular equations. A numerical comparison of the methods is made in Part II.

Extent of Charge Transfer.—The extent of charge transfer, *T*, is given by the weight of the charge-transfer configurations in the eigenfunction Ψ of the complex. If Ψ is normalised then [see eqn. (4)] $T = 1 - a_0{}^2$. From (5) and (9) one finds

$$T \approx 1 - (H_{01}/\Delta)^2 \qquad (13)$$

showing that charge transfer is less complete the greater the extent of resonance interaction between the electrophil orbital and the aromatic orbital, and more nearly complete the greater the value of Δ. In the case of the nitration some values of *T* are estimated in Part II by use of equation (13). The values vary from almost unity in the great majority of cases to a more moderate value for exceptional aromatic compounds such as benzene ($T = 0{\cdot}75$). Thus the formulæ in equations (3), implying complete charge transfer (*i.e.*,

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[28] H. C. Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.
[29] Fukui, Yonezawa, and Nagata, *Bull. Chem. Soc. Japan*, 1954, **27**, 423.
[30] Fukui, Yonezawa, and Nagata, *J. Chem. Phys.*, 1957, **27**, 1247.
[31] R. D. Brown, *Quart. Rev.*, 1952, **6**, 63.

$T = 1$), are an accurate representation of the charge distribution in the charge-transfer complexes.

Charge Transfer from All Occupied Orbitals.—In the preceding treatment it was supposed that the electron transfer involved only the highest occupied orbital of the aromatic compound. In some cases the highest occupied orbital is degenerate and in other cases the two highest occupied orbitals are nearly degenerate. When configurations arising from charge-transfer from degenerate uppermost filled orbitals are considered the solution of the secular equations having lowest energy is:

$$E_1 = H_{00} - \{\Delta + (\Delta^2 + 4\textstyle\sum)^{\frac{1}{2}}\}/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $\sum$ represents the sum of squares of resonance integrals over the degenerate orbitals:

$$\textstyle\sum = \sum_j H_{0j}^{\,2}$$

When charge-transfer from the two uppermost nearly degenerate orbitals is considered a cubic equation in the energy is obtained from the secular determinant. This is considered explicitly in Part II. It is not difficult to write down the equation for the energy when configurations arising from charge-transfer from all occupied orbitals are included in the treatment. It is:[32]

$$\left[W - \sum_j \left(\frac{H_{0j}^{\ddagger 2}}{W - \Delta_j^{\ddagger}}\right)\right] \Pi_k \, (W - \Delta_k^{\ddagger}) = 0 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and the most positive solution corresponds to the energy of the transition state for step (3*a*) where

$$W = H_{00}^{\ddagger} - E$$
$$\Delta_j^{\ddagger} = H_{00}^{\ddagger} - H_{jj}^{\ddagger} = A^{\ddagger} - I_j$$

and I_j is the ionisation potential of the aromatic compound for ionisation from the *j*th occupied molecular orbital. The summations and products in (15) are taken over all occupied molecular orbitals.

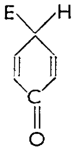
The activation energy for formation of the charge-transfer complex is then given by

$$\Delta E^{\ddagger} = X^{\ddagger} + Y^{\ddagger} - W^{\circ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

W° being the most positive solution of (15).

Intermediates Detected in Aromatic Substitution.—One of the features of aromatic substitution listed earlier [observation (vi)] was the isolation or detection of intermediates in substitution reactions. These have always been assumed to have a symmetrical structure (I), although there is no positive stereochemical evidence requiring this. The essential point of the present theory is that the charge-transfer complexes which are intermediates in the reaction have the unsymmetrical structure (II). There seems to be no difficulty in ascribing to the intermediates so far detected[6-12] unsymmetrical charge-transfer structure (II). In such structures no loss of aromaticity occurs. Furthermore in a quantum-mechanical investigation of this point Fukui *et al.*[29] showed that (I) normally corresponds to a local *maximum* in potential energy.

A possible exception might occur when the aromatic compound is an anion, such as in phenoxide. It is possible that the uncharged structure (V) is then a stable configuration owing to loss of electrostatic energy accompanying the formation of an uncharged covalent entity. However this would need to be more than enough to off-set the loss of aromaticity in such a structure.


(V)

Conclusion.—The present theory, involving unsymmetrical charge-transfer complexes, appears to account for the currently known features of aromatic electrophilic substitutions. Attention has been centred on uncharged aromatic systems and positively charged electrophils because charge transfer does not then appreciably alter the overall electrostatic properties, and hence electrostatic energy, of the interacting system. However

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[32] Dewar, *Proc. Camb. Phil. Soc.*, 1949, **45**, 638.

there is no difficulty in extending the present treatment to cases of uncharged electrophils such as SO_3, by including recognition of, for example, the dielectric properties of the solvent in facilitating the formation of an ion-pair configuration in the charge-transfer complex. In cases such as SO_3 a further interesting aspect might enter, namely that the lowest unfilled orbital of the electrophil may be sufficiently extensive to overlap simultaneously more than one $2p\pi$-orbital of the aromatic compound in the charge-transfer complex. This must inevitably happen in reactions such as ozonolysis, Diels–Alder addition, osmium tetroxide oxidation, etc., and it is hoped to extend the present treatment to these reactions in a subsequent paper. The charge-transfer complex mechanism is also applicable to nucleophilic substitution in aromatic compounds and to reactions of aromatic compounds with free radicals, as has been noted by Fukui *et al.*[29,30]

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