SULPHURYL CHLORIDE AS AN ELECTROPHILE

A thesis presented for the degree of
Master of Philosophy
in the Faculty of Science
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by

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Bedford College, London

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ABSTRACT

The reaction of sulphuryl chloride with a number of anilides in nitromethane at 25°C has been studied kinetically. It was concluded that although molecular sulphuryl chloride $(\overset{\delta+}{Cl} - \overset{\delta-}{SO_2Cl})$, is the major electrophile, molecular chlorine also contributes as the attacking electrophile.

$$SO_2Cl_2 \overset{K}{\rightleftarrows} SO_2 + Cl_2$$

The stoichiometry of the reaction is

$$ArH + SO_2Cl_2 \longrightarrow ArCl + SO_2 + HCl$$

A second order rate equation of the form

$$Rate = k_2 \left[SO_2Cl_2\right] \left[ArH\right]$$

was found; the reaction is kinetically first order with respect to each of the reactants.

The effect of the substituents, ($\rho = -5$) shows that a heterolytic electrophilic process is involved. The effect of solvents, which increase the rate of the reaction in the order nitromethane $\rangle$ o-dichlorobenzene $\rangle$ chlorobenzene $\rangle$ benzene, is also evidence for a heterolytic process.

The reaction of sulphuryl chloride with anthracene and some of its derivatives, and also with some derivatives of pyrene in chlorobenzene at 25°C has been studied. The stoichiometry of the reaction is

$$ArH + SO_2Cl_2 \longrightarrow SO_2 + HCl + ArCl.$$

The only effective electrophile was found to be molecular sulphuryl chloride $(\overset{\delta+}{Cl} - \overset{\delta-}{SO_2Cl})$ which attacks the ring in the rate determining step.

$$Rate = k_2 \left[ArH\right] \left[SO_2Cl_2\right]$$

This step is second order, first order with respect to each of the reactants. The magnitude of reaction constant ($\rho = -1.73$) for anthracenes

and ρ= about -2 for pyrenes indicates that the transition states in these heterolytic processes have acquired some positive charge. The effect of solvent on the rate (o-dichlorobenzene faster than chlorobenzene, which is faster than benzene) also confirms this deduction. The substituent effects show an electrophilic process in which electronic effects appear to be propogated by π -electron interactions.

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INTRODUCTION

Introduction

1. Heterolytic and homolytic bond formation and breaking:[1,2]

A covalent bond can be broken and formed in two ways. If it is broken in such a way that each species gets one bonding electron, making radicals, it is called homolysis; the reverse process, called colligation, is the combination of two radicals.

$$X:Y \underset{\text{colligation}}{\overset{\text{homolysis}}{\rightleftharpoons}} X\cdot + Y\cdot \qquad (1)$$

If the covalent bond is broken in such a way that one of the species takes both electrons and the other takes none, the process is called heterolysis and the products of this process are ions. The reverse reaction is called co-ordination.

$$X:Y \underset{\text{co-ordination}}{\overset{\text{heterolysis}}{\rightleftharpoons}} X:^{-} + Y^{+} \qquad (2)$$

X: (an electron-rich species) is called a nucleophile and Y (electron-deficient and seeking for electrons) is called an electrophile. Heterolytic processes are classified as nucleophilic or electrophilic reactions. Organic reactions can be classified as substitutions, additions, rearrangements and so on, and the characteristic reactions of aromatic systems are substitutions rather than additions.

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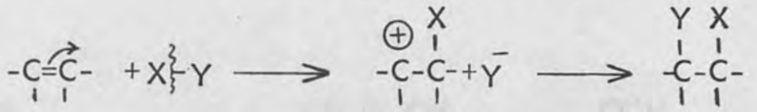
1.1 Additions:

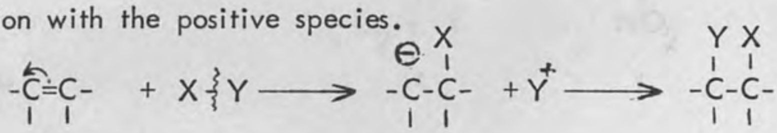
In this type of reaction two new covalent bonds are formed to a substrate, and this reaction can take place by three possible mechanisms.

1.1.1 Electrophilic addition: In this mechanism a positive species (or the positive end of a dipole) approaches the double or triple bond. In the first step a carbonium ion is formed and in the second step, the combination of carbonium ion with the negative species is involved.



$$-C{=}C- \;+ X{-}Y \longrightarrow -\overset{\oplus}{C}-\overset{X}{C}- + \bar{Y} \longrightarrow -\overset{Y}{C}-\overset{X}{C}- \qquad (3)$$

1.1.2 Nucleophilic addition: In this mechanism the first step involves the creation of a carbanion and the second step is a combination of this carbonion with the positive species.

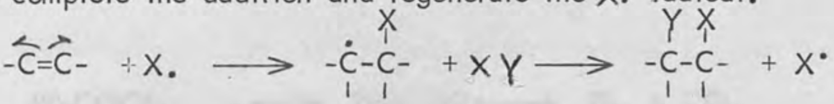


$$-C{=}C- \;+ X{-}Y \longrightarrow -\overset{\ominus}{C}-\overset{X}{C}- \;+ \overset{+}{Y} \longrightarrow -\overset{Y}{C}-\overset{X}{C}- \qquad (4)$$

1.1.3 Free radical addition: In the first step of this reaction the generated radical by the equation:

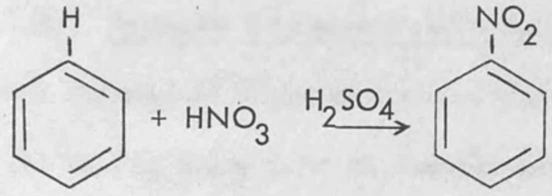
$$XY \longrightarrow X. + Y. \qquad (5)$$

approaches the double or triple bond, and the second step is an abstraction of Y to complete the addition and regenerate the $X.$ radical.



$$-C{=}C- \;+ X. \longrightarrow -\dot{C}-\overset{X}{C}- \;+ XY \longrightarrow -\overset{Y}{C}-\overset{X}{C}- \;+ X^{\bullet} \qquad (6)$$

1.2 Aromatic Substitutions[1-4] involve reactions in which hydrogen, or a substituent already present in the aromatic ring, is replaced by another group. Thus, the nitration of benzene to give nitrobenzene (eqn. (7)), the nitro-deiodination of p-iodoanisole to give 2,4-dinitroanisole[5] (eqn. (8)) and the reaction of hydroxide ion with chloro-2,4-dinitrobenzene to give 2,4-dinitrophenol[6] (eqn. (9)) are all aromatic substitution processes, as is the phenylation of benzene by Ph· to give biphenyl[7] (eqns. (10) (11)).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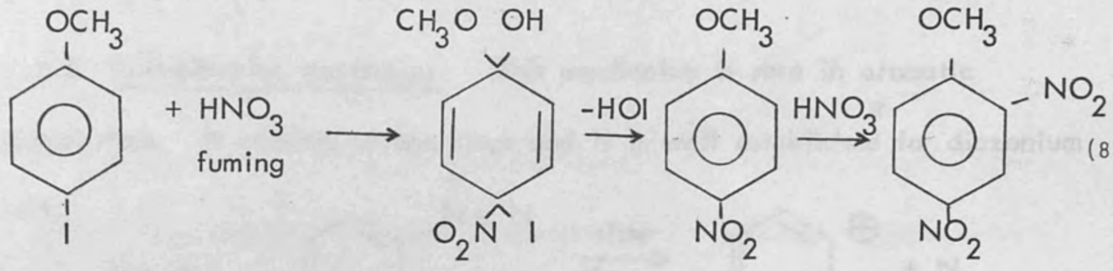
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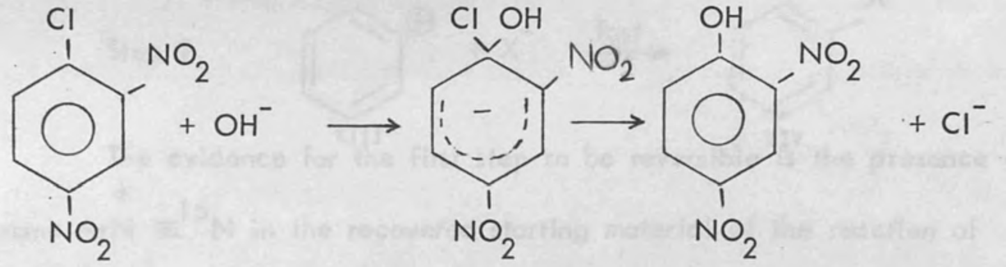
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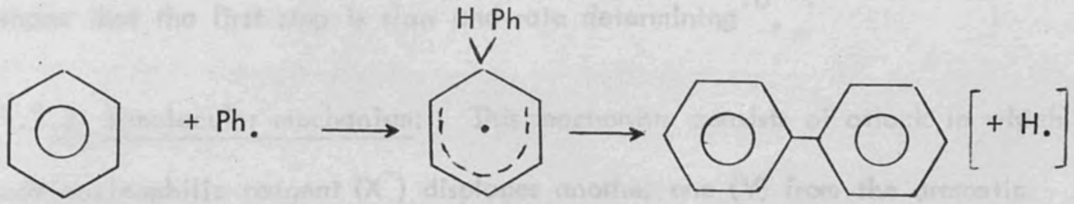
$$(PhCOO)_2 \longrightarrow 2PhCOO\bullet \longrightarrow Ph. + CO_2 \qquad (10)$$

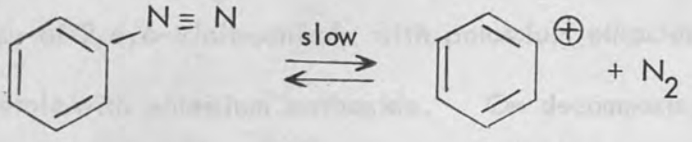

I X XI (11)

They are subdivided according to the nature of the attacking species and the kinetic form of the slow stages.

1.2.1 Aromatic Nucleophilic Substitution. In a nucleophilic substitution the nucleophile brings an electron pair to the substrate to form a bond, and the leaving group gains an electron pair. There are three general mechanisms for these reactions; SN_1 (unimolecular); SN_2 (bimolecular); and elimination addition (benzyne) mechanisms.

1.2.2. Unimolecular mechanism: This mechanism is rare in aromatic substitution. It consists of two steps and it is well established for diazonium salts.[8]

Step 1



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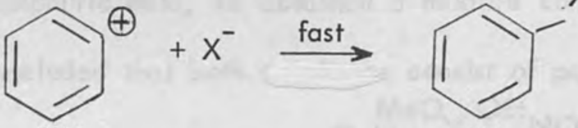
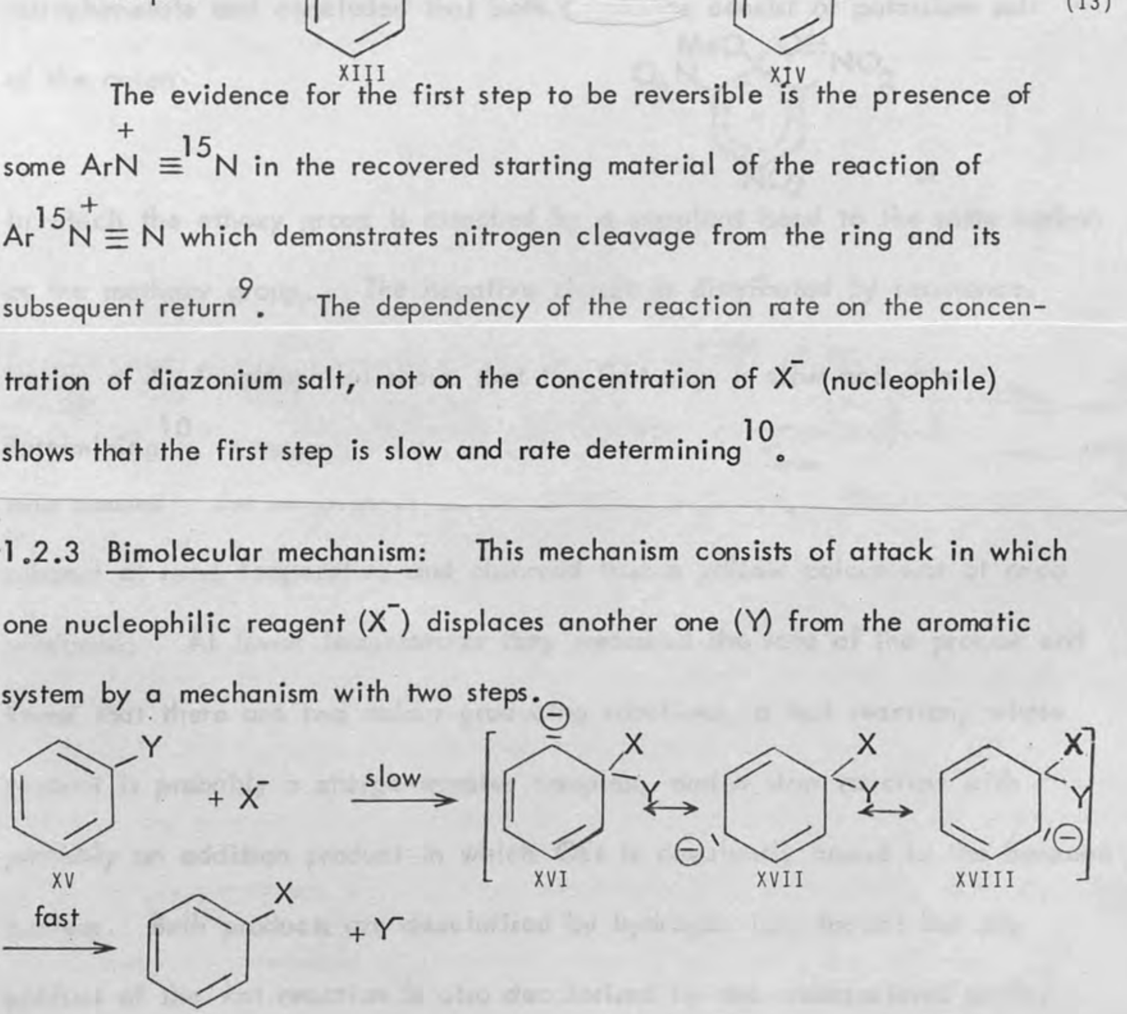
Step 2



XIII XIV (13)

The evidence for the first step to be reversible is the presence of some $Ar\overset{+}{N} \equiv {}^{15}N$ in the recovered starting material of the reaction of $Ar^{15}\overset{+}{N} \equiv N$ which demonstrates nitrogen cleavage from the ring and its subsequent return[9]. The dependency of the reaction rate on the concentration of diazonium salt, not on the concentration of X^- (nucleophile) shows that the first step is slow and rate determining[10].

1.2.3 Bimolecular mechanism: This mechanism consists of attack in which one nucleophilic reagent (X^-) displaces another one (Y) from the aromatic system by a mechanism with two steps.



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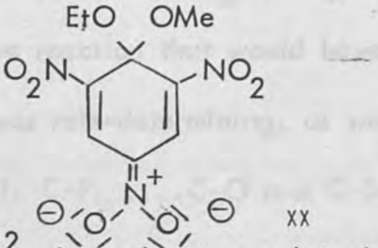
SN_2 reaction is usually first order with respect to both the concentration of substrate and the reagent (X^-), while the SN_1 reaction is first order with respect to the substrate[11]. In this mechanism the first step is usually slow and rate-determining. Some evidence for this mechanism includes the isolation of intermediates such as



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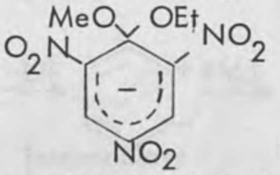
This structure was suggested by Meisenheimer[12] who isolated as solids the products of reaction of 2,4,6-trinitroanisole with potassium ethoxide and of 2,4,6-trinitrophenetole with potassium methoxide. On decomposing each of these with dilute sulphuric acid, he obtained a mixture containing trinitrophenetole and concluded that both specimens consist of potassium salt of the anion



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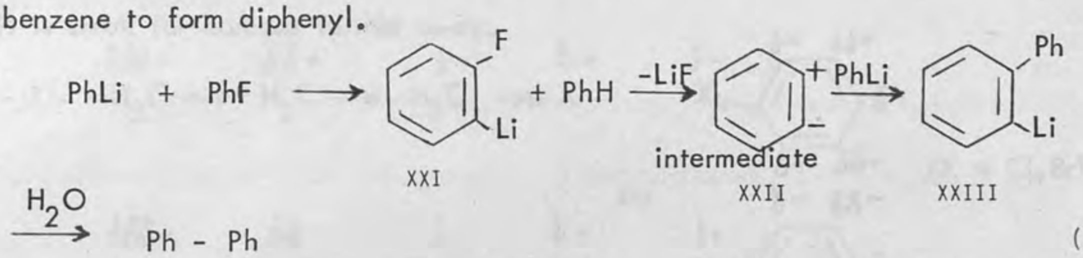
in which the ethoxy group is attached by a covalent bond to the same carbon as the methoxy group. The negative charge is distributed by resonance. Hammick and Foster[13] have found the infrared spectra of the two products to be identical. This structure is also supported by Ainscough and Caldin who studied[14] the reaction of sodium ethoxide with 2,4,6-trinitroanisole in ethanol at room temperature and observed that a yellow colour was at once produced. At lower temperatures they measured the rate of the process and found that there are two colour-producing reactions, a fast reaction, whose product is probably a charge-transfer complex, and a slow reaction with probably an addition product in which OEt is covalently bound to the benzene nucleus. Both products are decolorised by hydrogen ions (acids) but the product of the fast reaction is also decolorised by the undissociated acids.

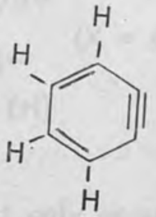
The effect of the leaving group on the reaction is another piece of evidence for this mechanism. In the study of the reaction of 1-substituted-2,4-dinitrobenzenes with piperidine in methanol, Bunnett and co-workers[15] have shown that the leaving group (Y) may be Cl, Br, I, SO_2Ph or *p*-nitrophenoxy, without the effect on rate of the reaction that would have been observed if bond-breaking of the Ar -Y was rate-determining, as was expected because hydrolysis of the bonds C-Cl, C-F, ...C-O and C-S occur at quite different rates. This shows that formation of the intermediate, a step in which the C-Y bond is not breaking, is the rate determining step.

1.2.4 Elimination-addition (benzyne) mechanism: This mechanism was first suggested by Witting et al[16] for the reaction of phenyl-lithium with fluoro-benzene to form diphenyl.



(15)

The intermediate was suggested to be represented as:



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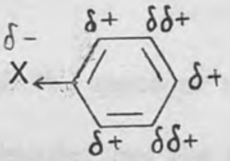
by Roberts, who called it "benzyne" which name is still accepted.

1.2.5 Aromatic Electrophilic Substitution[4] - These reactions involve the attack of an electrophile at a position with high electron density. The benzene ring is a source of electrons for electron seekers. The π -electrons in the benzene ring are holding each other somewhat more tightly than the π-electrons of a carbon-carbon double bond (C=C) in olefins, but are loosely held in comparison with σ-electrons and this makes them more available to electrophiles. The substituent already present in the ring determines the position of the attack of the new group. The electronic effect of the substituent may operate through space, σ-bonds, or π-bonds.

1.3 Electronic Effect of Substituent

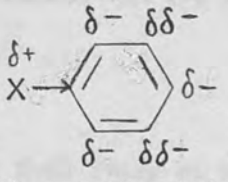
1.3.1 Inductive Effect[1-3] In a polar system in which there are species with different electronegativity, the species which tends to attract electrons shows a -I effect and the species which tends to repel electrons shows a +I effect. In inductive effects, the arrangement of the electrons does not change. The result is a polarisation of the bond and a slight positive charge on the next carbon. The effect is greater for adjacent bonds, but it is weak for carbons further away.

$$-I \qquad \overset{\delta\delta\delta+}{H_3C} \longrightarrow \overset{\delta\delta+}{H_2C} \twoheadrightarrow \overset{\delta+}{H_2C} \ggg \overset{\delta-}{X}$$



XXV (X = Cl, Br)

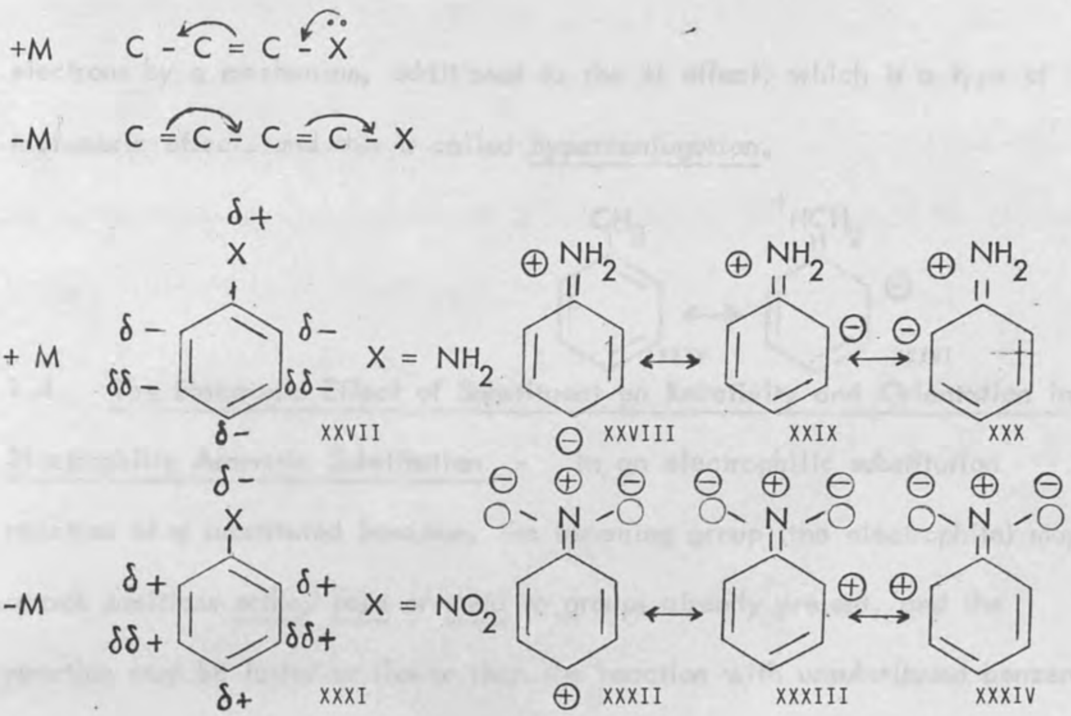
$$+I \qquad \overset{\delta\delta\delta-}{H_3C} \longleftarrow \overset{\delta\delta-}{H_2C} \twoheadleftarrow \overset{\delta-}{H_2C} \lll \overset{\delta+}{X}$$



XXVI (X = CH_3)

(X is an electronegative substituent such as Cl (-I) and CH_3 (+I)

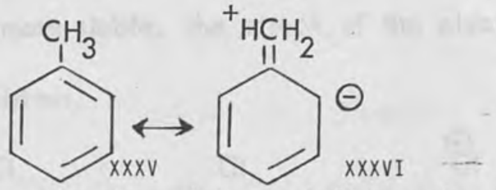
1.3.2 Mesomeric Effect (Resonance Effect)[1-3] This effect only occurs in unsaturated molecules and shows the ability of the substituent to rearrange the π-electron pairs in these molecules. If the substituent tends to donate electrons to the unsaturated system it shows an +M effect and if it withdraws electrons from the carbon system it shows an -M effect.



Inductive and Mesomeric Effects are time independent effects of electron displacement.

1.3.3 Field Effect - This effect operates through the space or solvent molecules and depends on the geometry of the molecule, not the nature of the bond.

1.3.4 Hyperconjugation - Baker and Nathan in their study of velocity of reaction of various p-alkyl substituted benzyl bromides with pyridine in dry acetone[17] found that all alkyl substituents increase the velocity of the reaction and that the velocity decreases in the order Me 〉 Et 〉 Pr^i 〉 Bu^t. Therefore methyl groups must be able to release electrons by an additional mechanism not available to the other alkyl groups or at least is very diminished in bulkier alkyl groups. It was suggested that when the methyl group is attached to a conjugated system, the electron pair of the C-H bond are not so localized (less than C-C) and the methyl group can release electrons by a mechanism, additional to the +I effect, which is a type of tautomeric effect, and this is called <u>hyperconjugation</u>.



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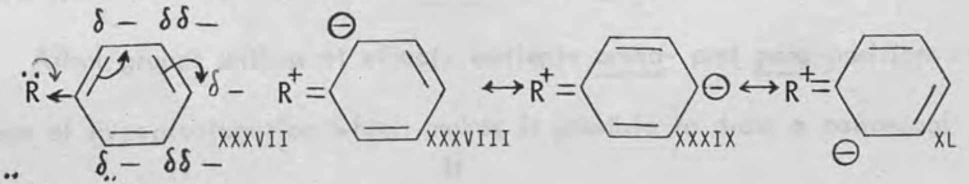
1.4 The Electronic Effect of Substituent on Reactivity and Orientation in Electrophilic Aromatic Substitution

- In an electrophilic substitution reaction of a substituted benzene, the incoming group (the electrophile) may attack positions <u>ortho</u>, <u>para</u> or <u>meta</u> to groups already present, and the reaction may be faster or slower than the reaction with unsubstituted benzene. If the reaction with the substituted benzene is faster than benzene, the substituent is an activating group; and if slower, it is called a deactivating group. Activating groups are <u>ortho</u>- and <u>para</u>- directing. Deactivating groups are generally <u>meta</u>-directing. Halogens are <u>ortho</u>-<u>para</u>-directing but deactivating groups which will be discussed on the next page.

Substituent groups with unshared unsaturated electrons on the atom attached to the ring, such as $\bar{O}$, $\ddot{N}H_2$, $\ddot{O}H$ (and halogens) have the possibility of conjugation with the ring and they are generally <u>ortho</u>- and <u>para</u>-directing, in spite of their negative inductive effect[1] (except $\bar{O}$).

(+M)



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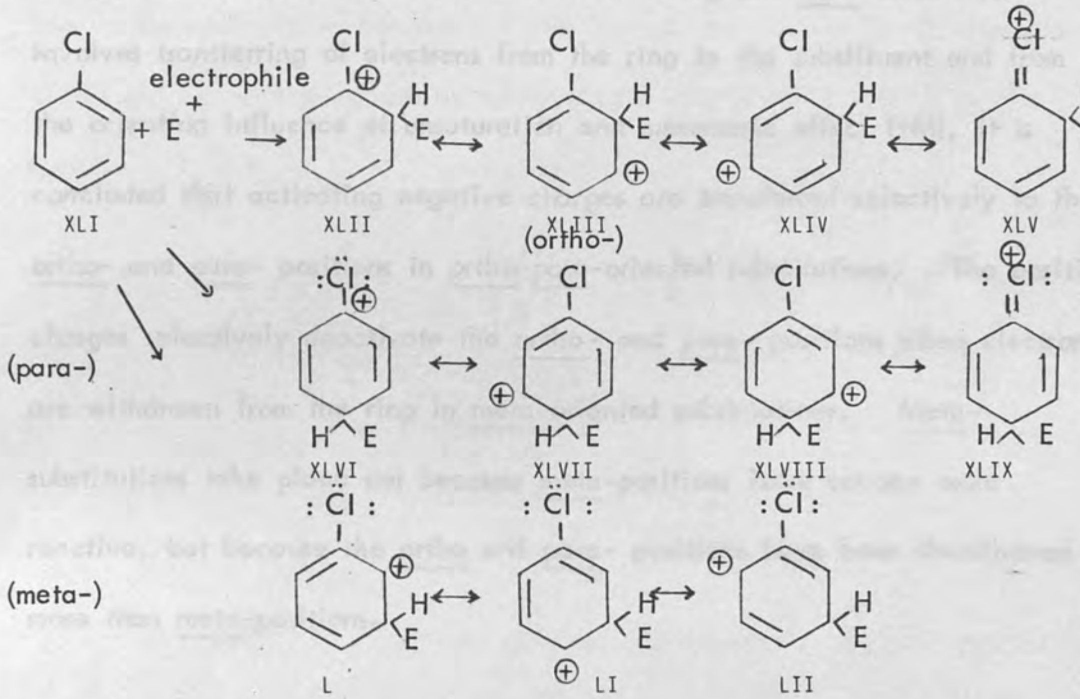
(R = $\ddot{N}H_2$, $\ddot{O}H$, etc.)

The unshared electrons take part in the conjugative electron displacement and the development of the negative charge on the <u>ortho</u>- and <u>para</u>-positions makes these positions more suitable for the attack of an electrophile.

Halogens, because of their strong inductive effect (-I) are deactivating but despite the positive conjugative effect (+M) involving a resonance hybrid of the arenium ion[4], which makes it more stable, the attack of the electrophile is directed to ortho and para positions.



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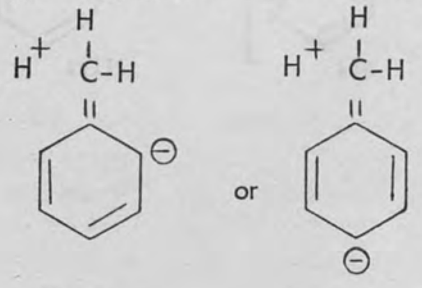
XLVI XLVII XLVIII XLIX (17)

L LI LII (18)

The +K effect may be subdivided into a +M effect which is a permanent condition of the molecule, and the +E effect, which is excited by the electrophile and which appears only when the electrophile attacks.

Substituents without unshared electrons, such as NO_2, NR_3^+, NH_3^+, COOH, have a -I effect and are meta-directing and deactivating.

Alkyl groups with a +I effect, activate ortho- and para-positions and also because of hyperconjugation which makes it possible to draw a canonical form.



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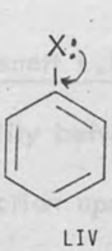
The result of study of orientation so far is that from the described influence of the electropolarity of substituents (±I effects), it follows that the ortho-para- orientation involves transferring of electrons (negative charge) from the substituents to the aromatic ring and meta-orientation involves transferring of electrons from the ring to the substituent and from the orienting influence of unsaturation and mesomeric effect (+M), it is concluded that activating negative charges are transferred selectively to the ortho- and para- positions in ortho-para-oriented substitutions. The positive charges selectively deactivate the ortho- and para- positions when electrons are withdrawn from the ring in meta-oriented substitutions. Meta-substitutions take place not because meta-positions have become more reactive, but because the ortho and para- positions have been deactivated more than meta-positions.



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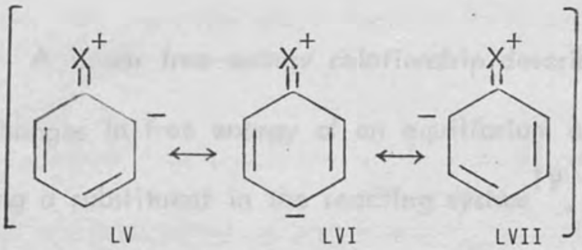

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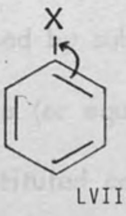

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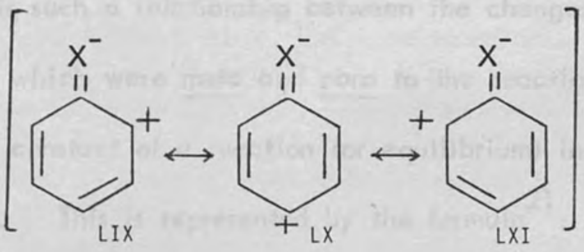

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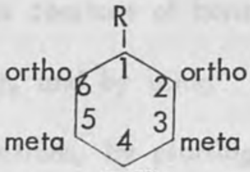
1.4.1 Partial Rate Factors

The orientation can also be discussed in terms of the partial rate factors. These factors are the ratio of the rates of substitution at one position in the benzene derivatives divided by the rate of substitution at one of the positions in benzene. The partial rate factors for substitution in the o-, m- and p- positions relative to a substituent R are given the symbols[18] f_o^R, f_m^R, f_p^R, respectively.

$$f_o^R = \frac{k_{o\text{-}R}}{k_H} = \frac{k_{C_6H_5R}}{(k_B/6)} \times \frac{\%\ \text{ortho}}{2 \times 100}$$



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$$f_m^R = \frac{k_{m\text{-}R}}{k_H} = \frac{k_{C_6H_5R}}{(k_B/6)} \times \frac{\%\ \text{meta}}{2 \times 100}$$

$$f_p^R = \frac{k_{p\text{-}R}}{k_H} = \frac{k_{C_6H_5R}}{(k_B/6)} \times \frac{\%\ \text{para}}{100}$$

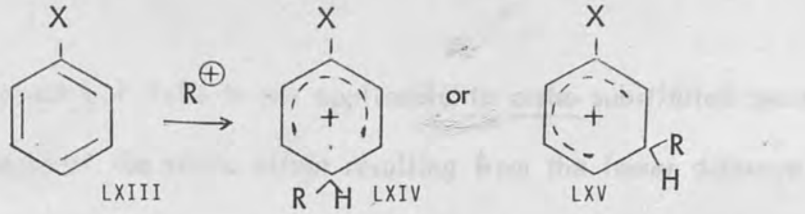
$k_{C_6H_5R}/(k_B/6)$ is the rate ratio of the substituted benzene to benzene in one position.

1.4.2 Hammett L.F.E.R.

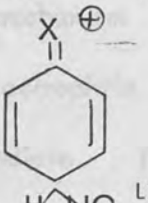
1.4.2 Hammett L.F.E.R. - A linear free-energy relationship describes a proportionality between the changes in free energy of an equilibrium or a rate of reaction upon changing a substituent in the reacting system[19]. Hammett found that[20] there is such a relationship between the changes in free energy caused by substituents which were meta and para to the reaction site, and the rate (or equilibrium) constant of a reaction (or equilibrium) involving phenyl-substituted compounds. This is represented by the formula[21]: $\log k/ko = \rho\sigma$, in which k is the rate (or equilibrium) constant of the substituted reactant e.g. substituted benzoic acid, and ko is that of the unsubstituted analogue, e.g. benzoic acid. σ is the substituent constant which is independent of reaction and it is the measure of the ability of the substituent to displace electrons to the reaction centre[19]. ρ is the reaction constant which is independent of the substituent and depends on the reaction conditions, the medium and the temperature and it is the measure of sensitivity of the reaction or equilibrium to a change in electron density. By giving a value of unity to ρ determined from the data of Dippy and co-workers[22], the difference between the logarithm of the ionisation constant[19] of a substituted benzoic acid and the logarithm of the ionisation constant of benzoic acid gives the value of the σ constant for that substituent, and by using these σ values ρ values have been derived for other reactions, by plotting the values of log k for a reaction of compounds with different substituents in the benzene ring, against the substituent constants σ, the result is a straight line (Hammett L.F.E.R.), the slope of which is the value of ρ. A negative value of ρ shows that a reaction is favoured by electron release and it indicates that the transition state involves some carbocationic character. A positive value of ρ shows that the transition state involved is favoured by electron donation.

A positive sign of σ indicates that the group is electron withdrawing and a negative value indicates electron donating properties.

Many reactions show good Hammett plots, but some reactions, those with strong electron demands in the transition state, show considerable scatter in the points comprising the line. The available data on aromatic nitration show serious deviation in the Hammet treatment[23], which was observed for substituted compounds with <u>ortho-para</u>-directing groups and it may be because these are able to stabilise the transition state



(19)

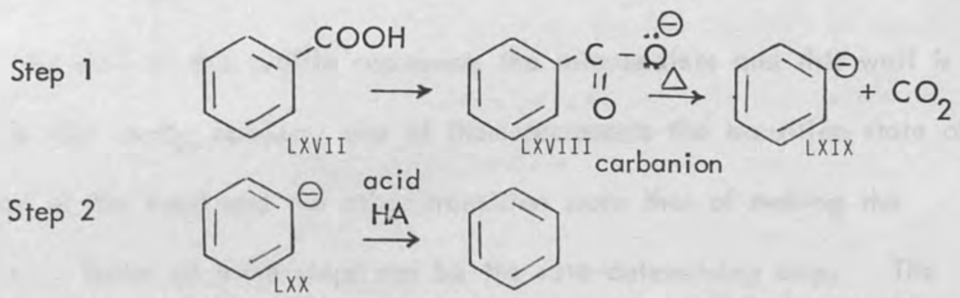
for p-substitution more than might be expected from their σ-constants. The effects might be ascribed to resonance structures of type  LXVI which could contribute relatively more to the stability of the transition state for p-substitution than for m-substitution or in the ground state. The deviations were small for p-CH_3 and p-F, moderate for p-Cl and p-Br and high for p-I.

De la Mare pointed out that the available halogenation results fail to follow the Hammett relationship.[24] He also attributed the deviation to the importance of resonance interactions in aromatic substitution. It was therefore proposed that(i) substituents which did not interact mesomerically with the reaction centre (meta-substituents) always give good Hammett plots (ii) that the deviations by para-substituents were proportional to the electron demand of the reaction, and (iii) that by a Hammett plot[25] using the rates of solvolysis of meta-substituted aryldimethyl carbinyl chlorides, one could use the experimentally observed rates of solvolysis of the para-compounds to derive new σ values called $\overset{+}{\sigma}$ for those troublesome substituents. A modified Hammett equation is obtained, $\log k/ko = \rho \cdot \overset{+}{\sigma}$ This was shown by Roberts and co-workers[23] in nitration of monosubstituted benzene, by De la Mare[24] in halogenation of monosubstituted benzenes by bromine and chlorine (in acetic acid) and by Illuminati and Marino[26] in bromination of monosubstituted derivatives of mesitylene, where a far better fit of Hammett plot arose with $\overset{+}{\sigma}$ values than with σ values.

The Hammett L.F.E.R. is not applicable to ortho substituted benzene derivatives because of the steric effect resulting from the lesser distance between the substituent in the ortho position to the reacting group.

1.4.3 Mechanism of Electrophilic Substitution[1-4] - The mechanism of electrophilic substitution involves the arenium ion. The electrophile attacks in the first step and makes a positively charged intermediate. The abstraction of the leaving group occurs in the second step. An alternative mechanism in which the leaving group departs before the arrival of the electrophile (like the SN_1 mechanism in nucleophilic substitution) is less common and it has been found only in reactions in which carbon is the leaving group, e.g. decarboxylation of aromatic acids[27]

$$\mathrm{ArCOOH} \xrightarrow[\text{quinoline}]{\text{Cu}} \mathrm{ArH} + \mathrm{CO_2}$$



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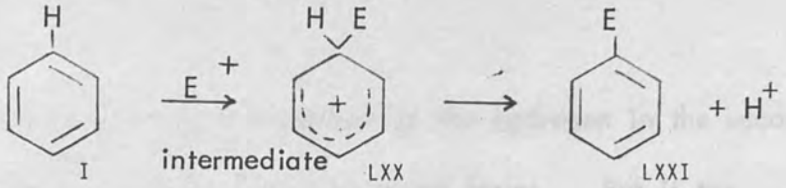
or when a strong acid is present, e.g. dehalogenation of aryl halides by Friedel-crafts catalysts[28].

$$\mathrm{ArX} \xrightarrow{\mathrm{AlCl_3}} \mathrm{ArH} \qquad (22)$$

Mechanisms analagous to the SN_2 process, the simultaneous attack of electrophile and departure of the leaving group, are not found at all. An electrophile which may be a positive ion or a dipole, attacks the ring and removes a pair of electrons from the ring to produce a carbonium.



(23)

In the intermediate the electrophile and the proton are bound to the aromatic carbon atom. Although it has less stabilisation energy than the original benzene system, some of this lost energy is returned by the electrophile (by using the π-electrons of the ring) and some of it by hyperconjugation of the hydrogen[29] with the rest of the system. The presence of an intermediate is shown by the energy diagram (potential energy vs. reaction co-ordinate profile)

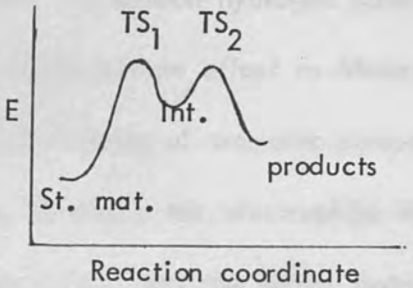


Fig. 1 Energy Diagram

The well of this profile represents the intermediate and this well is linked to two energy barriers, one of them represents the transition state of formation of the bond and the other transition state that of making the products. Either of these steps can be the rate-determining step. The intermediate can either lose the proton and goes to products or lose the electrophile and reverts to reactants. There are two pieces of evidence for the arenium ion mechanism, the isotope effect and the isolation of the intermediates.

1.4.4 <u>Isotope Effect</u> - If the hydrogen whose place will be taken by an electrophile, is changed to deuterium or tritium, a primary isotope effect will be found in the one-step mechanism or in a two-step mechanism if the rate-determining step involves departure of the hydrogen in the second step, and the compound with light hydrogen reacts faster. But if the second step is faster, the first step is rate determining and there is no sign of an isotope effect,

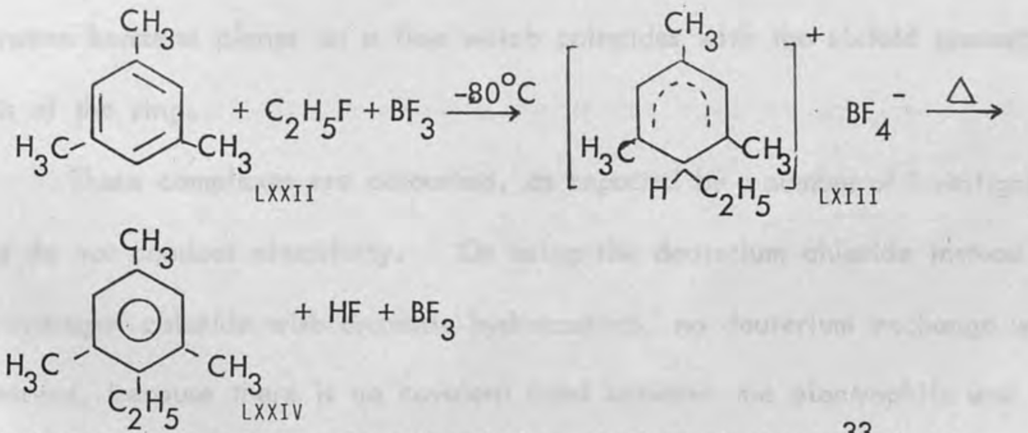
$$\mathrm{ArH} + \mathrm{E}^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left[\mathrm{Ar}\begin{array}{l}\diagup \mathrm{H}\\ \diagdown \mathrm{E}\end{array}\right]^{+} \tag{24}$$

$$\left[\mathrm{Ar}\begin{array}{l}\diagup \mathrm{H}\\ \diagdown \mathrm{E}\end{array}\right]^{+} \xrightarrow{k2} \mathrm{ArE} + \mathrm{H}^{+} \tag{25}$$

because in the arenium ion mechanism the carbon-hydrogen bond is not breaking in the slow step. There is no isotope effect as Melander[30] found out in the study of nitration of a series of aromatic compounds containing small amounts of tritium, in which the electrophile did not prefer to displace the light hydrogen rather than the heavy isotope and it was concluded that the departure of the proton was not kinetically significant. The observed isotope effect in some reactions such as: meta-nitration of tritiated nitrobenzene, toluene, bromobenzene, p-nitrobromobenzene, naphthalene, by Melander[30], k_H/k_T ratio being about 1.3 was a secondary isotope effect, not arising from breaking of the C-H bond and therefore not from a primary isotope effect.

If in the arenium-ion mechanism (S_E2 mechanism) the second step proceeds more slowly than the first one, a kinetic isotope effect would be expected[31], but in most electrophilic substitution reactions the primary isotope effect was not observed. Thus, the second step involving the release of hydrogen is faster than the first one, and the observed isotope effect could be from the reversibility of step 1 (equation 24). The rate of the reversion of $(\mathrm{Ar}^{+}\begin{array}{l}\diagup \mathrm{H}\\ \diagdown \mathrm{E}\end{array})$ to ArH (reactant) should be almost the same as the rate of reversion of $\left[\mathrm{Ar}^{+}\!<^{D}_{E}\right]$ to ArD or $\left[\mathrm{Ar}^{+}\!<^{T}_{E}\right]$ to ArT because the C-H bond is not breaking in this step, but the rate of making the products (i.e. $\left[\mathrm{ArHE}^{+}\right]$ and $\left[\mathrm{ArDE}^{+}\right]$ going to ArE should be different (faster for the first one). If $k_2 \gg k_1$ this does not matter and the rate determining step is the first step $k_1\left[\mathrm{ArH}\right]\left[\mathrm{E}^{+}\right]$, and in this case if $k_2 \ll k_{-1}$ the reversion to reactant has nearly the same rate for (ArHE^{+}), $(\mathrm{ArED})^{+}$ and $(\mathrm{ArET})^{+}$, but the rate of reactions producing products (ArE and H^{+} or D^{+} or T^{+}), k_2, for $(\mathrm{ArED})^{+}$ and $(\mathrm{ArET})^{+}$ is less than that for $(\mathrm{ArHE})^{+}$ thus a larger proportion of $(\mathrm{ArHE})^{+}$ goes to products than (ArDE^{+}) and the partition factor for (ArDE^{+}) is less than that for (ArHE^{+}), $(k_2/k_{-1})_{(\mathrm{ArHE})^{+}} > (k_2/k_{-1})_{(\mathrm{ArDE})^{+}}$ and the overall reaction is faster for ArH and a weak isotope effect is found although C-H bond breaking is not well developed in the rate determining step.

1.4.5 <u>Isolation of arenium ion intermediate</u> - Some arenium ions have been isolated, for example[32] in the reaction of mesitylene with ethyl fluoride and BF_3 (as a catalyst) at -80°C, an isolatable intermediate with m.p. of -15°C was obtained which after heating was altered to ethyl mesitylene.



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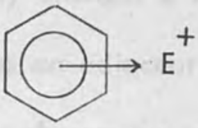
Such intermediates are coloured and they conduct electricity[33] (evidence for the presence of positive and negative ions). Electrophiles can form a loose addition complex without making a bond to any particular carbon,



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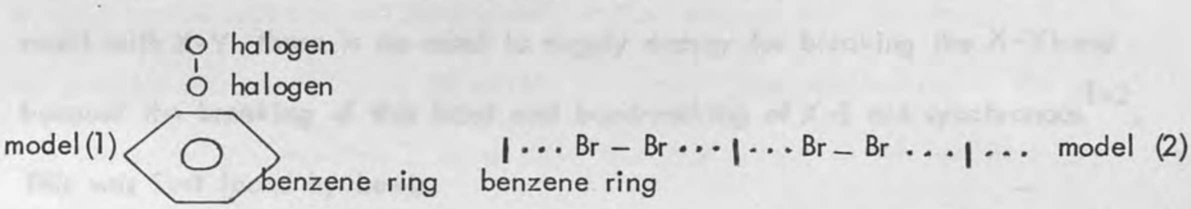
but to the π-electron cloud. This sort of complex is called a charge transfer complex, π-complex, or outer complex.

The stereochemistry of these complexes is important when they serve as intermediates. Among the various proposed models for the aromatic halogen complexes, the axial model is suggested by the infrared studies of E.E. Ferguson[34]. In this model, halogen atoms are situated on the sixfold



axis of the benzene ring (model (1)). This model is supported by x-ray works of Hassel and co-workers[35]. Their work showed that the crystals consist of chains of alternating benzene and halogen (model (2)) molecules, the aromatic planes are all parallel to each other and the halogens symmetrically placed between benzene planes on a line which coincides with the sixfold symmetry axis of the ring.

These complexes are colourless, as reported by a number of investigators[36] and do not conduct electricity. On using the deuterium chloride instead of hydrogen chloride with aromatic hydrocarbons, no deuterium exchange was observed, because there is no covalent bond between the electrophile and the ring, while formation of an arenium ion with DCl and $AlCl_3$ causes deuterium exchange; the relative stabilities of these two sorts of complexes is different: the π -complex stability does not change much with methyl group substitution, but σ -complex stability changes a lot. This difference can be explained. A methyl group stabilises an adjacent positive charge. In a σ -complex a great amount of positive charge is present in the ring. In a π -complex a small amount of positive charge is spread over the whole of the ring and a methyl group can stabilise it equally on any position but in the σ -complex the ion is a hybrid of three canonical forms and the charge is localised on three carbons. When methyl group is attached to one of these three carbons it stabilises the charge on that position.

1.4.6 Transition State - In a reaction path when an electrophile (E) is to react with X-Y there is no need to supply energy for breaking the X-Y bond because the breaking of this bond and bond-making of X-E are synchronous[1-2]. This was first found by Lewis.

$$E + X\text{-}Y \quad = \quad E - X + Y \qquad (27)$$

As (E) is getting closer to X-Y the interaction between (E) and the bond electrons of X-Y will supply the required energy for breaking the X-Y bond and the reverse of that is the reaction between X-E and Y. But between the initial state (reactants) and the final state (products) there is a configuration like E .... X .... Y which is called the transition state, having the greatest amount of energy: in a two-step reaction the energy diagram involves two transition states and an intermediate is represented by the valley between the transition states.

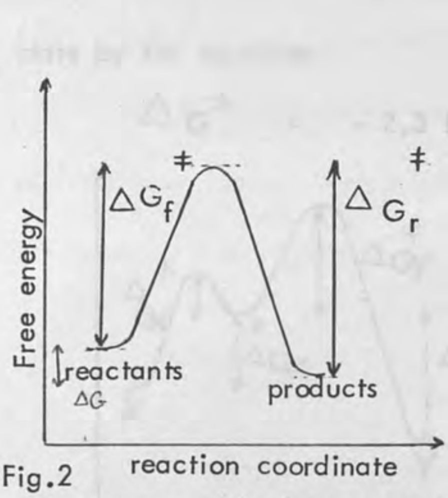


Fig.2
Free energy profile for one-step reaction.

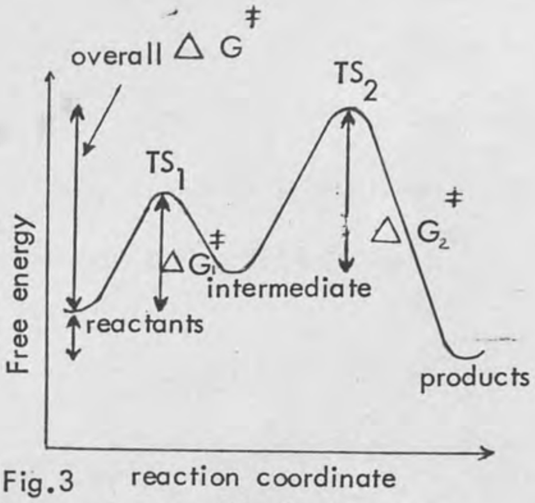


Fig.3
Free energy profile for two-step reaction.

The reaction co-ordinate is a function of all the space co-ordinates of the reacting system, and each point on the reaction co-ordinate specifies the geometrical properties of the system[4]. A reaction takes place if the free energy of the products is lower than the free energy of the reactants (negative ΔG). The free energy is related to two factors, enthalpy change ΔH and entropy change ΔS by the equation:

$$\Delta G = \Delta H - T \Delta S$$

ΔH measures the evolved or absorbed heat during a reaction (at constant pressure) and ΔS is the degree of disorder of the system. High entropy (the less order) and low enthalpy are the best conditions in a system; having a negative ΔG is not sufficient for a reaction to take place[1], but a free energy of activation must be added. For the reverse reaction the free energy of activation is equal to ($\Delta G + \Delta G_f^{\ddagger}$). $\Delta G^{\ddagger}$ is related to ΔH , the enthalpy of activation, and $\Delta S^{\ddagger}$, the entropy of activiation, by the equation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$$

and is related to the equilibrium constant between initial state and transition state by the equation

$$\Delta G^{\ddagger} = -2.3\ RT \log K^{\ddagger}$$

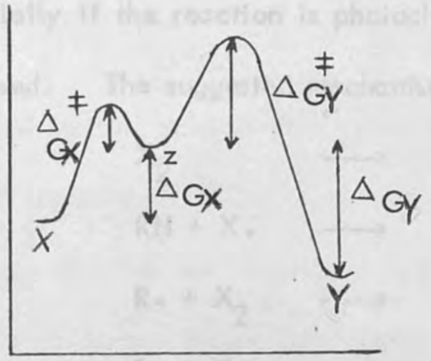


Fig.4 Free energy profile

A compound may go to two different products $Z \begin{smallmatrix} \nearrow X \\ \searrow Y \end{smallmatrix}$. Before the equilibrium is reached, X may be produced more quickly than Y, because $\Delta GX^{\ddagger}$ is smaller than $\Delta GY^{\ddagger}$ (but Y may be thermodynamically more stable; $\Delta GY > \Delta GX$), thus the production of X is faster and it is kinetically controlled. But when the equilibrium is established, X reverts to Z more easily and faster than Y ($\Delta GY > \Delta GX$) and the reaction is thermodynamically controlled (more stable compound will be produced in larger amount). The geometry of the transition state is similar to that of the molecule to which it is closer in free energy.

In two-step mechanisms the geometry of the transition state is thought to resemble the geometry of the intermediate more than that of the products or reactants. This is called the Hammond postulate. In a reversible reaction the mechanism of the reverse reaction must proceed along the same route as the forward reaction. This is called the principle of microscopic reversibility.

1.5 Chlorination by molecular chlorine

Molecular chlorine is easily able to sustain free radical chain reactions, especially if the reaction is photochemically activated or free radical initiators are used. The suggested mechanism for free radical substitution is[37]:

$$X_2 \longrightarrow 2X\cdot \qquad (28)$$

$$RH + X\cdot \longrightarrow R\cdot + XH \qquad (29)$$

$$R\cdot + X_2 \longrightarrow RX + X\cdot \qquad (30)$$

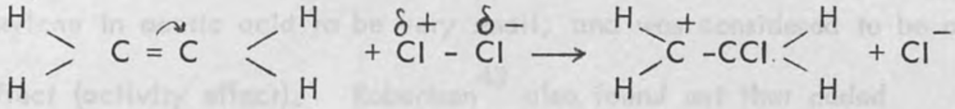
$$R\cdot + X\cdot \longrightarrow RX \qquad (31)$$

Substitution between a paraffin like neopentane and chlorine easily occurs photochemically with a free radical mechanism[60].

$$Cl_2 + C(CH_3)_4 \longrightarrow (CH_3)_3\ CCH_2Cl + HCl \qquad (32)$$

With unsaturated compounds addition usually prevails, e.g. benzene gives tetra- and hexa-chloride adducts.

With olefinic compounds, e.g. ethylene addition occurs by a heterolytic mechanism[38] (two-stage process).



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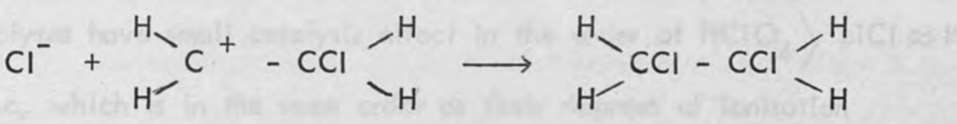

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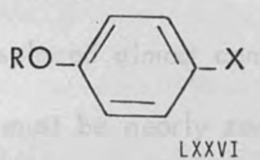
Bradfield and Jones[39] studied the chlorination of some ethers of the types



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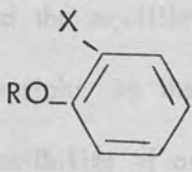
and



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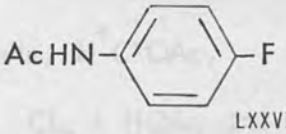
$X = Cl,\ CO_2H,\ NO_2$

$R = CH_3, C_2H_5, n\text{-}Pr,\ Bu^t, CH_2Ph,\ Pr^i$

and of some anilides[40] of the type



LXXVIII

$Ac = CH_3CO,\ C_6H_5CO,\ C_6H_5SO_2$

in 99% acetic acid at 20°C, and they concluded that the velocity coefficients were only slightly altered by a change in the relative concentrations of ether and chlorine, and the effect of the medium on the rate of the reaction was shown by a rapid increase of the velocity with increasing water content of the media. The rise of rate for an alternation from 1% to 2% of water being almost as much as that for a temperature increase of 10°C. They also found the kinetic form

$$\text{Rate} = k\left[ArH\right]\left[Cl_2\right]$$

De la Mare and Robertson[41] found the same second order kinetic form in their studies of chlorination of naphthalene, benzene and some substituted alkyl-benzenes (Me , Et, Pr^i, Bu^t) in acetic acid. Robertson et al[42] showed the catalytic effect of perchloric acid on the chlorination of m-xylene in acetic acid to be very small, and was considered to be a salt effect (activity effect). Robertson[43] also found out that added electrolytes have small catalysis effect in the order of $HClO_4 \rangle LiCl \approx HCl \rangle NaOAc$, which is in the same order as their degrees of ionisation (conductivities). From these observations and also the slight influence of chloride ions (as added HCl or LiCl) it was concluded that a mechanism involving Cl^+ ions is not possible and the equilibrium, $Cl^+ + Cl^- \rightleftarrows Cl_2$ (35) is displaced almost completely to the right, so the concentration of Cl^+ ions must be nearly zero, and the possibility of an initial presence of Cl^+ (reactive reagent) is zero, because in that case the formed hydrochloric acid would destroy the reactive reagent, so that substitution would show a strong negative auto catalysis. Chlorine acetate (ClOAc) or the protonated molecule, $H^{+}ClOAc$,

$$Cl_2 + HOAc \rightleftarrows ClOAc + H^{+} + Cl^{-} \rightleftarrows HCl + ClOAc \qquad (36)$$

cannot be an essential intermediate since the addition of HCl does not reduce the rate, and the equilibrium

$$Cl_2 + HOAc \rightleftarrows ClOAcH^{+} + Cl^{-} \qquad (37)$$

cannot be involved because of the small observed effect of added chloride ion.

De la Mare and co-workers[44] confirmed these results and the conclusion that molecular chlorine is the effective electrophile, by preparing chlorine acetate which was immediately decomposed by chloride ions and whose chlorination reactions were strongly catalysed by mineral acids. The slight catalysis by electrolytes and the fact that the rate of the reaction increases with increase in the polarity of the solvent (e.g. more aqueous media) shows that the transition state involving compound and chlorine molecule is more dipolar than the ground state involving neutral starting materials.

Dewar and Mole[45] measured the rate constants of the chlorination of polynuclear compounds such as diphenyl, naphthalene, phenanthrene and benzene in acetic acid and also in a mixture of acetic acid-carbon tetrachloride (1:3 v/v). Pyrene was also studied in this mixed solvent as the chlorination of pyrene (the most reactive hydrocarbon in this series) was too fast in acetic acid to be measured and that of benzene in the mixed solvent was too slow. The reactions were of the second order, (Rate = $k_2 [ArH][Cl_2]$), and the studies were carried out under first order conditions (excess of hydrocarbon), and the rate constant, k_2, was obtained by application of the pseudo-first order equation:

$$k_2 t = \frac{-2.303}{[ArH]_0} \log_{10} [Cl_2]_t$$

where $[ArH]_0$ is the initial concentration of hydrocarbon and $[Cl_2]_t$ is the chlorine concentration at time t. The straight-line obtained showed the reaction to be of the first order with respect to the chlorine concentration. The rate of chlorination of hydrocarbons were much higher in acetic acid than in carbon tetrachloride-acetic acid.

Andrews and Keefer[46] studied the chlorination of pentamethylbenzene with chlorine in carbon tetrachloride and of benzene in trifluoroacetic acid. In the chlorination of pentamethylbenzene, reaction, once started, accelerated because of a catalytic role of hydrogen chloride, shown by adding hydrogen chloride initially to the reaction mixture. The reactions are first order with respect to each of the reactants and 3/2 or mixed - first order and second order with respect to hydrogen chloride. They were also first order with respect to iodine monochloride which is a much more effective catalyst than hydrogen chloride. The reaction product of benzene with chlorine in trifluoroacetic acid at room temperature is chlorobenzene. The reaction is first order with respect to each of the reactants and the activation energy for chlorination increases as the polarity of the medium is increased (being higher in trifluoroacetic acid than in carbon tetrachloride), which may be because of an increase in desolvation energy of the reactants, a polar solvent favours the ionization of the halogen-halogen bond of a hydrocarbon halogen complex ($ArHX_2$) in the rate-determining step. They also studied the rate of reaction of toluene, benzene and m-xylene in different solvents[47] and showed that the rate of nuclear chlorination varies with solvent in the order 1,2-dichloroethane $\ll$ acetic anhydride $\approx$ acetic acid $\approx$ acetonitrile $<$ nitromethane $\ll$ trifluoroacetic acid, and the activation energies vary in the order acetic acid $>$ acetic anhydride $>$ acetonitrile $>$ nitromethane.

Table 1

Second order rate coefficient for reaction of ArH with Cl_2 in various solvents

ArH	Solvent	Temp.	$10^3 \times K_2$ (1 mol^{-1} sec^{-1})
Toluene	acetic acid	25.2	0.82
Toluene	acetic anhydride	25.0	0.35
Toluene	acetonitrile	25.0	1.36
Toluene	nitromethane	25.0	10.80
Benzene	acetonitrile	25.0	0.00091
Benzene	nitromethane	25.0	0.0068
Benzene	trifluoroacetic acid	25.0	6.8
m-Xylene	acetic acid	25.8	375
m-Xylene	acetonitrile	25.2	1530

Table 2

Activation energies for aromatic hydrocarbon chlorination

Compound	Solvent	E_a (k cal/mole)
Toluene	Ethylene dichloride	large
Toluene	Acetic acid	13
Toluene	Acetic anhydride	9.1
Toluene	Acetonitrile	7.9
Toluene	Nitromethane	5.6
m-Xylene	Acetonitrile	4.6
m-Xylene	Acetic Acid	7.7
p-Xylene	Acetonitrile	9.4
Benzene	Trifluoroacetic acid	11.4

The rate of chlorination of toluene in ethylene dichloride is very slow at room temperature if a polar catalyst such as hydrogen chloride is not used. The reaction is first order with respect to hydrocarbon, halogen and the catalyst. In acetic acid, acetic anhydride, acetonitrile and nitromethane, the reaction proceeds relatively rapidly in the absence of any catalyst. The activation energy in nitromethane is low, so the rate in this solvent is much higher than in the other solvents. The activation energy for the reaction of toluene with chlorine in nitromethane is over 2 k cal/mole less than that for the same reaction in acetonitrile, although the dielectric constants for both solvents are the same (37.5). Stock and Himo[48] also found second order rate coefficients in their kinetic studies of the chlorination of some alkylbenzenes such as benzene, toluene, t-butylbenzene and p-xylene in various solvents like nitrobenzene, nitromethane, acetonitrile, acetic acid and chlorobenzene at 25°C.

Table 3

Second-order rate coefficients (10^4k_2; l.mol.$^{-1}$s^{-1}; 25.0°) for reaction of ArH and chlorine

ArH/Solvent	$MeNO_2$	$PhNO_2$	MeCN	Ac_2O	PhCl
PhH	0.059	-	-	-	-
PhMe	131	45	15	2.44	0.013
Ph^tBu	30.7	9.58	5.8		0.0036
p-$C_6H_4Me_2$	723		110		

Although the rate of chlorination of toluene (or t-butylbenzene) in nitromethane was almost 10^4 times that in chlorobenzene, the relative rate $k_{p\text{-Me}}/k_{p\text{-}^t\text{Bu}}$ was similar in each solvent. (However, this relative rate was larger than that in aqueous acetic acid), and this shows that the Baker-Nathan order is produced by a polar effect rather than a solvent effect.

In most of the kinetic studies of molecular chlorination, acetic acid has been used as a solvent (usually with some water content). Jones and Bradfield[49], and Jones[50] investigated the chlorination of a large number of ethers and anilides in 99% acetic acid at 20°C to study substituent effects in electrophilic substitution. Jones[51] measured the rate of nuclear chlorination of some ethers of the type $\underline{p}\text{-RO}\cdot C_6H_4X$ at various temperatures between 15° and 35°C, where R is an alkyl or substituted benzyl group and X is F, Cl, COph, OCOph and NO_2. Analysis of the results on the basis of the equation $k = PZe^{-E/RT}$, where k is the velocity coefficient and E is the activation energy; PZ is a compound term (P = phase term, which is approximately constant, Z is number of collisions between reacting molecules) and T is the temperature, confirms that changes in the velocity of chlorination of these compounds are due to changes in the energy of activation, which in the ethers studied varies from 9.850 to 14.650 cals/mole.

The chlorination of alkylbenzenes in acetic acid has been studied by various groups of workers and they have obtained second order rate coefficients. (Table 4)

Table 4

Second order rate coefficient ($10^3 k_2$ l.mol^{-1} s^{-1}) for reaction of ArH with Cl_2 in acetic acid

ArH/Reference	a	b	c	d
Benzene	-	0.00154	0.0069	0.0013
Toluene	0.47	0.53	0.60	0.485
t-Butylbenzene		0.135		
p-Di-t-butylbenzene		0.462		
p-t-Butyltoluene		2.28		
p-Xylene	3.05	3.20	4.22	
1,2,3,5-Tetramethylbenzene			4190	
m-Xylene		285	337	
o-Xylene	6.35	3.23	7.9	

a - At 24°C in 99.9% aqueous acetic acid, de la Mare and P.W. Robertson, J.C.S. (1943), 279.

b - At 25°C, 99.87% aq.. acetic acid, Brown and Stock, J.A.C.S. 79, (1957), 5175

c - At 25.2°C, purified acetic acid, R.M. Keefer and L.J. Andrews, J.A.C.S. 79, (1957), 4348.

d - At 25°C, water content 0.05%, P.B.D., de la Mare and M. Hassan J.C.S. (1958), 1519.

The first kinetic study of chlorination of acetanilides such as mono- and poly-methyl-acetanilides with molecular chlorine as the electrophile (in acetic acid containing 0.14% water, at 16°C), was made by Orton and King[52]. The chlorine is produced from the addition of hydrochloric acid to N-acetyl-N-chloroamino-2,4-dichlorobenzene (which is not chlorinated significantly under the reaction conditions).

$$C_6H_5NClAc \ + \ HCl \ \rightleftarrows \ C_6H_5NHAc \ + \ Cl_2 \qquad (38)$$

Then the nuclear chlorination takes place

$$C_6H_5NHAc \ + \ Cl_2 \ \longrightarrow \ ClC_6H_4NHAc \ + \ HCl \qquad (39)$$

The rate is dependent on the concentration of anilide and chlorine

$$\text{Rate} \ = \ k_2 \ \left[ArH\right]\left[Cl_2\right]$$

The reaction medium affects the rate of chlorination a great deal. The rates of reactions of acetanilides in more dilute acetic acid (more water content) are higher.

Table 5

Velocity coefficient k_2 ($l \ mol^{-1} \ min^{-1}$) of chlorination of some anilides in AcOH + H_2O at 20°C

Anilide	(H_2O)=1%	(H_2O)=0.14%
Formanilide	9.2	4.95
Acetanilide	62.2	40.0
Benzanilide	69.1	42.0

As Orton and Jones[54] have shown, there is an equilibrium between chlorine, anilide, chloroamine and hydrogen chloride.

$$ArNHAc \ + \ Cl_2 \ \rightleftarrows \ ArNClAc \ + \ HCl \qquad (40)$$

In glacial acetic acid, the equilibrium lies entirely to the left hand side of the equation, but in aqueous acetic acid the position shifts further to the right as the proportion of water is increased. Thus in 95% acetic acid 80% of the chloro amine is converted to molecular chlorine. This figures falls to 20% in 75% acetic acid, and is near zero in 50% aqueous acetic acid. Although in dilute acetic acid there is considerable difference between the rates of chlorination of anilides, in glacial acetic acid there is not much difference.

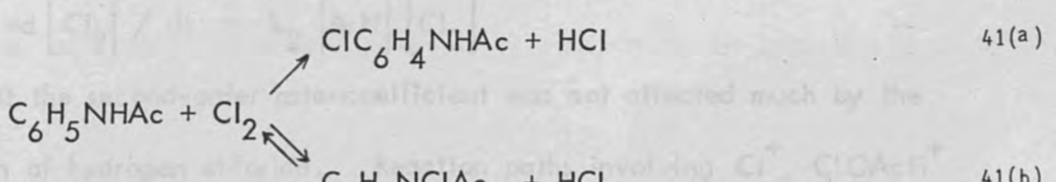
Orton and Williams and Soper have measured[55] the relative rates of C- and N-chlorination of some anilides in 40% aqueous acetic acid at 18°C and they obtained the following results.

Table 6

The velocity coefficients of N- and C- chlorination (k, l mol^{-1} min^{-1}) of some anilides

Anilides	k_N	k_C	mean k_N/k_C
o-Chloroacetanilide	286	27.5	10.46
m-Chloroacetanilide	172	3,140	0.056
p-Chloroacetanilide	115	135	0.863
p-Bromoacetanilide	123	116	1.06
Aceto-o-toluidide	140	1,390	0.111
Aceto-p-toluidide	2,540	18,500	0.14
Acetanilide	96	11,000	0.134

They concluded that the position of the equilibrium 41(b)



$$C_6H_5NHAc + Cl_2 \rightarrow ClC_6H_4NHAc + HCl \qquad 41(a)$$

$$C_6H_5NHAc + Cl_2 \rightleftharpoons C_6H_5NClAc + HCl \qquad 41(b)$$

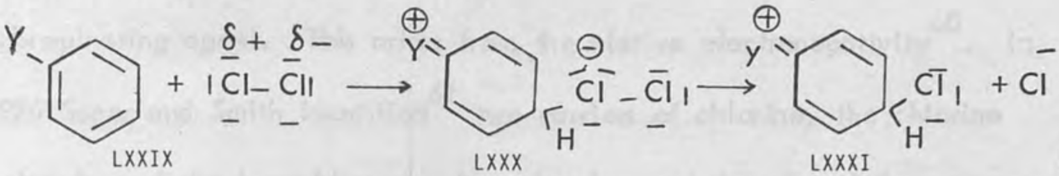
depends on the composition of the medium and the constitution of the anilide, as it was concluded before by Orton and King[52] who showed that for chlorination of p-chloroacetanilide the ratio of N-chlorination to C-chlorination in 30% acetic acid is 0.93:1; in 50% acetic acid, 1.25:1; and in 65% acetic acid, 1.55: 1, and for acetanilide with the same concentration of acetic acid the ratios are 0.082; 0.08 and 0.083. De la Mare and Hassan also studied[56] the chlorination of some anilides such as 4-methyl and 2-methyl and 2,6-dimethyl-acetanilide, acetanilide, 4-acetamidodiphenyl and 1,4-diacetamidobenzene with chlorine in acetic acid (water content 0.05%) at 25°C, and they found second order rate coefficients, (k_2, l mol.$^{-1}$ sec^{-1}) for the reactions which are as follows: 1.53, 0.193, 0.0118, 0.93, 0.248, 0.231.

Dusouqui and Hassan[57] and de la Mare, Hassan and Swedland[58] have obtained second order rate coefficients (k_2, l mol^{-1} sec^{-1}) for the chlorination of 3-chloroacetanilide (0.215), 4-chloroacetanilide (0.01), 3-nitro-acetanilide (5.7×10^{-5}) and phenyl benzoate (3.2×10^{-6}).

1.5.1 <u>Mechanism of chlorination by molecular chlorine</u> - In the kinetic studies of chlorination with solutions of chlorine in acetic acid and in other solvents (e.g. nitrobenzene, chloroform) it was shown that the effective electrophile is molecular chlorine, the rate of chlorination has the kinetic form:

$$-d\left[Cl_2\right] / dt = k_2 \left[ArH\right]\left[Cl_2\right]$$

and that the second-order rate-coefficient was not affected much by the addition of hydrogen chloride. Reaction paths involving Cl^+, $ClOAcH^+$ or ClOAc (as mentioned before) are inconsistent with the kinetic form, because of the absence of either powerful catalysis by acid and anticatalysis by base or anticatalysis by chloride ion which is required if Cl^+, $ClOAcH^+$ or ClOAc were involved in the reaction path. The result is consistent with reaction through molecular chlorine.



(42)

If LXXX is the intermediate, then an entity such as the solvent may be required to remove the chloride ion (Cl^-) and if this is the rate determining step, then the rate should be different in different solvents[47].

All the electrolytes accelerate the reaction, the Table shows the effect of electrolytes (0.05m) on the rates of chlorination of naphthalene and m-xylene at 24°C in acetic acid, found by Robertson[41-42], and depending on the ionization power of the electrolyte.

Added electrolyte	None	$HClO_4$	H_2SO_4	HCl	NaOAc
Relative rate of substitution	1	1.9	1.4	1.2	1.2

The small catalysis by electrolytes and the increase in rate by the addition of the water content of the solvent, presumably is because the transition state of the reactions involves polarization of both the chlorine molecule and the aromatic compound. The transition state is therefore more polar than the reactants, and the reaction is facilitated by increase in the ionizing power of the media[59].

1.6 Chlorination by chlorinating species other than molecular chlorine:

Some reagents other than molecular chlorine are used for chlorination such as: ClF, $ClNHCOCH_3$ (mentioned before), Cl-OH and SO_2Cl_2. Chlorine fluoride provides electrophilic chlorine and acts as a chlorinating species, although iodine chloride acts as iodinating and bromine chloride as a brominating agent. This arises from the relative electronegativity[60]. In 1926 Soper and Smith identified[61] two carriers of chlorine, the chlorine molecule and the hypochlorous acid molecule, and they found the rate equation:

$$R = k\,[ClOH]\,[OPh^-]$$

for aqueous chlorination of phenol by hypochlorite, and that hydrochloric acid, which produces elemental chlorine, increases the rate a great deal.

$$Rate = k\,[HOCl]\,[H^+]\,[Cl^-]\,[PhO^-] \;=\; k\,[Cl_2]\,[OPh^-]$$

In 1950 de la Mare and his co-workers[62] studied aromatic chlorination in aqueous hypochlorous acid, acidified by perchloric acid or sulphuric acid. This system contained a strong chlorinating agent. The rate equation,

$$Rate = k\,[ArH][ClOH][H^+]$$

was found in the chlorination of benzene and toluene and suggested that the true electrophile could be written as Cl^+. On increasing the reactivity of the aromatic compounds, the equation becomes:

$$Rate = k\,[ClOH]\,[H^+]$$

This was understood to mean that as soon as the effective electrophile is produced, the aromatic compound takes it in a comparatively fast reaction which therefore does not take part in the determination of the rate. De la Mare and co-workers[62] suggested that rate of chlorination depends on the pre-equilibrium process

$$ClOH \;+\; H_3O^+ \;\underset{}{\overset{fast}{\rightleftarrows}}\; ClOH_2^{\;+} \;+\; H_2O \qquad (43)$$

$$Cl\text{-}OH_2^{\;+} \;\xrightarrow{slow}\; Cl^+ \;+\; H_2O \qquad (44)$$

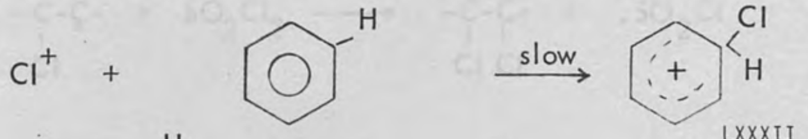
The dependency of rate to the Hammett acidity function, ho , at high concentration of acid, instead of (H^+), supports the first step of the equilibrium, and the ortho/para ratio of chlorination of toluene and t-butylbenzene supports the second step, as the ortho/para ratios by various chlorinating agents, cationic and molecular chlorine, decrease for both hydrocarbons by going from Cl^+ to Cl_2 [63].

Table 7

Isomer proportions (%) in the chlorination of toluene and t-butylbenzene by various chlorinating agents

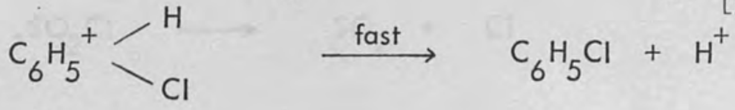
		Cl^+	Cl_2
Toluene			
	ortho-	75	60
	meta-	2.2	0.5
	para-	23	39.5
t-butylbenzene			
	ortho-	-	22
	meta-	-	2.1
	para-	42	76

which is the order of increasing size of the substituting agent (steric hindrance) and the observation cannot be interpreted if the cationic chlorinating agent, taken to be Cl^+, was $HOClH^+$. De la Mare and co-workers also found that, in the chlorination of even more reactive aromatic compounds, the concentration reappears as a factor in the rate expression. This means that these compounds do not wait for the chlorinium ion, Cl^+, to form but take chlorine directly from the hypochlorous acidium ion, $ClOH_2^+$. The mechanism of chlorination by attack of free chlorinium ion is suggested to be



LXXXII

(45)



$$C_6H_5^{+}\langle^{H}_{Cl} \xrightarrow{\text{fast}} C_6H_5Cl + H^+$$

(46)

The mechanism of halogenation by attack of free halonium ion was first suggested by Melander[64], who found that in the bromination of benzene containing tritium, with iodine as catalyst and without a solvent, the displacement of the proton by bromine is not appreciably faster than that of tritium, and de la Mare et al[65] showed that in chlorination and bromination the second step does not determine the rate and a primary isotope effect is not observed when benzene and hexadeuterobenzene were brominated by acidified aq. hypobromous acid in accordance with the kinetic equation

$$\text{Rate} = k\,[\text{ArH}]\,[\text{HOBr}]\,[\text{H}^+]$$

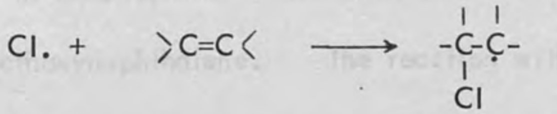
The rates were identical as required by the above scheme.

1.7 Sulphuryl Chloride as an electrophile -

Sulphuryl chloride can chlorinate compounds such as aliphatics and aromatic hydrocarbons, homolytically, in the dark in the presence of a catalyst, e.g. benzoyl peroxide, far more rapidly and more conveniently than using elementary chlorine and light. Many of the chlorination reactions of sulphuryl chloride have been understood in terms of free radicals; chlorine atoms are formed by homolysis:

$$SO_2Cl_2 \longrightarrow Cl. + .SO_2Cl \qquad (47)$$

and these set up a chain reaction:



$$Cl. + \;>C{=}C< \;\longrightarrow\; -\underset{|}{\overset{|}{C}}-\underset{Cl}{\overset{|}{C}}- \qquad (48)$$

$$-\overset{|}{\underset{Cl}{C}}-\overset{|}{C}- + SO_2Cl_2 \longrightarrow -\overset{|}{\underset{Cl}{C}}-\overset{|}{\underset{Cl}{C}}- + .SO_2Cl \qquad (49)$$

$$.SO_2Cl \longrightarrow SO_2 + .Cl \qquad (50)$$

The attack of side chains in alkylbenzenes is catalysed by benzoyl peroxide as reported by Kharash and Brown[66].

$$C_6H_5\text{-CO - O.OCO.}C_6H_5 \longrightarrow 2CO_2 + 2C_6H_5^{\bullet} \quad (51)$$

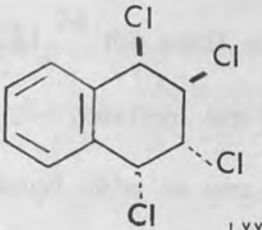
$$C_6H_5^{\bullet} + SO_2Cl_2 \longrightarrow .SO_2Cl + C_6H_5Cl \quad (52)$$

$$.SO_2Cl \longrightarrow SO_2 + Cl. \quad (53)$$

$$Cl^{\bullet} + RH \longrightarrow R^{\bullet} + HCl \quad (54)$$

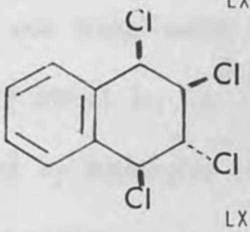
$$R^{\bullet} + SO_2Cl_2 \longrightarrow RCl + {}^{\bullet}SO_2Cl \quad (55)$$

They also suggested that the reaction of sulphuryl chloride with aliphatic compounds at 80° involves homolytic substitution[67]. This does not seem to be the only mechanism involved in chlorination. The convenient nuclear chlorination of some less reactive compounds by using Lewis acid catalysts such as aluminium chloride has been studied by Silberrad et al[68]. The orientation of attack of phenols[69] and of phenol ethers[70] suggests attack by electrophilic sulphuryl chloride. Thus resorcinol (1,3-dihydroxybenzene) gives 4-chlororesorcinol, and p-cresol (4-methylphenol) gives 2-chloro-4-methylphenol. The reaction of sulphuryl chloride with some aromatic ethers and with naphthalene and some of its derivatives have been studied by Bolton, de la Mare and Suzuki[71]. They showed that sulphuryl chloride gives products typical of electrophilic chlorination in the attack of 3,5-dimethyl anisole and of 2-methoxynaphthalene. The reaction with naphthalene gives 1-chloro naphthalene (ca. 93%) and some adducts, e.g. naphthalene-α-tetrachloride (ca. 4%)



LXXXIII

and naphthalene-δ-tetrachloride (ca. 3%)



LXXXIV

and by using less reactive derivatives such as monochloronaphthalene, the reaction does not occur detectably. The reaction with anisole is slower than that with 2-methoxynaphthalene, 3,5-dimethylanisole or 1,3-dimethoxybenzene. They later showed[72] that the rate of chlorination of anisole was affected markedly both by alkyl-substituents, in the order anisole $<$ m-methylanisole $<$ 3,5-dimethylanisole $<$ 2,3,5-trimethylanisole, and the presence of a more solvating solvent. Nitrobenzene caused the reaction to proceed at about 10,000 times of that in benzene, the sequence order being benzene $<$ chlorobenzene $<$ o-dichlorobenzene $<$ nitrobenenze, which shows that the transition state is more dipolar than reactants (i.e. evidence for the presence of positive and negative charges) and the reaction involves a heterolytic process. The sensitivity of the rate to the substituent groups, increasing with increasing electron donating power of the group, shows that an electrophilic process is involved. A detailed study of the substituent effects upon the rate of chlorination of m-dimethoxybenzene in chlorobenzene at 25°C[73] confirmed the electrophilic nature of the reagent ($\rho = -4$), the high negative value of ρ shows that the development of positive charge is involved in the transition state and it is a reason for proposing a heterolytic mechanism of the reaction. In the study of the reaction of substituted toluenes and ethylbenzenes with sulphuryl chloride at 40°C in CCl_4[74] the small value of the reaction constant 0.56 and 0.49, indicates that the reactions are homolytic processes. The substitution reaction with sulphuryl chloride was extended to a study of alkyl benzenes in nitromethane[75]. This was complicated by the presence of two modes of reaction, one involving direct attack by $\overset{\delta+}{Cl} - \overset{\delta-}{SO_2Cl}$ and the second having as its slow stage the attack by molecular chlorine. Although molecular chlorine formed in the pre-equilibrium,

$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2 \qquad (56)$$

contributes to some extent, but the principle electrophile is sulphurylchloride.

1.7.1 Kinetic form and mechnism of chlorination by sulphuryl chloride -

From the kinetic studies of chlorination of some aromatic compounds by sulphuryl chloride at room temperature, as was mentioned[71,72,73,75] so far, it was concluded that the reactions follow the kinetic form

$$-d\left[SO_2Cl_2\right]/dt = d\left[HCl\right]/dt = k_2\left[ArH\right]\left[SO_2Cl_2\right]$$

and four possible electrophiles can be suggested:

Cl_2, Cl^+, $ClSO_2^+$ and SO_2Cl_2

Molecular chlorine derived from the reaction:

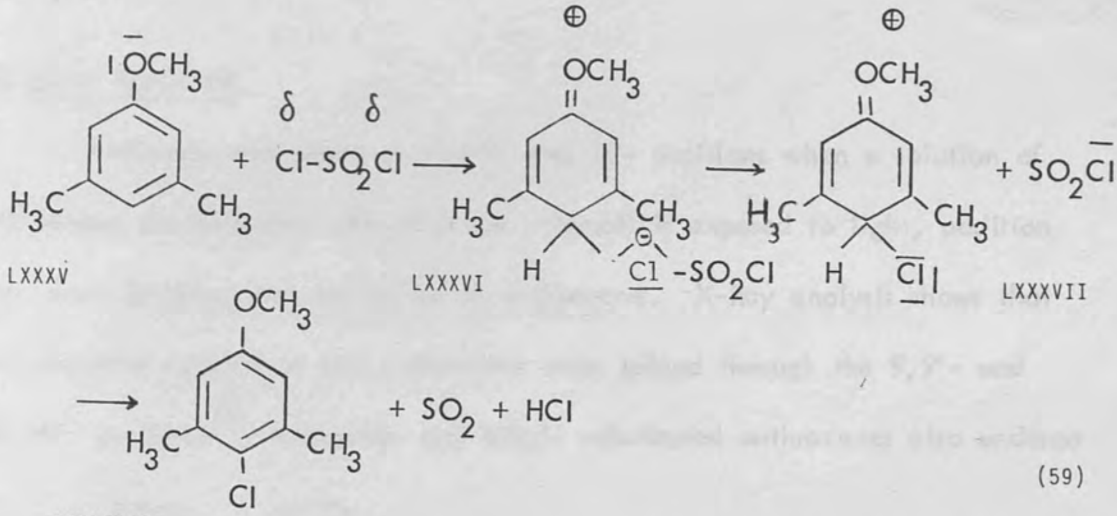
$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2 \qquad (56)$$

cannot be the effective electrophile since the formed sulphur dioxide during the reaction or the initially added sulphur dioxide does not affect the rate of the reaction, neither Cl^+ nor $ClSO_2^+$ derived from pre-equilibrium:

$$ClSO_2Cl \rightleftarrows Cl^+ + SO_2Cl^- \qquad (57)$$

$$ClSO_2Cl \rightleftarrows Cl^- + SO_2Cl^+ \qquad (58)$$

are the effective electrophiles, because if either of these pre-equilibria were present, the formed hydrogen chloride would have an effect on the rate, (which was not observed) since chloride ion would repress the relevant equilibrium to the left and set up a new equilibrium $Cl^+ + Cl^- \rightleftharpoons Cl_2$, (35) which decreases the rate of the reaction by consuming Cl^+ (assumed electrophile). From these results it was concluded that the effective electrophile in chlorination with sulphuryl chloride is molecular sulphuryl chloride, through the scheme:



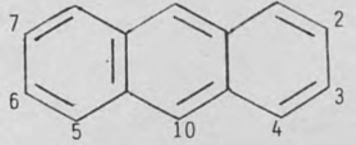
(59)

and the rate determining step involves the attack of the electrophile (SO_2Cl_2) upon the aromatic compound.

1.8 Polynuclear aromatic compounds[76a]

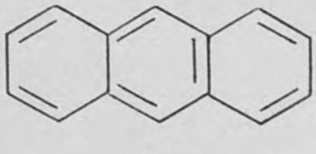
1.8.1 Anthracene

In anthracene, $C_{14}H_{10}$, the three benzene rings condensed linearly. X-Ray examination of its crystal[77], shows that anthracene molecule is flat and it is a hybrid of a number of structures such as:



LXXXIX a

$\longleftrightarrow$



LXXXIX b

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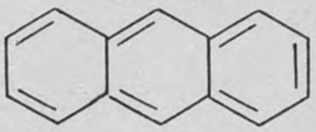
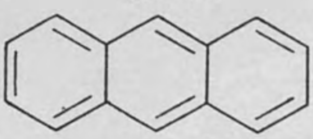


LXXXIX c

$\longleftrightarrow$

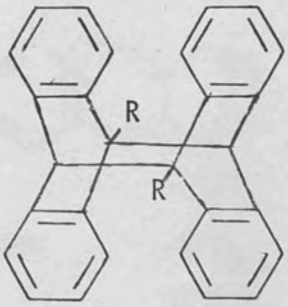


LXXXIX d

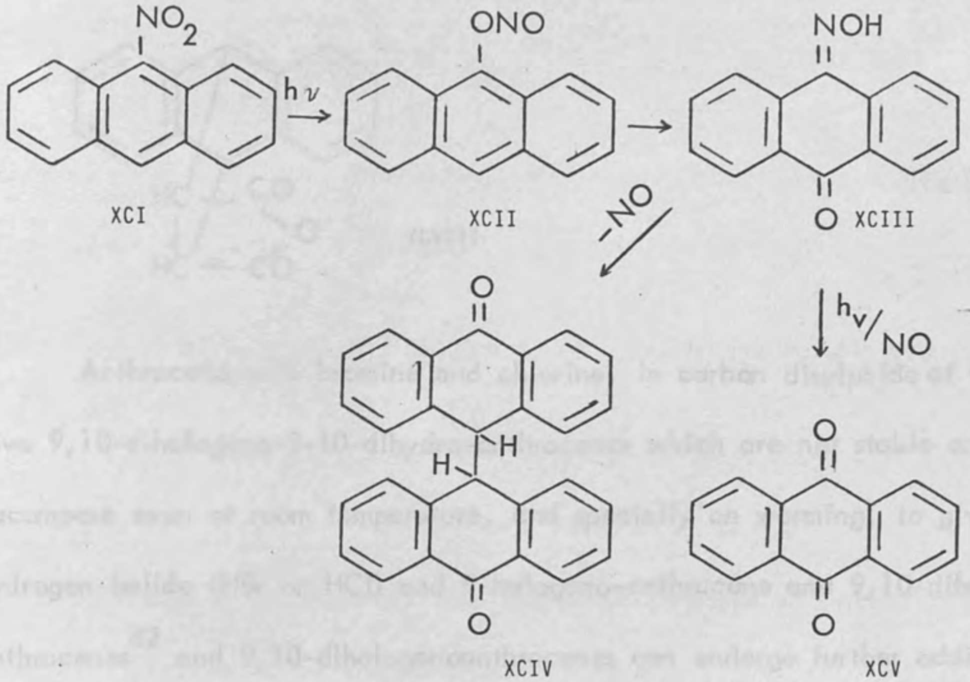
in which 14-electrons are distributed in various ways among 16 bonds in three hexagons. Although the molecule of anthracene is planar, when it is saturated at 9 and 10 positions, it is no longer planar and the X-ray analysis has shown that the two benzene rings in 9,10-dihydroanthracene are folded about the 9,10-axis with an angle of 145° instead of 180° in anthracene.

Addition Reactions

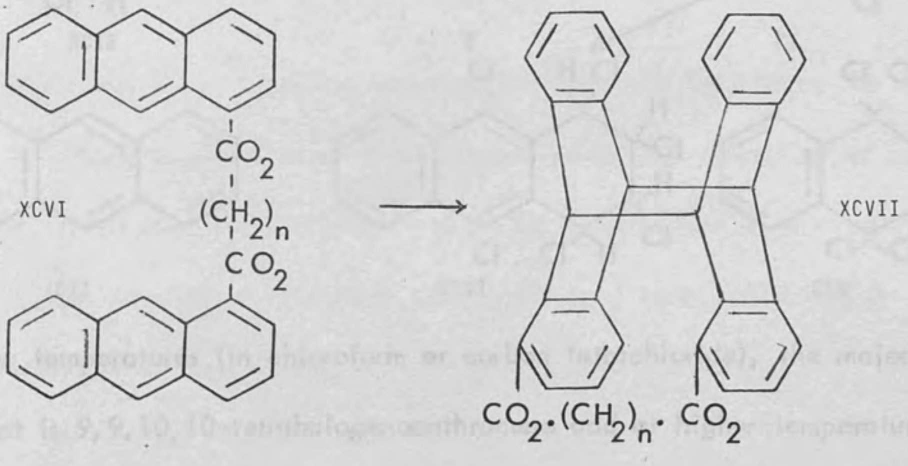
Additions take place to the 9- and 10- positions when a solution of anthracene (in benzene, chloroform or ethanol) is exposed to light, addition can occur between two molecules of anthracene. X-Ray analysis shows that the structure consists of two anthracene units joined through the 9,9'- and 10,10'- positions[78], halogeno- and alkyl- substituted anthracenes also undergo dimerization (R = halogen or alkyl), but 9,10-disubstitution supresses dimerization[79]. Photolysis of 9-nitroanthracene in degassed solutions gives anthraquinone and 10,10'-bianthrone through the mechanism scheme:



XC

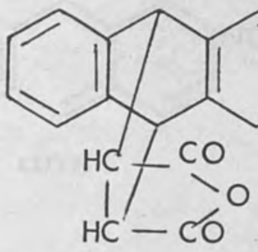


Intramolecular cyclisation products are formed by irradiation of 1,1'-dianthracenes or 2,2'-dianthracenes[80].



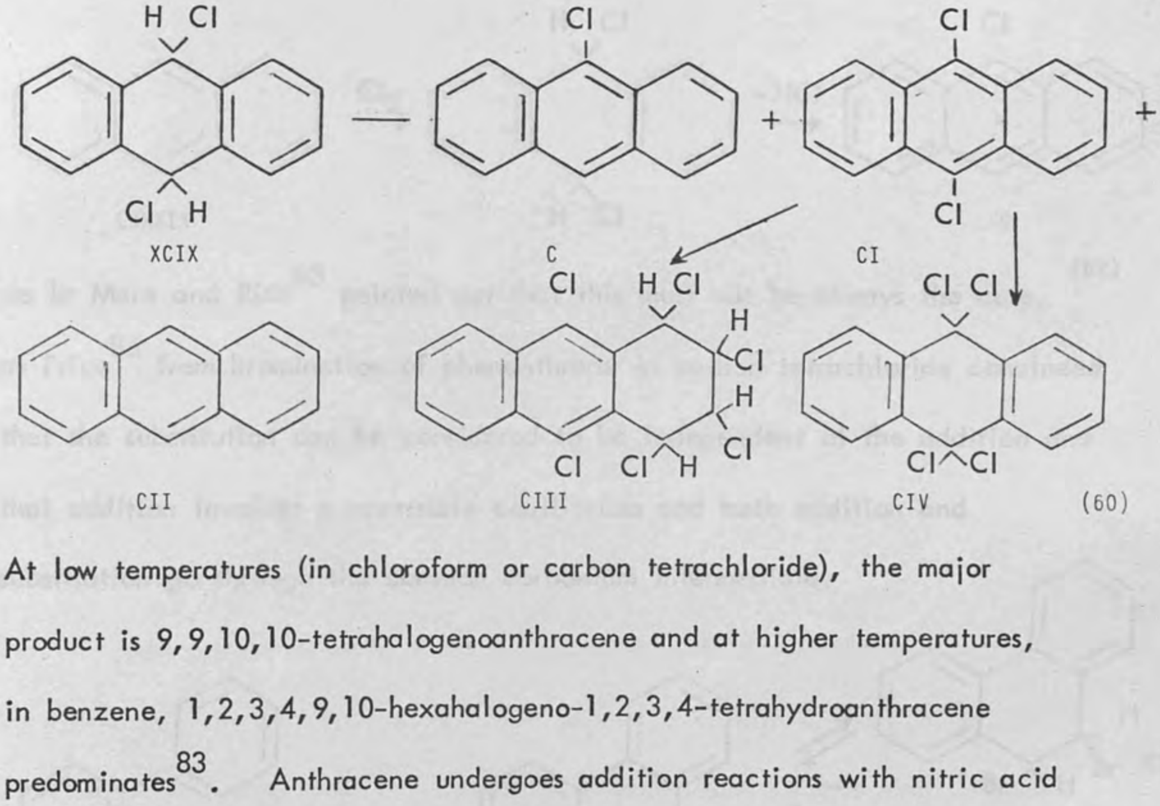
Thermal cycloaddition reactions also occur (as well as photolytic ones).

If anthracene is heated with maleic anhydride in xylene, a crystalline adduct, *cis* 9,10-dihydroanthracene-9,10-*endo*succinic anhydride, m.p. 261-262°C is formed[81]. Addition reactions readily occur with halogens.



XCVIII

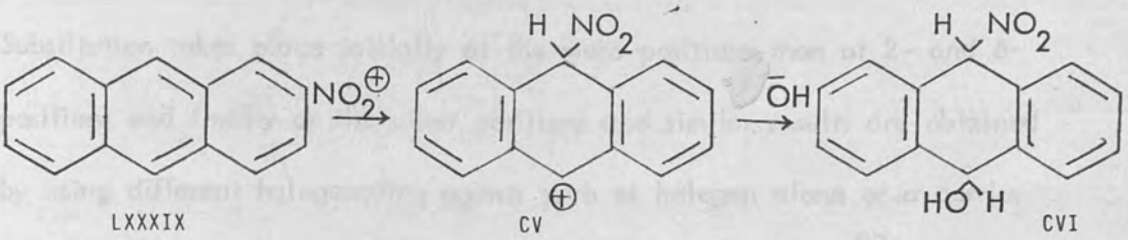
Anthracene with bromine and chlorine, in carbon disulphide at 0° give 9,10-dihalogeno-9-10-dihydro-anthracenes which are not stable and decompose even at room temperature, and specially on warming, to give hydrogen halide (HBr or HCl) and 9-halogeno-anthracene and 9,10-dihalogeno-anthracenes[82] and 9,10-dihalogenoanthracenes can undergo further addition.



XCIX C CI

CII CIII CIV (60)

At low temperatures (in chloroform or carbon tetrachloride), the major product is 9,9,10,10-tetrahalogenoanthracene and at higher temperatures, in benzene, 1,2,3,4,9,10-hexahalogeno-1,2,3,4-tetrahydroanthracene predominates[83]. Anthracene undergoes addition reactions with nitric acid in mild conditions (with concentrated nitric acid oxidation takes place to give anthraquinone[84]). The initial product is 10-hydroxy-9-nitro-9,10-dihydroanthracene, through a carbonium species,

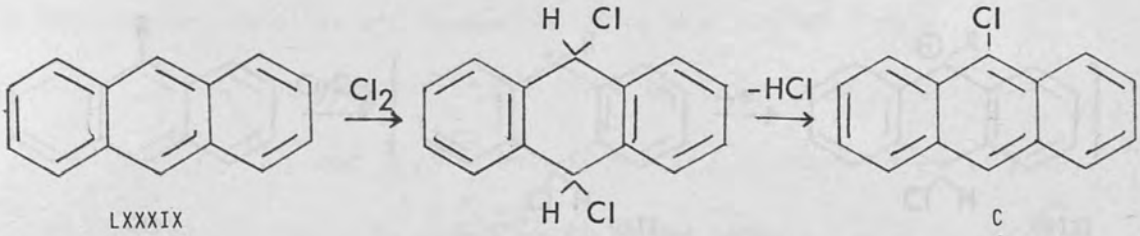


(61)

with alkali it loses water and alcohol to form stable 9-nitroanthracene, m.p. 146°.

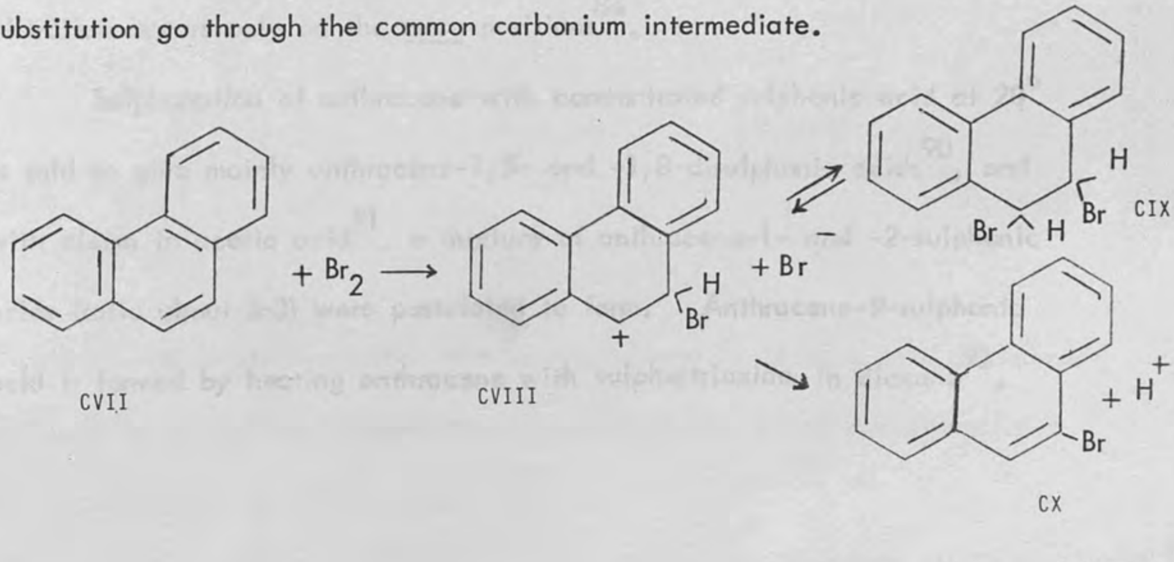
Substitution Reactions.

Although it is frequently said that substitution in phenanthrene and anthracene proceed by addition followed by elimination,



(62)

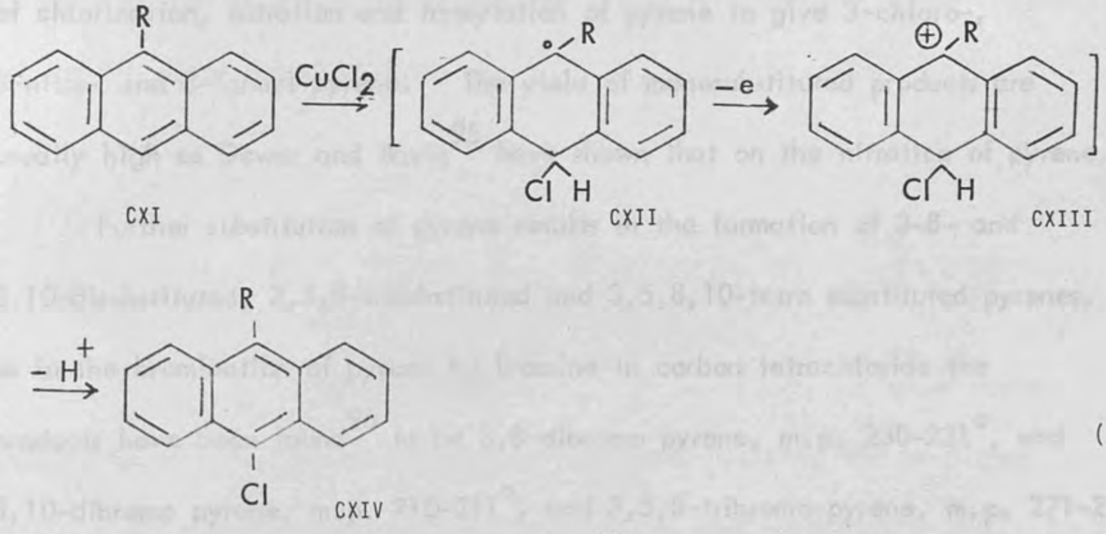
de la Mare and Ridd[85] pointed out that this must not be always the case, as Price[86] from bromination of phenanthrene in carbon tetrachloride concluded that the substitution can be considered to be independent of the addition and that addition involves a reversible equilibrium and both addition and substitution go through the common carbonium intermediate.



(63)

Substitution takes place initially at the meso-positions then at 2- and 6-positions and finally at the other positions and similar results are obtained by using different halogenating agents such as halogen alone or a carrier ($SbCl_5$) or a reagent like sulphuryl chloride (in nitrobenzene)[87]. 9-Alkyl- and 9-aryl-anthracenes undergo halogenation with cupric halides to form 10-halogenated derivatives[88].

9-Alkoxy and 9-acyloxyanthracenes also undergo the same reactions[89], through an intermediate radical which is thought to become oxidised by the cupric halide to a carbonium ion and deprotonation follows which leads to the formation of halogenated anthracene:



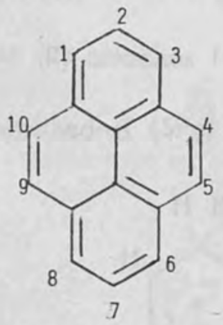
CXI CXII CXIII CXIV (64)

Nitration occurs only on the meso-positions[84].

Sulphonation of anthracene with concentrated sulphonic acid at 20° is said to give mainly anthracene-1,5- and -1,8-disulphonic acids[90], and with oleum in acetic acid[91], a mixture of anthracene-1- and -2-sulphonic acids (ratio about 5:3) were postulated to form. Anthracene-9-sulphonic acid is formed by heating anthracene with sulphurtrioxide in dioxane[92].

1.8.2 Pyrene[76b]

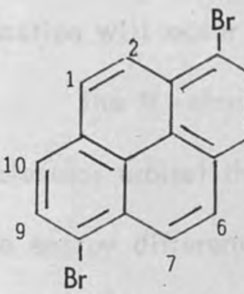
Pyrene, $C_{16}H_{10}$, forms colourless plates, m.p. 150°, b.p. 392°, in the crystal the pyrene molecule is slightly non-planar, probably as the result of packing forces[93].



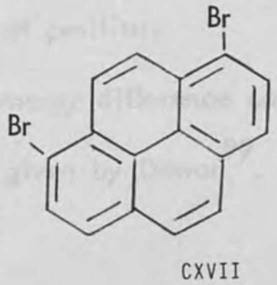
CXV

Substitution reactions. Electrophilic attack of pyrene occurs at the 3-position. This was concluded by Vollmann and co-workers[94] in their study of chlorination, nitration and formylation of pyrene to give 3-chloro-, 3-nitro- and 3-formyl-pyrene. The yield of monosubstituted products are usually high as Dewar and Bavin[95] have shown that on the nitration of pyrene.

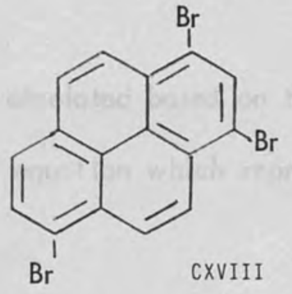
Further substitution of pyrene results in the formation of 3-8- and 3,10-disubstituted, 3,5,8-trisubstituted and 3,5,8,10-tetra substituted pyrenes, as in the bromination of pyrene by bromine in carbon tetrachloride the products have been found[96] to be 3,8-dibromo pyrene, m.p. 230-231°, and 3,10-dibromo pyrene, m.p. 210-211°, and 3,5,8-tribromo-pyrene, m.p. 271-272°.



CXVI



CXVII

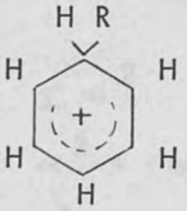


CXVIII

3-chloro- and 3-bromo-pyrenes have been prepared by using cupric chloride and bromide in boiling chlorobenzene in good yields, which the mechanism was concluded to be a radical process[97].

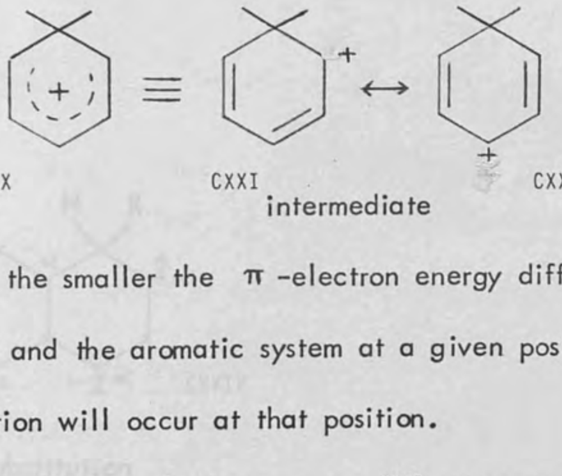
1.9 M.O. calculations in aromatic substitution

In aromatic substitution, the rate of the reaction depends on the activation energy which is the energy difference between the aromatic system and the transition state. Wheland[98] suggested that the transition state is a state where the reagent (R) attaches itself to one carbon of the ring, and that carbon becomes tetrahedral (SP_3) and out of conjugation with the rest of the aromatic system.



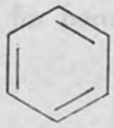
CXIX

So the transition state has one conjugated carbon less than the original system and we can write the structures:



CXX CXXI CXXII

intermediate



I

original system

Thus the smaller the π-electron energy difference between the transition state and the aromatic system at a given position, the more rapidly the reaction will occur at that position.

The π-electron energy difference can be calculated based on the molecular orbital theory given by Dewar[99]. The equation which represents the energy difference is:

$$\Delta E = 2\beta\,(\Sigma\,\alpha)$$

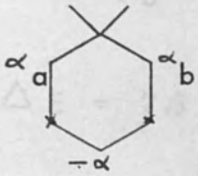
in which β is the resonance integral and α is the non-bonding molecular orbital coefficient (NBMO) and α can be calculated from the equation:

$$q = \sum \alpha^2$$

where q is the probability of finding the electron near the nucleus: in any system the total charge $\sum \alpha^2$ is equal to unity so

$$1 = \sum \alpha^2$$

The calculation of α and energy difference around SP3 carbon atom for benzene and α - and β - substitution in naphthalene is given below:



CXXIII

$$1 = \sum \alpha^2$$

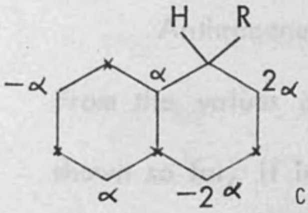
$$1 = \alpha^2 + \alpha^2 + \alpha^2$$

$$\alpha = \frac{1}{\sqrt{3}}$$

$$\Delta E = 2\beta(\alpha_a + \alpha_b)$$

$$\Delta E = 2\beta(\alpha + \alpha) = \frac{2\beta 2}{\sqrt{3}} \quad 2.31\beta$$

for benzene



CXXIV

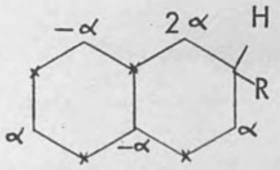
α -substitution

$$1 = \sum \alpha^2 = (2\alpha)^2 + (2\alpha)^2 + \alpha^2 + \alpha^2 + \alpha^2 = 11\alpha^2$$

$$\alpha = \frac{1}{\sqrt{11}}$$

and $\sum \alpha$ around SP^3 carbon atom is $(\alpha + 2\alpha)$ so:

$$\Delta E = 2\cdot\beta\cdot 3\alpha = \frac{6\beta}{\sqrt{11}} = 1.81\beta \qquad \text{for } \alpha\text{-substitution.}$$



CXXV

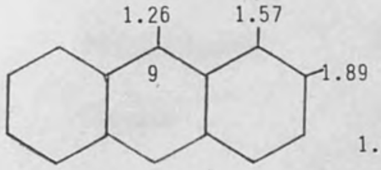
β -substitution

$$1 = \Sigma \alpha^2 = (2\alpha)^2 + \alpha^2 + \alpha^2 + \alpha^2 + \alpha^2 = 8\alpha^2$$

$$= \frac{1}{\sqrt{8}} = \frac{1}{2\sqrt{2}}$$

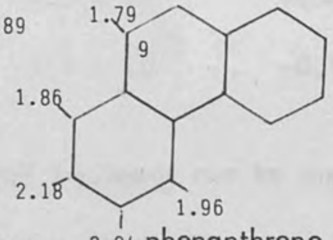
$$\Delta E = 2\beta(2\alpha + \alpha) = \frac{6\beta}{2\sqrt{2}} = 2.12\beta \text{ for } \beta\text{-substitution}$$

For some other aromatic systems the energy difference around every position (SP_3 carbonation) has been calculated, e.g.

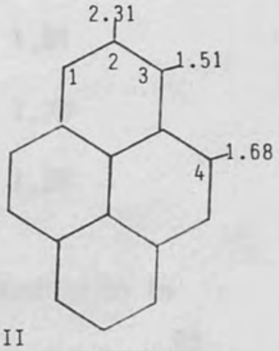


CXXVI

Anthracene



CXXVII phenanthrene



CXXVIII pyrene

From the values of energy difference for some of the aromatic compounds shown so far, it is predicted that the rate of substitution at different positions and for different compounds is in the order:

benzene $\langle$ naphthalene (2 $\langle$ 1) $\langle$ phenanthrene (9) $\langle$ anthracene (9)

pyrene (3 $\rangle$ 4 $\rangle$ 2), which is experimentally confirmed.

If we plot the π -electron energy differences of some hydrocarbons (at the positions at which substitution is expected to occur), against logarithms of the rate constants of a substitution reaction of these hydrocarbons, a linear relationship will be observed, (fig. 5 and 6).

Table 8

The second order rate constant of chlorination with Cl_2 in acetic acid at 20°C[100]

	k_2 ($l\ mol^{-1} s^{-1}$)	$\log k_2$	$\Delta E/\beta$
Benzene	6.8×10^{-7}	-6.167	2.31
Naphthalene	5.21×10^{-2}	-1.28	1.81
Phenanthrene	4.45×10^{-1}	-0.342	1.79

Table 9

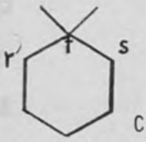
The second order rate constants of chlorination of ArH[45] with chlorine in acetic acid-carbon tetrachloride (3:1 v/v)

	k_2 ($l\ mol^{-1} s^{-1}$)	$\log k_2$	$\Delta E/\beta$
Naphthalene	1.9×10^{-4}	-3.72	1.81
Phenanthrene	1.3×10^{-3}	-2.88	1.79
Pyrene	7.1×10^{-1}	-0.14	1.51

The molecular orbital treatment can be applied to substitution in aromatic hydrocarbons by using Wheland's model for the transition state[95]. The activation energy ΔE should be shown by:

$$\Delta E = C_X - 2\beta\,(a_{or} + a_{os}) = C_X - \beta N_t \qquad (1)$$

where C_X is a constant characteristic of the reagent X, β is the carbon-carbon resonance integral, and a_{or}, a_{os} are the coefficients of the atomic orbitals of atoms adjacent to that (t)



CXXIX

at which the reaction occurs in the non-bonding molecular orbital of the transition state, N_t is therefore a direct measure of the relative reactivity of a given position in a hydrocarbon, and it is termed the "reactivity number" of atom (t). The smaller the N_t the greater the reactivity is. Because the equation (1) holds regardless of the reagent, thus orientation in hydrocarbons should be the same for all types of reagents (e.g. electrophile, nucleophile and radical).

The obtained relative rates of methylation reaction of a number of hydrocarbons with methyl radicals, show such an agreement. From equation (1) equation (2) can be written:

$$RT \quad \log_n k/ko = - \beta \, (N^o - N_t) \qquad (2)$$

where ko is the velocity constant and N^o reactivity number for substitution in benzene and k and N_t the same quantities for substitution at the most reactive position in hydrocarbons.

Table 10 shows that the experimental results for methylation[101] are in good agreement with the equation (2).

Table 10

Comparison of observed and predicted reactivities for methylation of hydrocarbons

Hydrocarbon	log k/ko	N^o-N_t	(log k/ko)/(N^o-N_t)
Diphenyl	0.70	0.24	2.9
Naphthalene	1.34	0.50	2.7
Phenanthrene	1.43	0.51	2.8
Chrysene	1.76	0.64	2.8
Pyrene	2.10	0.80	2.6
Benzanthracene	2.67	0.96	2.8
Anthracene	2.91	1.04	3.1
Naphthacene	3.97	1.28	

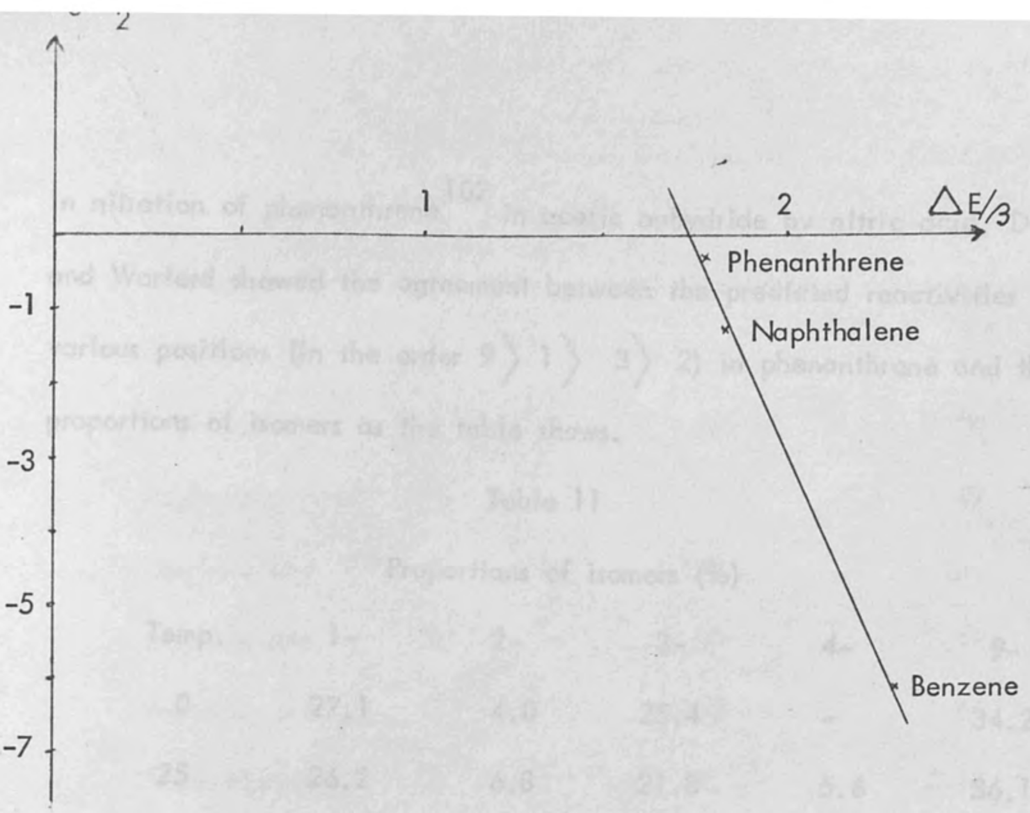


Fig. 5 Plot of $\log_{10}k_2$ against $\Delta E/\beta$ for chlorination of hydrocarbons by molecular chlorine in AcOH

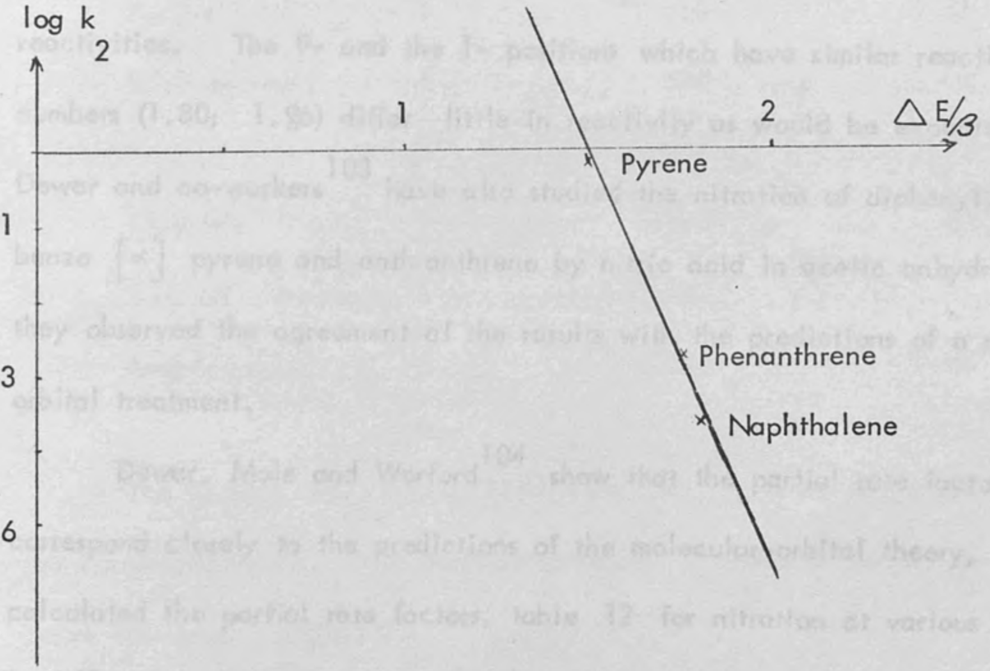


Fig. 6 Plot of $\log_{10}k_2$ against $\Delta E/\beta$ for chlorination of some hydrocarbons by Cl_2 in AcOH–CCl_4.

In nitration of phenanthrene[102] in acetic anhydride by nitric acid, Dewar and Warford showed the agreement between the predicted reactivities of the various positions (in the order $9 \rangle 1 \rangle 3 \rangle 2$) in phenanthrene and the proportions of isomers as the table shows.

Table 11

Proportions of isomers (%)

Temp.	1-	2-	3-	4-	9-
0	27.1	4.0	25.4	-	34.2
25	26.2	6.8	21.8	5.6	36.1
35	24.7	5.3	22.9	-	33.4

The proportions of isomers are different from what was reported by Schmidt and Heimle which were not in good agreement with the predicted reactivities. The 9- and the 1- positions which have similar reactivity numbers (1.80; 1.86) differ little in reactivity as would be expected. Dewar and co-workers[103] have also studied the nitration of diphenyl, chrysene, benzo [α] pyrene and anthanthrene by nitric acid in acetic anhydride and they observed the agreement of the results with the predictions of a molecular orbital treatment.

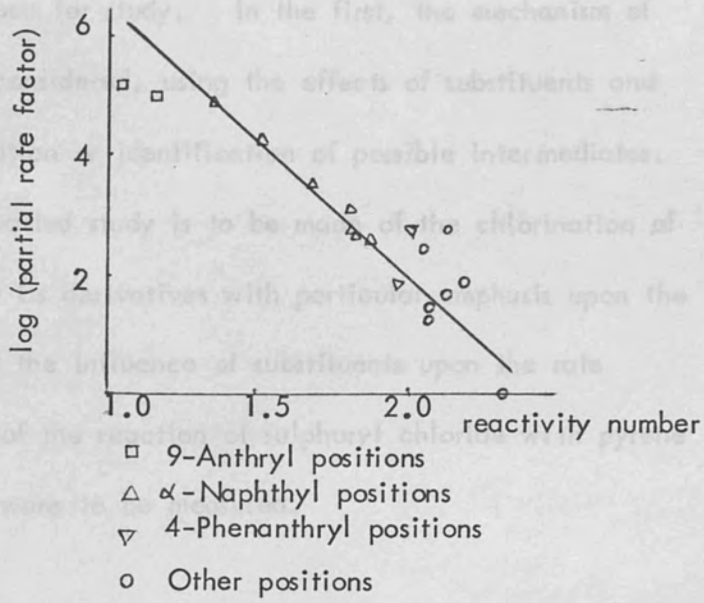
Dewar, Mole and Warford[104] show that the partial rate factors correspond closely to the predictions of the molecular-orbital theory, they calculated the partial rate factors, table 12 for nitration at various positions in different hydrocarbons from the obtained data of their studies of the relative reactivities of a number of hydrocarbons by competitive method[105] and the proportions of isomers found in nitration of those hydrocarbons.

Table 12

Hydrocarbon	position	partial rate factor	reactivity number
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	600	2.00
Triphenylene	2	600	2.12
Chrysene	2	3,500	1.67
Benzo (α) pyrene	6	108,000	1.15
Anthanthrene	6	156,000	1.03

The plot of $\log_{10}$ ki/ko (calculated from the data in the table) against the corresponding reactivity numbers (equation 2) shows a straight line and a linear relationship, (fig. 7).

Fig. 7 Plot of $\log_{10}$ ($k\,k_o$) against N_i for nitration of hydrocarbons by nitric acid in acetic anhydride



Agreement is not perfect as is shown in the graph where some of the points do not lie on the line. By using β'_x, a smaller parameter instead of β, a better agreement will be obtained $\beta'_x = \beta - \beta_x$ 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.

1.10 Scope of the present work:

Two aspects of the heterolytic chlorination of aromatic systems by sulphuryl chloride were chosen for study. In the first, the mechanism of attack of acetanilides was considered, using the effects of substituents and solvents as well as the isolation or identification of possible intermediates.

In the second, a detailed study is to be made of the chlorination of anthracene and a number of its derivatives with particular emphasis upon the kinetics of the reaction and the influence of substituents upon the rate and also the rate constants of the reaction of sulphuryl chloride with pyrene and some of its derivatives were to be measured.

EXPERIMENTAL

2.1 Instrumentation

The following methods were used for identification of the products throughout the work:

a) Infrared spectroscopy: A Perkin-Elmer 197 spectrophotometer was used for recording the spectra.

b) Nuclear magnetic resonance spectroscopy: All ^1H n.m.r. spectra were recorded on a Perkin-Elmer R12B instrument, at 60 MHz. T.M.S. (Tetra Methyl Silane) was used as the internal standard.

c) Thinlayer Chromatography: Alumina and Silica gel TLC plates having a thickness of 0.25 mm were used. Plates were examined under ultraviolet light.

d) Gas Liquid Chromatography: This was carried out on a Pye 104 instrument, using a flame ionisation detector and nitrogen as carrier gas.

Identification of the reaction products was achieved by comparing the reaction times with those of authentic samples under exactly the same conditions. The columns which were used for identification of the products of reaction of sulphuryl chloride with anthracenes and acetanilides were:

AP-15C	(15% Apiezon L, supported on 100-120 mesh celite, 9 ft x 1/8 inch O.D. column)
OV-1	(1% Methyl silicone gum, supported on 100-120 mesh, 5 ft x 1/8 inch O.D. column)
OV-1	better results were obtained.

e) Densities of the solvents were measured using a Worden's pycnometer, the volume of which was determined at 25°C using boiled out, deionized water.

f) n_D^{20} Refractive indices were measured using an Abbe '60' Refractometer, degree scale model.

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f) n_D^{20} Refractive indices were measured using an Abbe '60' Refractometer, degree scale model.

2.1.1 Purification of the solvents and sulphuryl chloride:

Nitromethane was purified by fractional distillation and dried with sodium sulphate. After column chromatography on alumina it was again dried with calcium chloride and redistilled.

	lit.	exp.
b.p.	101°/760 mm Hg	101°/760 mm Hg
d	1.354 g/cm^3	1.354 g/cm^3
n_D^{20}	1.3935	1.3822

Chlorobenzene was dried with calcium chloride and fractionally distilled. Material recovered from the kinetic runs was steam distilled first and then dried with calcium chloride and fractionally distilled.

	lit.	exp.
b.p.	132°/760 mm Hg	131°/760 mm Hg
d	1.064 g/cm^3	1.064 g/cm^3
n_D^{20}	1.5248	1.5244

Sulphuryl chloride was fractionally distilled. After discarding the first portion (containing free chlorine and sulphur dioxide) some solid carbon dioxide was added to the still pot and distillation was continued, when a colourless product b.p. 69°/760 mm Hg was obtained[72] lit. b.p. 69.1/760 mm Hg.

2.1.2 Preparation of starting materials:

Acetanilides. Some of the acetanilides were commercial materials and some others were prepared by acetylation of the relevant amines[106].

o-Bromoaniline (0.022 mole 3.78g) was acetylated by refluxing it with acetic anhydride (0.021 mole, 2 ml) and glacial acetic acid (0.035 mole, 2 ml), and a few mg of zinc dust for thirty minutes. The product was recrystallised from dilute alcohol (using charcoal); 3.4g, 72% pure o-bromoacetanilide m.p. 96° (lit m.p. 96°) was obtained.

m-Bromoacetanilide was similarly prepared from acetylation of m-bromoaniline (38.2g, 24.2 ml, 0.18 mole) giving m-bromoacetanilide (38.5g, yield 81%) m.p. 87-87.5°, lit. m.p. 87.5°.

o-Trifluoromethylacetanilide was made from acetylation of o-trifluoroaniline (7.2g, 0.05 mole) using sulphuric acid, when o-trichloromethylacetanilide (7.2g, 0.035 mole) was obtained, m.p. 94°C (lit. m.p. 94-95°, C.A. (1954) 48, 8194g).

o-Fluoroacetanilide was prepared from acetylation of o-fluoroaniline (5g, 0.045 mole) using hydrochloric acid (10 ml), acetic anhydride (5.1 ml, 0,0497 mole) and sodium acetate (6.6g/20 ml H_2O, 0.08 mole). o-Fluoroacetanilide m.p. 80°C (5.3 g, 78%) was obtained (lit. m.p. 80°).

p-Methoxyacetanilide. p-Methoxynitrobenzene was reduced to p-methoxyaniline by the method used to reduce nitrobenzene to aniline[107]. Tin (5g, 0.08 mole) and hydrochloric acid (20 ml) were used to reduce p-methoxynitrobenzene (7.6g, 0.05 mole). p-Anisidine (4.3g, 70%) was obtained, m.p. 55° (lit. m.p. 57°). Acetylation of this amine gave p-methoxyacetanilide, which was recrystallised from water after column chromatography, m.p. 128°C (lit. m.p. 130-132°C).

2.1.3 Preparation of authentic materials

2-chloro-4-bromo acetanilide was prepared[108] by passing molecular chlorine into a cooled solution of aceto-p-bromoanilide (0.05 mole, 10.7g) in glacial acetic acid and anhydrous sodium acetate (0.05 mole, 4.1g) at room temperature. The product was recrystallised from alcohol to give aceto-2-chloro-4-bromoanilide (11.3g, 91%) m.p. 151° (lit. m.p. 151°). This compound was then converted into the corresponding aniline (4-bromo-2-chloroaniline m.p. 73° lit. m.p. 73°C) for gas chromatographic study by dissolving the acetanilide in a mixture of alcohol and hydrochloric acid (5 ml) and refluxing it for about eight hours. Then sodium hydroxide was added.

Aceto-2-bromo-4-chloroanilide[108] 4-Chloro-acetanilide (8.4g, 0.05 mole) and anhydrous sodium acetate (4.1g, 0.05 mole) in acetic acid were mixed and a solution of bromine (8g, 0.05 mole) in acetic acid (80 ml) was added slowly. After heating for 5 hours on a water-bath the mixture was diluted with water and filtered and the residue crystallised from alcohol. 2-Bromo-4-chloroacetanilide (11.43g, 92%) m.p. 136°C was obtained (lit. m.p. 137°C). The anilide was then hydrolysed[109]. The product was recrystallised from alcohol giving 2-bromo-4-chloroaniline m.p. 67°C (lit. m.p. 69°C).

N.B. To study the g.l.c. of the products, acetanilides were converted into anilines by hydrolysing them. To hydrolyse the acetanilides the acetanilide (0.5 to 1g) was refluxed with 10-20 ml of concentrated hydrochloric acid for two hours[109]. The aniline was recovered by diluting it with water and addition of 5% sodium hydroxide until alkaline and then it was filtered and recrystallised from alcohol.

2.1.4. Preparation and purification of anthracenes

Anthracene was commercial material which was purified by recrystallisation from alcohol m.p. 218°C (lit. m.p. 216°[138a], lit. m.p. 218°[138b]).

9-Bromo-anthracene was prepared[110] by refluxing anthracene (4.45g, 0.025 mole) with copper (II) bromide (0.05 mole) in chlorobenzene (100 ml) for 1 hour. The crude product (5g, 77.5%) was then chromatographed on alumina, eluting with petroleum ether (b.p. 40°-60°) to give 9-bromoanthracene m.p. 85-90°C and some 9,10-dibromoanthracenes observed by t.l.c. After fractional recrystallisation, 9-bromoanthracene m.p. 99-101° was obtained (lit. 98-99° & 101°)[139].

9-Chloroanthracene[110] was prepared by a similar method using copper (II) chloride, the major product being 9-chloroanthracene (3.62g, 68%) m.p. 105-106° (lit. 104-106°) and the minor product 9,10-dichloroanthracene m.p. 212-214°C (lit. 212-214°C).

9-Nitroanthracene was prepared by the method of C.E. Brown and coworkers[111] using anthracene (19.9g, 0.112 mole). The crude orange 9-nitroanthracene (20.6g, 92%) was obtained after washing with 10% sodium hydroxide and warm water, and by recrystallisation from acetic acid, pure 9-nitroanthracene was obtained as bright orange-yellow needles (16g) m.p. 145-146°C (lit. m.p. 145-146°).

9-Anthraldehyde was prepared by the method of L.F. Fieser, J.L. Hartwell and J.E. Jones[112] using anthracene (23.1g, 0.13 mole). The obtained solid was washed with 6N hydrochloric acid and water. The crude solid (20g, 75%) m.p. 97-100° was recrystallised from acetic acid to give 9-anthraldehyde m.p. 104.5-105° C (lit. m.p. 104.5-105°C).

9-Methoxyanthracene - It was prepared by the modified method used by J.S. Meek et al[113] using anthrone (7.6g, 0.09 mole) and methyl-p-toluenesulphonate (14g, 0.075 mole). The crude product (6g, 64%) m.p. 95-96°C was recrystallised from isopropanol (using charcoal). Column chromatography on alumina raised the m.p. to 97-98°C (lit. m.p. 97-98°C).

Anthrone used in this method was prepared[114] from reduction of anthraquinone (12g, 0.057 mole) in acetic acid (90 ml), granulated tin (11.3g, 0.095 mole) and hydrochloric acid (30 ml). The crude product (10.05g, 82%) m.p. 153°C was recrystallised from a mixture of 3:1 benzene and petroleum ether (b.p. 60-80°) (100 ml) to give anthrone (7.63g) m.p. 155°C (lit. m.p. 155.5°).

9-Methylanthracene was prepared by two methods:

Method 1 - The conversion of anthrone into 9-methyl anthracene[88α]. Anthrone (3.5g, 0.018 mole) in benzene was treated with the Grignard reagent (0.054 mole) derived from 0.5g magnesium in dry ether reacted with 3g CH_3I in 5 ml dry ether[115]. The crude product was chromatographed on alumina and recrystallised from light petroleum. Both the yield (1.2g, 31%) and the m.p. (90°C, lit. m.p. 100°C) were low.

88b

Method 2 - 9-Anthraldehyde (10g, 0.05 mole) was reduced to 9-methyl anthracene by refluxing it with diethylene glycol (100 ml), sodium hydroxide (10 ml) and 85% hydrazine hydrate (10g) for 2½ hours. The cooled mixture was diluted with water and filtered. The precipitate (8.1g, 88%) was recrystallised from methanol after column chromatography on alumina to give 9-methylanthracene (6g, 64%) m.p. 100°C (lit. m.p. 100°).

9-Benzoylanthracene (anthraphenone) was prepared by using aluminium-chloride (12g, 0.055 mole) as a catalyst in the reaction of benzoylchloride (11.5g, 0.025 mole) in ethylene dichloride (100 ml) with anthracene[116]

(8.9g, 0.05 mole). The crude product (10g 71%) was chromatographed on alumina (eluting with petroleum ether, b.p. 40-60°) and crystallised from acetic acid and recrystallised from ethylacetate. The purity of the compound was shown by its N.M.R. spectrum, its sharp m.p. 148°C (lit. 148°) and by t.l.c.

9-Cyanoanthracene (9-anthranitrile) was prepared from the relevant oxime[117]. To prepare the oxime a solution of 9-anthraldehyde (5.5g, 0.025 mole) in alcohol (65 ml) was treated with hydroxylamine hydrochloride (2.1g in water (25 ml) to give 5.1g, 86% of the oxime. A solution of the oxime (5.1g) in acetic acid (25 ml) was boiled under reflux for 15 min. The resulting solid was washed with acetic acid and petroleum ether and recrystallised from acetic acid. 9-Cyanoanthracene (4.81g, 95%) m.p. 177.5-179° was obtained (lit. m.p. 177.5-179°).

2-Chloroanthracene. 2-Chloroanthraquinone was prepared by the method used for[118] making 1-chloroanthraquinone, using potassium anthraquinone-2-sulphonate (0.03 mole, 10g), concentrated hydrochloric acid (43 ml) and sodium chlorate (10g, 0.095 mole). 2-Chloroanthraquinone (5.55g, 70%) m.p. 209-210° was obtained. The m.p. raised to 212.5°C by recrystallisation from alcohol (lit. m.p. 212.4°)[140]. 2-Chloroanthraquinone (4.36g, 0.018 mole) was reduced to 2-chloroanthracene with zinc in ammonia solution (0.088 mole) by the method used for the reduction of 1,5-dichloroanthraquinone[119]. The m.p. of the product (3g, 79%) 200-220°C was raised to 223°C after column chromatography on alumina and two recrystallisations from n-propyl alcohol (lit. m.p. 223°C)[141].

9-Acetamidoanthracene was also prepared from reduction of 9-nitroanthracene (1g, 0.0044 moles) in 20 ml acetic acid to 9-aminoanthracene[120] by heating it with a solution of stannous chloride (10g, 0.05 moles) in concentrated hydrochloric acid (10 ml). 9-Acetamidoanthracene (0.94g, 90%) m.p. 148-150° (lit. m.p. 145-150°) was obtained from acetylation of the obtained amine[106], but because it is not soluble in chlorobenzene its kinetic study was not possible in this solvent.

2.1.5 Preparation of authentic materials

9-Chloro-10-methoxyanthracene - To a solution of 9-methoxyanthracene[121] (2g, 0.01 mole) in benzene was slowly added phosphorus pentachloride (2g, 0.01 mole) down the condensor. The mixture was boiled for about one hour, then concentrated under vacuum, and it was left in a watch glass to crystallise (m.p. 138-140°). After recrystallisation from ligroin yellow crystals m.p. 148-152°C were obtained. (lit. m.p. 154°)

9-Bromo-10-chloroanthracene was prepared from chlorination of 9-bromo anthracene[139] (2g, 0.008 mole in 10 ml chloroform) by sulphuryl chloride (2 ml 0.024 mole). The obtained solid (2g, 85%) m.p. 204-206° was recrystallised from chloroform to give 9-bromo-10-chloroanthracene m.p. 207-209°C (lit. m.p. 207°).

9-Benzoyl-10-Chloroanthracene was prepared[122] by chlorination of 9-benzoyl-anthracene (5.6g, 0.02 mole) by a solution of chlorine in carbon tetrachloride (20 ml, 7.5% w/v 0.0) mole). The obtained solid was crystallised successively from glacial acetic acid, benzene, and ethyl acetate. m.p. 164-165° (lit. m.p. 164-165°C).

2.1.6 Preparation and purification of pyrenes

Pyrene - The commercially available pyrene was purified by recrystallisation from absolute alcohol to give m.p. 148-149°C lit. m.p. 148-149°C.

3-Chloropyrene - Pyrene (5g, 0.025 mole) in carbon tetrachloride (50 ml) was treated with sulphuryl chloride (3.4g, 0.015 mole) in carbon tetrachloride[123] (10 ml). After 48 hours at room temperature most of the solvent was removed, the rest was evaporated and the residue (2g, 34%) was recrystallised three times from alcohol using charcoal to give 3-chloropyrene (1.11g, 19%), m.p. 119-120°C (lit. m.p. 119-120°, lit. yield 17%).

3-Benzoylpyrene - To a solution of pyrene (5.05g, 0.025 mole) and benzoyl chloride (3.75g) in dry benzene (50 ml) aluminium chloride was added[124] (5g, 0.0375 mole) at room temperature, keeping the temperature at about 35° for an hour then the mixture was hydrolysed at room temperature and the benzene removed by steam distillation. The solid residue was filtered and extracted with benzene then dried by calcium chloride and the solvent was removed. The crude product (6g, 79%) m.p. 107-110° was recrystallised from alcohol and then twice from a mixture of alcohol and benzene (1:1) to give 3-benzoyl pyrene, m.p. 126.5-127.5°C (lit. m.p. 128°).

3-Bromopyrene - This compound was prepared from bromination of pyrene (5g, 0.025 mole) with bromine in carbon tetrachloride by the procedure used by W.H. Gumprecht[125]. The obtained crude material (5g, 70%) was recrystallised from benzene-alcohol, a colourless product m.p. 93-94°C was obtained (lit. m.p. 94.5-95.5°C).

Pyrene-3-aldehyde - Phosphorus oxychloride (27g) was added dropwise over 2 hours to a mixture of form-N-methylaniline (27g) in ortho-dichlorobenzene (20 ml) keeping the temperature below 25°C, then powdered pyrene (20g, 0.099 mole) was added[124] with shaking and the mixture was heated to 90-95° for two hours under reflux. The deep-red solution precipitated a red complex on cooling. This product was washed with benzene and decomposed with water, The crude aldehyde (21.6g, 95%) m.p. 120° was recrystallised from alcohol to give a bright yellow material m.p. 125-126° (lit. m.p. 126°).

2.2 Kinetic Study

For studying the kinetic runs standard solutions of a compound and of sulphuryl chloride in the solvent were made and thermostated. To show the absence of free chlorine in the sulphuryl chloride solution, one part of the solution was added to aqueous potassium iodide. No iodine was liberated. To show the absence of sulphur dioxide one part of the solution was added to a known volume of standard iodine solution and then titrated with sodium thiosulphate. Titration showed that no iodine was reduced by the reagent solution. To study the reaction a known volume and known concentration of the thermostated sulphuryl chloride solution was added to a solution of the substrate of known concentration. A known volume of this solution was taken out in intervals and poured in water to stop the reaction and titrated with standard iodine solution. An example of a kinetic study is given below.

Table 13

$[I^2] = 0.1N$ $[SO_2Cl_2] = 0.106M$ [p-Chloroacetanilide] = 0.05M

Time (s)	188	300	549	696	904	1115	1449
V_{I^2} (cm^3)	5.6	6.3	7.2	7.8	8.2	8.8	9.3
$\log \frac{a-x}{b-x}$	0.5149	0.5685	0.6601	0.744	0.817	0.97	1.184
$10^2 k_2$ (l mol^{-1} s^{-1})	1.843	1.828	1.63	1.738	1.642	1.85	1.98

Mean $k_2 = 1.79 \pm 0.12 \times 10^{-2}$ l mol^{-1} s^{-1}

2.2.1 Standardisation of solutions of sulphuryl chloride - Sulphuryl chloride solutions were made by weight and then analysed by measuring the concentration of liberated sulphur dioxide produced in the reaction of an excess of substrate (acetanilide or anthracene). 1-2 mls of the standard solution (SO_2Cl_2 in CH_3NO_2 or C_6H_5Cl) were added to 0.2-0.5g of the substrate (in the solvent) and left for at least 24 hours, then it was washed with water to dissolve the liberated sulphur dioxide and titrated with a standard iodine solution. From that the concentration of sulphuryl chloride was calculated and the requisite volume of this solution was taken out to make the desired concentration of sulphuryl chloride to pour in the standard solution of substrate to start the reaction. To measure the molarity of the sulphuryl chloride by hydrolysing it, 1 ml of the standard solution was poured in some water then titrated with standard sodium hydroxide (0.1N), then the molarity of sulphuryl chloride solution was calculated, for example, 40.9 ml of NaOH (0.102N) was used in titration of the obtained solution, from hydrolysis of SO_2Cl_2:

$$\frac{40.9 \times 0.102}{1000} = \text{moles NaOH which is equal to } 4[SO_2Cl_2]$$

$$\text{so} \quad \frac{1}{4}\left(\frac{40.9 \times 0.102}{1000}\right) = 1.04 \times 10^{-3} \text{ moles } SO_2Cl_2 \text{ in 1 ml solution}$$

and $1.043 \times 10^{-3} \times 1000 = 1.043$ M SO_2Cl_2

2.2.2 Stoichiometric analysis - To find out the stoichiometry of the reaction , determination of hydrogen chloride and sulphur dioxide formed during the reaction of sulphuryl chloride with aromatic compounds is necessary. To determine these, 0.1 mole of substrate (acetanilides or anthracenes) in 20 ml solvent (nitromethane or chlorobenzene) was treated with 0.1 mole of sulphuryl chloride solution in an iodine flask and left for at least 24 hours. The reaction mixture was washed with water several times to extract sulphur dioxide and hydrogen chloride from the organic layer, and the aqueous layer after being washed with ether was kept to use for identification of the products of the reaction. To determine the formed hydrogen chloride a solution of silver nitrate (0.1N) was made and standardised with standard sodium chloride solution (0.1N). Then 25 ml of the aqueous solution were titrated with silver nitrate solution and the amount of hydrogen chloride was calculated from the titre.

To determine the liberated sulphur dioxide, a standard solution of iodine (0.1N) was made and standardised against standard sodium thiosulphate solution. Then 20 ml of the aqueous solution was titrated with iodine solution (0.1N) using commercially available iodine indicator (Iotect). The percentage of the formed sulphur dioxide was calculated from the titre (Table 14.)

Table 14

Substrate	[ArH] mole	$[SO_2Cl_2]$	formed Cl^- mole	obtained SO_2 mole
Acetanilide	0.1	0.1	0.099	0.097
o-Chloroacetanilide	0.1	0.1	0.098	0.095
p-Methoxyacetanilide	0.1	0.1	0.099	0.098
p-Nitroacetanilide	0.1	0.1	0.088	0.082
Anthracene	0.002	0.002	0.0014	0.0013
9-Methylanthracene	0.002	0.002	0.0018	0.0016
9-aldehydeanthracene	0.002	0.002	0.0016	0.0014
2-methylanthracene	0.002	0.002	0.0012	0.0012

DISCUSSION

3.1.1 Acetanilides -

The yields of sulphur dioxide and hydrogen chloride and identity of the products (table 15) show that the stoichiometry of the reaction is:

$$ArH + SO_2Cl_2 \longrightarrow ArCl + SO_2 + HCl \qquad (65)$$

Table 15

The major organic products of the reaction of sulphuryl chloride with acetanilide in nitromethane at 25°C

Starting Material	Product	lit m.p.	exp. m.p.	Yield
p-Chloroacetanilide	2,4-dichloroacetanilide	143-146°	144-146°	78%
o-Chloroacetanilide	2,4-dichloroacetanilide	143-146°	144-145°	80%
p-Acetotoluidide	2-chloro-4 aceto-toluidide	118°	117-118°	99%
Acetanilide	4-chloroacetanilide	169.5°	170°	98%
o-Nitroacetanilide	4 chloro-2-nitroacetanilide	104°	103-104°	74%
p-Nitroacetanilide	2-chloro-4 nitroacetanilide	139°	138°	72%
m-Nitroacetanilide	4-chloro-3-nitroacetanilide	150(145°)	149°	72%
p-Bromoacetanilide	(2-chloro-4-bromoacetanilide (4-chloro-acetanilide	151° 169.5°	146-151°	78%
m-Chloroacetanilide	3,4-dichloroacetanilide	121°	120-121°	98%

The rate of reaction does not alter much by changing the concentration of the reactants (table 16).

Table 16

Second order rate constants for the chlorination of substituted acetanilides (SO_2Cl_2/CH_3NO_2, 25°)

Substituent	[ArH]	$[SO_2Cl_2]$	k_2 ($l\ mol^{-1}\ sec^{-1}$)
p-chloro	0.05	0.1016	$1.79 \pm 0.12 \times 10^{-2}$
	0.05	0.1016	$1.7 \pm 0.3 \times 10^{-2}$
	0.05	0.1016	$1.97 \pm 0.16 \times 10^{-2}$
	0.1	0.1016	$1.63 \pm 0.13 \times 10^{-2}$
p-bromo	0.05	0.1	$1.22 \pm 0.18 \times 10^{-2}$
	0.05	0.1	$1.49 \pm 0.16 \times 10^{-2}$
	0.05	0.1	$1.249 \pm 0.4 \times 10^{-2}$
Hydrogen	0.01	0.01	21
	0.01	0.01	40
o-nitro	0.05	0.1	$2.68 \pm 0.2 \times 10^{-3}$
	0.05	0.05	$2.67 \pm 0.15 \times 10^{-3}$
p-methyl	0.01	0.01	about 12
p-methoxy	0.01	0.01	$\rangle$ 7
p-nitro	0.02	0.02	$2.14 \pm 0.29 \times 10^{-3}$
	0.05	0.014	$3.06 \pm 0.16 \times 10^{-3}$
m-chloro	0.1	0.1	$0.53 \pm 0.09 \times 10^{-3}$
m-nitro	0.1	0.1	$1.63 \pm 0.45 \times 10^{-3}$
	0.05	0.1	$2.27 \pm 0.3 \times 10^{-3}$
	0.05	0.05	$2.21 \pm 0.3 \times 10^{-3}$
o-chloro	0.1	0.725	$4.76 \pm 0.22 \times 10^{-2}$
	0.05	0.1	$3.1 \pm 0.4 \times 10^{-2}$

Table 17

The influence of SO_2 upon the rate of chlorination of some anilides (SO_2Cl_2/CH_3NO_2, 25°)

Substituent	$[SO_2]$	[ArH]	$[SO_2Cl_2]$	k_{obs} ($l\ mol^{-1}\ s^{-1}$)
o-chloroacetanilide	-	0.01	0.01	0.935 ± 0.09
	-	0.01	0.01	0.923 ± 0.09
	0.0038	0.01	0.01	0.563 ± 0.0048
	0.0047	0.01	0.01	0.51 ± 0.087
	0.0069	0.01	0.01	0.39 ± 0.208
	0.0082	0.01	0.01	0.38 ± 0.08
o-fluoroacetanilide	-	0.01	0.01	1.84 ± 0.2
	-	0.01	0.01	1.68 ± 0.18
	-	0.01	0.01	1.7 ± 0.21
	0.0079	0.01	0.01	0.548 ± 0.073
	0.0075	0.01	0.01	0.54 ± 0.13
	0.0045	0.01	0.01	0.80 ± 0.0013
	0.048	0.01	0.01	0.722 ± 0.092
	0.0062	0.01	0.01	0.635 ± 0.1
o-trifluoromethylacetanilide	-	0.01	0.01	5.12 ± 0.4×10^{-2}
	-	0.01	0.01	5.0 ± 0.65×10^{-2}
	7.8×10^{-3}	0.01	0.01	5.25 ± 1.0×10^{-2}
	-	0.01	0.01	7.29 ± 1.0×10^{-2}
	4.7×10^{-3}	0.01	0.01	7.25 ± 0.34×10^{-2}
	7.7×10^{-3}	0.01	0.01	5.02 ± 0.7×10^{-2}
o-bromoacetanilide	-	0.01	0.01	0.813 ± 0.1
	-	0.01	0.01	0.813 ± 0.046
	0.01	0.01	0.01	0.288 ± 0.019
	0.0122	0.01	0.01	0.283 ± 0.058
	0.0069	0.01	0.01	0.36 ± 0.039
	0.00485	0.01	0.01	0.41 ± 0.05

Table 16 indicates that the reaction is generally a second order process involving one molecule of each reagent, and so a bimolecular mechanism.

$$\text{Rate} = k_2 \left[\text{ArH}\right]\left[SO_2Cl_2\right]$$

But this equation cannot be strictly applied since sulphuryl chloride decomposes in nitromethane to some extent. The equilibrium constant (k) of the dissociation process in nitromethane

$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2 \qquad (56)$$

has been determined[75], k = 6.8 ± 0.8 x 10^{-4} l mol^{-1} at 18° and k = 1.6 ± 0.2 x 10^{-3} l mol^{-1} at 25°C.

There are four possible electrophiles, chlorinium ion Cl^+, chlorosulphonium ion $ClSO_2^+$, molecular chlorine, Cl_2, and molecular sulphuryl chloride SO_2Cl_2.

Chlorinium ion and chlorosulphonium ion cannot be the effective electrophiles since there is no observed decrease in the rate of the reaction with time which otherwise would have been observed because of the effect of formed chloride ion.

Molecular chlorine contributes slightly in the chlorination by sulphuryl chloride in nitromethane since the initially added sulphur dioxide only retards the reaction and does not stop it. Bolton concluded that, in the chlorination of alkylbenzenes[75], molecular chlorine is not the only effective electrophile and that the principal electrophile is in fact molecular sulphuryl chloride. However, the sensitivities of the two reagents towards substituent effects may differ and so the conclusion is not necessarily general.

From the reaction schemes,

$$SO_2Cl_2 \overset{K}{\rightleftarrows} SO_2 + Cl_2 \quad \text{pre equilibrium} \quad K = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$

$$Cl_2 + ArH \xrightarrow[slow]{k_\beta} ArCl + HCl \quad \text{rate determining} \qquad (66)$$

$$SO_2Cl_2 + ArH \xrightarrow[slow]{k_\alpha} ArCl + HCl + SO_2 \quad \text{rate determining} \qquad (67)$$

the rate equation:

$$\text{Rate} = k_\alpha \left[SO_2Cl_2\right]\left[ArH\right] + k_\beta \left[Cl_2\right]\left[ArH\right]$$

results. If K is not large $\left[Cl_2\right] \ll \left[SO_2Cl_2\right]$ and we can write:

$$\text{Rate} = k_\alpha \left[SO_2Cl_2\right]\left[ArH\right] + k_\beta \; K \frac{\left[SO_2Cl_2\right]\left[ArH\right]}{\left[SO_2\right]}$$

$$\text{Rate} = \frac{dx}{dt} = \left[ArH\right]\left[SO_2Cl_2\right]\left(k_\alpha + K \frac{k_\beta}{x}\right)$$

$$\text{Rate} = \frac{dx}{dt} = \left(k_\alpha + \frac{k_\beta K}{x}\right)(a - x)(b - x)$$

$$\text{Rate} = \frac{dx}{dt} = \text{kobs} \; (a - x) \; (b - x)$$

$$\text{kobs} = k_\alpha + \frac{k_\beta K}{x}$$

$$K = \frac{\left[SO_2\right]\left[Cl_2\right]}{\left[SO_2Cl_2\right]}$$

$$\left[SO_2\right] = \frac{K\left[SO_2Cl_2\right]}{\left[Cl_2\right]}$$

$$k_{obs} = k_\alpha + \frac{k_\beta \; \left[Cl_2\right]}{\left[SO_2Cl_2\right]}$$

where x = concentration of product at time t and is equal to that of formed sulphur dioxide, a is the concentration of aromatic compound, and b is the concentration of sulphuryl chloride. A plot of k_{obs} against $\left[Cl_2\right]$. (calculated from $\left[Cl_2\right] = \frac{K\left[SO_2Cl_2\right]}{\left[SO_2\right]}$, $K = 1.6 \times 10^{-3}$ and the initial concentrations of SO_2Cl_2 and SO_2) gives k_α as the intercept and then k_β can be calculated from the equation $k_{obs} = k_\alpha + (K \frac{k_\beta}{x})$ by applying relevant values of k_{obs} and concentration of added sulphur dioxide, $[SO_2]$

Table 18

$[SO_2Cl_2] = 0.01M$, $[\underline{o}\text{-F } C_6H_4NHAc] = 0.01M$

k_{obs}	$[\text{added } SO_2]/M$	$[Cl_2] \times 10^3$
1.84 ± 0.2	-	-
1.68 ± 0.18	-	-
1.70 ± 0.21	-	-
0.514 ± 0.073	0.0079	2.02
0.548 ± 0.13	0.0075	2.13
0.8 ± 0.0013	0.0045	3.55
0.722 ± 0.092	0.0048	3.33
0.635 ± 0.1	0.0062	2.6

$[SO_2Cl_2] = 0.01M$, $[\underline{o}\text{-Br}C_6H_4NHAc] = 0.01M$

k_{obs}	$[SO_2]/M$	$[Cl_2] \times 10^3$
0.813 ± 0.1	-	-
0.813 ± 0.046	-	-
0.288 ± 0.019	0.01	1.6
0.283 ± 0.058	0.0122	1.31
0.36 ± 0.039	0.0069	2.32
0.41 ± 0.05	0.00485	3.3

$[SO_2Cl_2] = 0.01M$, $[\underline{o}\text{-Cl}C_6H_4NHAc] = 0.01M$

k_{obs}	$[SO_2]/M$	$[Cl_2] \times 10^3$
0.935 ± 0.07	-	-
0.928 ± 0.09	-	-
0.563 ± 0.048	0.0038	4.2
0.51 ± 0.087	0.0047	3.4
0.39 ± 0.208	0.0069	2.32
0.38 ± 0.08	0.0082	1.95

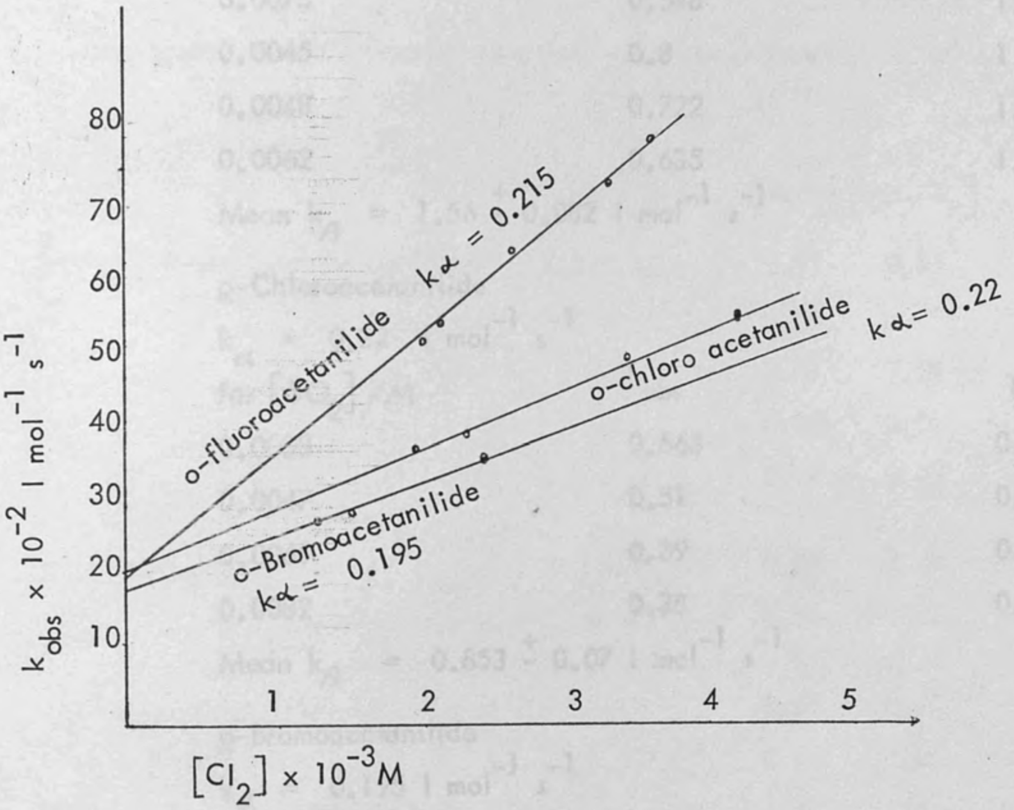


Fig. 8 The plot of k_{obs} against $[Cl_2]$

The obtained values of k_α for the reaction of these three compounds are used to calculate k_β (Table 19).

Table 19

o-Fluoroacetanilide

$k_\alpha = 0.215$ l mol^{-1} s^{-1}

for $[SO_2]$/M	k_{obs}	k_β
0.0079	0.514	1.47
0.0075	0.548	1.56
0.0045	0.8	1.64
0.0048	0.722	1.52
0.0062	0.635	1.56

Mean k_β = 1.56 ± 0.082 l mol^{-1} s^{-1}

o-Chloroacetanilide

k_α = 0.22 l mol^{-1} s^{-1}

for $[SO_2]$/M	k_{obs}	k_β
0.0038	0.563	0.81
0.0047	0.51	0.85
0.0069	0.39	0.73
0.0082	0.38	0.82

Mean k_β = 0.853 ± 0.07 l mol^{-1} s^{-1}

o-Bromoacetanilide

k_α = 0.195 l mol^{-1} s^{-1}

for $[SO_2]$/M	k_{obs}	k_β
0.01	0.288	0.581
0.012	0.283	0.66
0.0069	0.36	0.71
0.00485	0.41	0.561

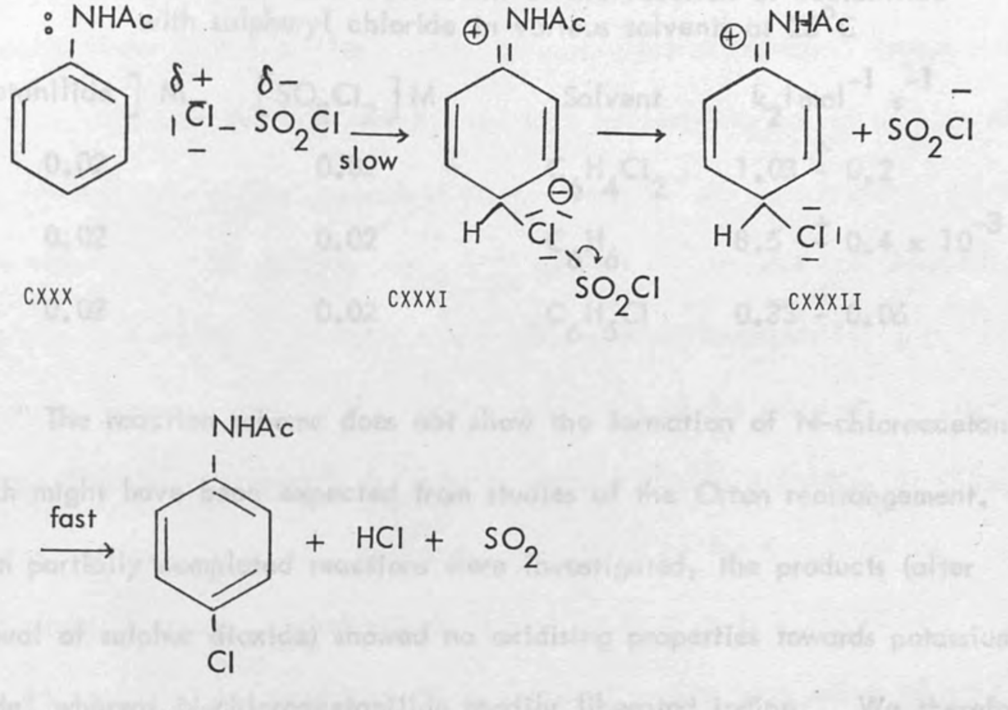
Mean k_β = 0.65 ± 0.046 l mol^{-1} s^{-1}

The high value of k_{β} shows that in the case of these compounds molecular chlorine as the effective electrophile contributes more than what was reported for the reaction of sulphuryl chloride with alkylbenzenes, and the effective electrophile is not only molecular sulphuryl chloride, but molecular chlorine as well. No influence of added sulphur dioxide was found on the rate of reaction of o-trifluoromethylacetanilide, acetanilide and p-acetotoluidide, (Table 20) although the rates of reaction of the last two compounds were too great to allow accurate determination of k_2.

Table 20

	$[SO_2]$	$[ArH]$	$[SO_2Cl_2]$	k_2 l mol^{-1} s^{-1}
o-Trifluoromethylacetanilide	7.8×10^{-3}	0.01	0.01	5.25
	4.7×10^{-3}	0.01	0.01	7.25
	7.7	0.01	0.01	5.2
	-	0.01	0.01	5.27
	-	0.01	0.01	5.12
Acetanilide	-	0.01	0.01	> 40
	0.007	0.01	0.01	> 40
p-Acetotoluidide	-	0.01	0.01	> 12
	0.007	0.01	0.01	> 12

The proposed reaction scheme for sulphuryl chloride being the effective electrophile is:



CXXX CXXXI CXXXII

CXXXIII

(68)

The rate determining step is the step in which the electrophile SO_2Cl_2 attacks the ring and the absence of isotope effect, as in the study of reactions of sulphuryl chloride with toluene and p-deuteriotoluene in nitromethane[75] it has been shown that hydrogen and deuterium were replaced at the same rates, indicating that the abstraction of hydrogen does not occur in the rate-determining step. The sensitivity of the reaction rate to changes in the solvent (Table 21), the rate being higher in more polar solvents, shows the ionic nature of the transition state and an evidence for heterolytic mechanism.

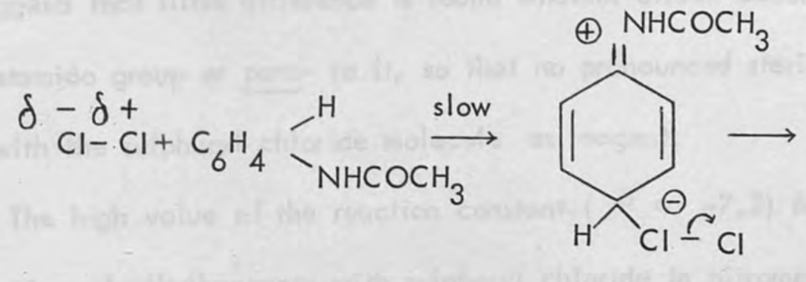
Table 21

The second order rate coefficient of the reaction of acetanilide with sulphuryl chloride in various solvents at 25°C

[Acetanilide] M	$[SO_2Cl_2]$ M	Solvent	$k_2 \, l \, mol^{-1} \, s^{-1}$
0.02	0.02	$C_6H_4Cl_2$	1.03 ± 0.2
0.02	0.02	C_6H_6	$8.5 \pm 0.4 \times 10^{-3}$
0.02	0.02	C_6H_5Cl	0.33 ± 0.06

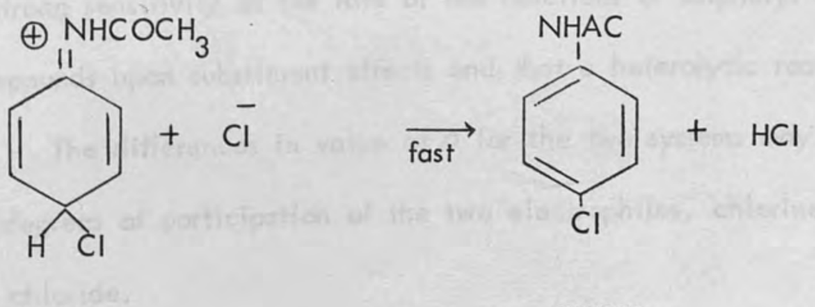
The reaction scheme does not show the formation of N-chloroacetanilide, which might have been expected from studies of the Orton rearrangement. When partially completed reactions were investigated, the products (after removal of sulphur dioxide) showed no oxidising properties towards potassium iodide, whereas N-chloroacetanilide readily liberated iodine. We therefore deduced that reaction did not proceed through the N-chloroamide.

The reaction scheme for molecular chlorine being the effective chloride is:



CXXXIV

(69)



CXXXII

CXXXIII

(70)

3.1.2 Substituent Effects

The obtained rate coefficients in the reactions of sulphuryl chloride with acetanilides in nitromethane show that the electron releasing groups such as methyl, increase the rate and the electron withdrawing groups such as nitro group, retard the reaction, which is an evidence for the electrophilic nature of the reaction. By plotting $\log_{10} k_{obs}$ against σ^+ (substituent constant) for o-bromo, o-chloro-, o-nitro- and o-trifluoromethylacetanilide, (fig. 10), considering them as meta to the position of attack of the reagent, or plotting the logarithms of k_2, against σ^+, for p-Me-, p-MeO-, p-chloro, m-chloro p-bromo, p-nitro, m-nitro*, considering the attack at the 6-position of acetanilides (* assuming total attack at position 6 in m-X C_6H_4.NHAc) (fig. 9), a reaction constant of -5 is obtained. The high value of ρ (> 1) indicates that the reaction mechanism is heterolytic, and the negative sign of ρ shows that the reaction is involving a carbocationic transition state.

The similarity in size of ρ obtained under these two steps of conditions also suggests that little difference is found whether attack occurs ortho- to the acetamido group or para- to it, so that no pronounced steric effect is found with the sulphuryl chloride molecule as reagent.

The high value of the reaction constant ($\rho = -7.2$) for the reaction of a number of alkylbenzenes with sulphuryl chloride in nitromethane[75] also shows a strong sensitivity of the rate of the reactions of sulphuryl chloride in these compounds upon substituent effects and that a heterolytic reaction is involved. The differences in value of ρ for the two systems may reflect different degrees of participation of the two electrophiles, chlorine and sulphuryl chloride.

Table 22

Substituent effects upon the attack at the 6-position of acetonitrile (SO_2Cl_2, CH_3NO_2, 25°)

Substituent	σ	σ^+	$\log_{10} k_2$
m-Me	-0.069	-0.066	ca. 1.08
m-OMe	0.115	0.047	ca. 0.8
H	-	-	ca. 0.8
p-Cl*	0.226	0.114	- 0.3
m-Cl	0.373	0.399	- 1.75
m-Br	0.393	0.405	- 1.92
m-NO_2	0.71	0.674	- 2.50
p-NO_2*	0.778	0.79	- 2.66

*Assuming total attack at position σ in m-x.C_6H_4.NH.AC

Table 23

Substituent effects upon the rate of chlorination of some anilides (SO_2Cl_2, CH_3NO_2, 25°)

Substituent*	k_{obs}	log k_{obs}	$\sigma\ m^+$
o-F	1.69	0.23	-0.35
o-Cl	1.069	0.029	0.4
m-Br	0.81	-0.092	0.41
o-CF_3	0.4	-0.398	0.52
o-NO_2	0.029	-1.54	0.67

*Assuming the total attack at m-position to substituents.

Fig. 9 Hammett L.F.E.R. for reaction of sulphuryl chloride with substituted acetanilides (MeNO$_2$, 25°)

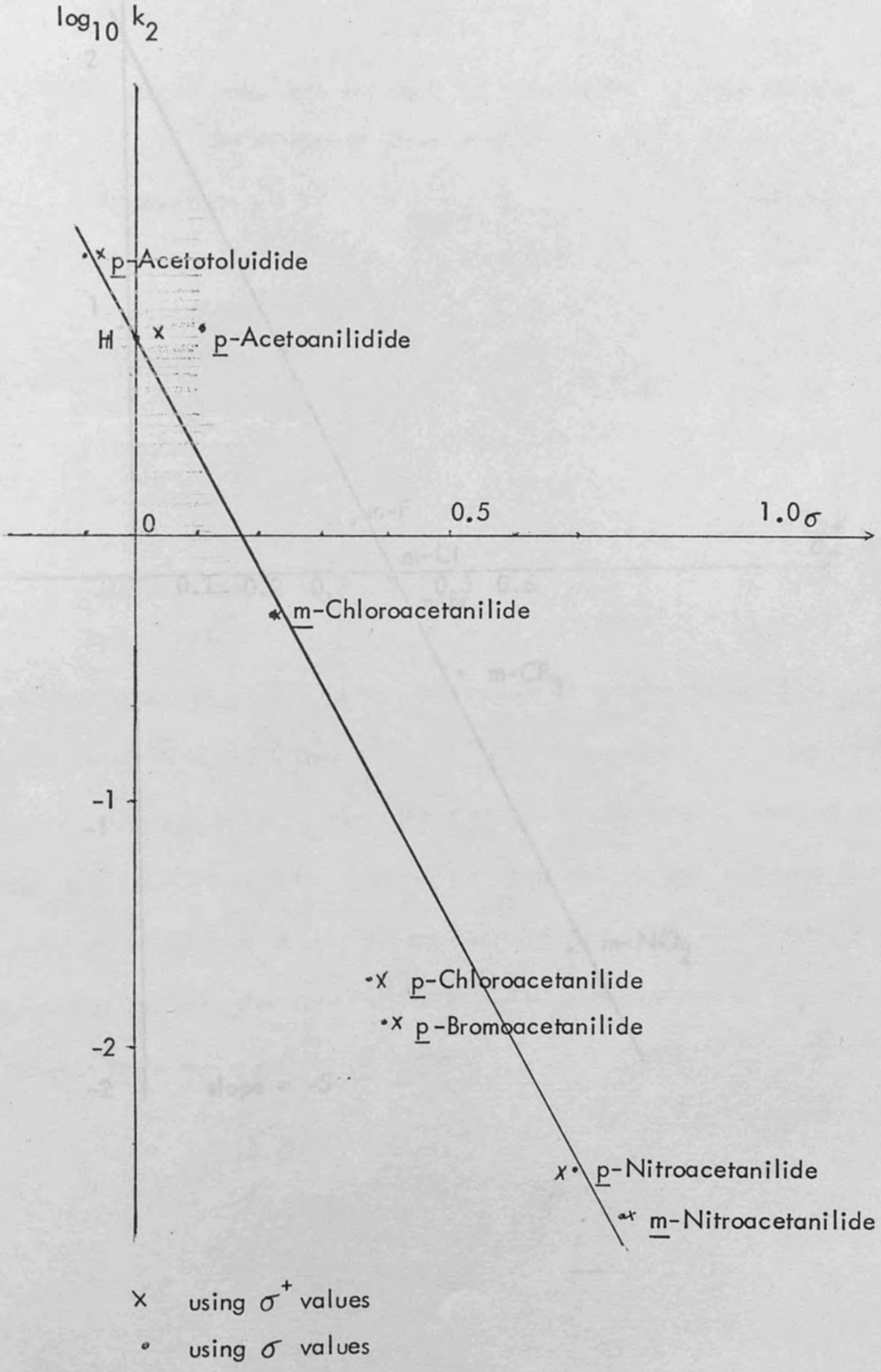
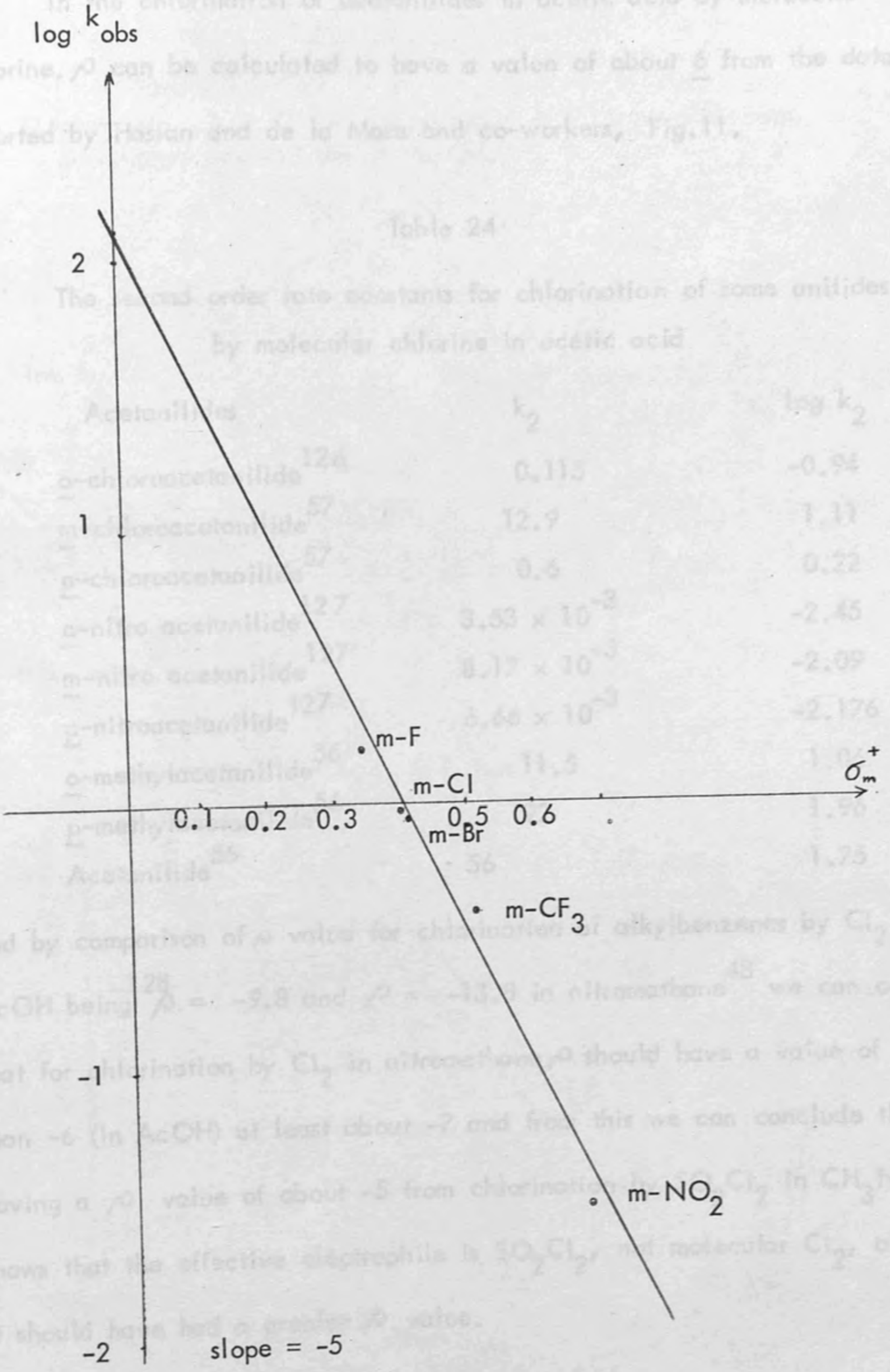


Fig.10 Hammett L.F.E.R. for reaction of sulphuryl chloride with some substituted acetanilides ($MeNO_2$, 25°)



In the chlorination of acetanilides in acetic acid by molecular chlorine, ρ can be calculated to have a value of about 6 from the data reported by Hassan and de la Mare and co-workers, Fig.11.

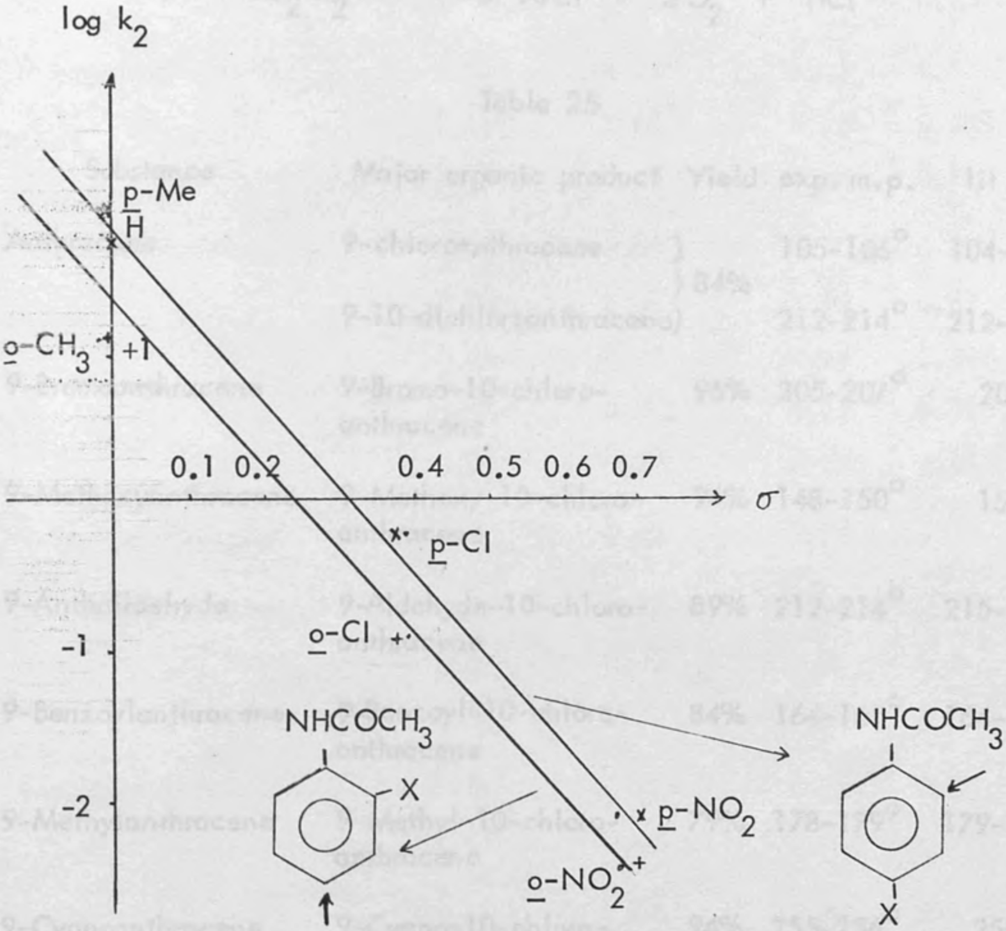
Table 24

The second order rate constants for chlorination of some anilides by molecular chlorine in acetic acid

Acetanilides	k_2	$\log k_2$
o-chloroacetanilide[126]	0.115	-0.94
m-chloroacetanilide[57]	12.9	1.11
p-chloroacetanilide[57]	0.6	0.22
o-nitro acetanilide[127]	3.53×10^{-3}	-2.45
m-nitro acetanilide[127]	8.12×10^{-3}	-2.09
p-nitroacetanilide[127]	6.66×10^{-3}	-2.176
o-methylacetanilide[56]	11.5	1.06
p-methylacetanilide[56]	92	1.96
Acetanilide[56]	56	1.75

and by comparison of ρ value for chlorination of alkylbenzenes by Cl_2 in AcOH being[128] $\rho = -9.8$ and $\rho = -13.8$ in nitromethane[48] we can conclude that for chlorination by Cl_2 in nitromethane ρ should have a value of greater than -6 (in AcOH) at least about -7 and from this we can conclude that having a ρ value of about -5 from chlorination by SO_2Cl_2 in CH_3NO_2 shows that the effective electrophile is SO_2Cl_2, not molecular Cl_2, otherwise it should have had a greater ρ value.

Fig. 11 Hammett L.F.E.R. for the reaction of chlorine with some substituted acetanilides in AcOH.



x , + Using σ values

o Using σ$^+$ values

3.2.1 Anthracene Derivatives

The obtained amount of sulphur dioxide and hydrogen chloride and the identification of the products (Table 25) show that the stoichiometry of the reaction of sulphuryl chloride with anthracenes in chlorobenzene at 25°C is:

$$ArH + SO_2Cl_2 \longrightarrow ArCl + SO_2 + HCl \qquad (65)$$

Table 25

Substance	Major organic product	Yield	exp. m.p.	lit m.p.
Anthracene	9-chloroanthracene	84%	105-106°	104-106°
	9-10-dichloroanthracene		212-214°	212-214°
9-Bromoanthracene	9-Bromo-10-chloro-anthracene	96%	205-207°	207°
9-Methoxyanthracene	9-Methoxy-10-chloro-anthracene	94%	148-150°	154°
9-Anthraldehyde	9-Aldehyde-10-chloro-anthracene	89%	212-214°	215-216°
9-Benzoylanthracene	9-Benzoyl-10-chloro-anthracene	84%	164-165°	164-165°
9-Methylanthracene	9-Methyl-10-chloro-anthracene	79%	178-179°	179-180°
9-Cyanoanthracene	9-Cyano-10-chloro-anthracene	94%	255-256°	255°
9-Nitroanthracene	9- Nitro-10-chloro-anthracene	84%	208-210°	220-221°

The second order rate constant of the reaction does not change much on changing the concentration of the reactants (Table 26).

Table 26

Rates of the reaction of sulphuryl chloride with anthracene and its derivatives in chlorobenzene at 25°C

Substance	[ArH] M	[SO_2Cl_2] M	k_2/l mol^{-1} sec^{-1}
9-Methoxyantrhacene	0.02	0.02	$9.2 \pm 0.025 \times 10^{-3}$
	0.03	0.02	$8.3 \pm 0.63 \times 10^{-3}$
	0.02	0.02	$8.36 \pm 0.63 \times 10^{-3}$
	0.03	0.02	$8.08 \pm 0.25 \times 10^{-3}$
9-Cyanoanthracene	0.025	0.025	$7.12 \pm 0.9 \times 10^{-4}$
	0.025	0.025	$6.79 \pm 0.285 \times 10^{-4}$
	0.04	0.02	$7.46 \pm 0.7 \times 10^{-4}$
9-Nitroanthracene	0.04	0.04	$4.2 \pm 0.61 \times 10^{-5}$
	0.05	0.05	$3.95 \pm 0.67 \times 10^{-5}$
	0.04	0.02	$4.24 \pm 0.086 \times 10^{-5}$
	0.022	0.022	$4.35 \pm 0.29 \times 10^{-5}$
	0.04	0.04	$4.285 \pm 0.48 \times 10^{-5}$
9-Bromoanthracene	0.02	0.02	$7.79 \pm 0.38 \times 10^{-4}$
9-Methylanthracene	0.02	0.02	$4.18 \pm 0.73 \times 10^{-3}$
	0.02	0.02	$4.3 \pm 0.6 \times 10^{-3}$
	0.02	0.01	$3.81 \pm 0.309 \times 10^{-3}$
9-Benzoylanthracene	0.02	0.02	$6.648 \pm 0.37 \times 10^{-4}$
	0.03	0.02	$5.606 \pm 0.175 \times 10^{-4}$
9-Anthraldehyde	0.02	0.02	$2.45 \pm 0.195 \times 10^{-4}$
	0.02	0.02	$2.64 \pm 0.56 \times 10^{-4}$
	0.04	0.02	$2.28 \pm 0.25 \times 10^{-4}$
2-Chloro-anthracene	0.02	0.02	$4.8 \pm 0.67 \times 10^{-4}$
	0.03	0.02	$5.4 \pm 0.49 \times 10^{-4}$
	0.02	0.02	$4.87 \pm 0.51 \times 10^{-4}$

Table 26 (continued)

Substance	$[ArH]$ M	$[SO_2Cl_2]$ M	k_2/l mol^{-1} sec^{-1}
2-Methylanthracene	0.0216	0.0216	$1.4 \pm 0.084 \times 10^{-3}$
	0.0216	0.0216	$1.33 \pm 0.17 \times 10^{-3}$
	0.03	0.0216	$1.356 \pm 0.136 \times 10^{-3}$
	0.03	0.0216	$1.350 \pm 0.212 \times 10^{-3}$
			$1.338 \pm 0.19 \times 10^{-3}$
Anthracene	0.04	0.0224	$2.22 \pm 0.23 \times 10^{-3}$
	0.0224	0.0224	$2.465 \pm 0.19 \times 10^{-3}$
9-Anthraldehyde*	0.03	0.02	$3.05 \pm 0.9 \times 10^{-2}$
	0.03	0.02	$2.3 \pm 0.33 \times 10^{-2}$
	0.02	0.02	$3.05 \pm 0.10 \times 10^{-2}$
Anthracene*	0.01	0.01	$2.30 \pm 0.23 \times 10^{-2}$
	0.01	0.01	$2.12 \pm 0.071 \times 10^{-2}$
	0.01	0.016	$2.13 \pm 0.18 \times 10^{-2}$
	0.01	0.0185	$2.48 \pm 0.16 \times 10^{-2}$
	0.01	0.0086	$2.36 \pm 0.23 \times 10^{-2}$

*containing radical initiators

This indicates that the reaction is a second order process involving one molecule of each reagent and a bimolecular mechanism.

$$\text{Rate} = k_2 \, [ArH][SO_2Cl_2]$$

Four possible electrophiles can be suggested:

Molecular chlorine - the absence of the effect of initially added sulphur dioxide or the formed sulphur dioxide during the reaction (Table 27) shows that molecular chlorine formed by the dissociation of sulphuryl chloride is not the true electrophile and is not a process which determines the chlorination.

$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2 \qquad (56)$$

Table 27

Substance	[ArH] M	$[SO_2Cl_2]$ M	$[SO_2]$ M	k_2 l mol^{-1} s^{-1}
Anthracene	0.02	0.02	0.0052	$2.41 \pm 0.18 \times 10^{-3}$
	0.03	0.02	0.0080	$2.33 \pm 0.21 \times 10^{-3}$
	0.02	0.02	0.000	$2.46 \pm 0.14 \times 10^{-3}$

Chlorinium ion (Cl^+) and chlorosulphonium ion ($ClSO_2^+$) - neither of these ions can be the true electrophile since according to the equilibria:

$$SO_2Cl_2 \rightleftharpoons Cl^+ + SO_2Cl^- \qquad (57)$$

$$SO_2Cl_2 \rightleftharpoons ClSO_2^+ + Cl^- \qquad (58)$$

the formed chloride ion (Cl^-) would directly repress the second equilibrium and with Cl^+ from the first equilibrium would set up a new equilibrium:

$$Cl^+ + Cl^- \rightleftharpoons Cl_2 \qquad (35)$$

and a regular decrease in the rate of the reaction should be observed as the reaction proceeds. This was not observed in the reaction of sulphuryl chloride with anthracenes. Molecular sulphuryl chloride was the only possible effective electrophile as it was reported before for the reactions of sulphuryl chloride with alkylbenzenes in nitromethane[75] and a number of aromatic ethers[73] in chlorobenzene.

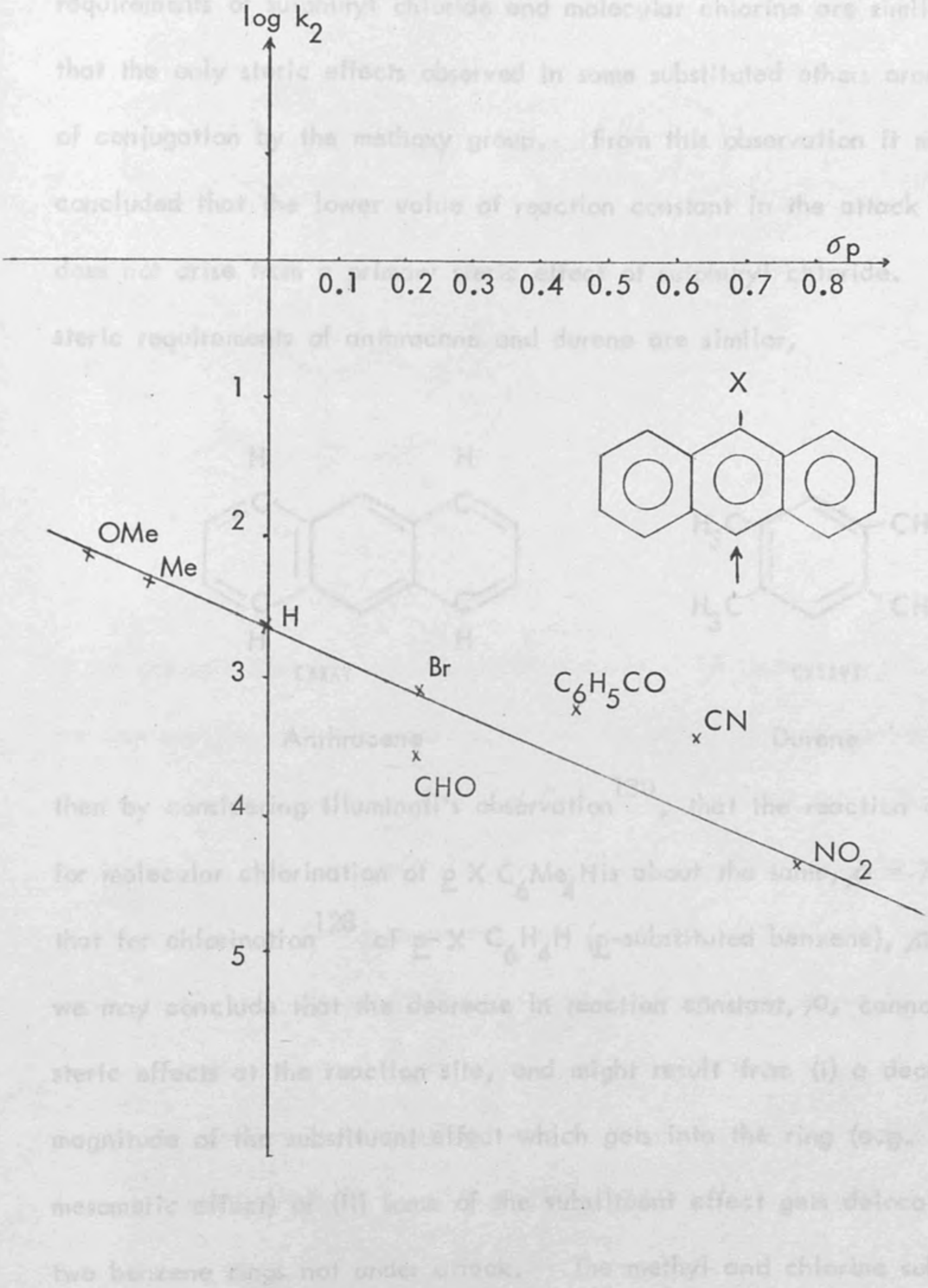
3.2.2 Effects of substituents upon the rate of reaction

By assuming total attack para to the substituent, the substituent effect has been studied. The correlation between the substituent constant, σ, and the second order rate coefficient is shown in Table 26. The results show a slope, ρ, of -1.7 ± 0.3, which is lower than the value of the reaction constant, ρ is -4 ± 0.2, for the reaction of sulphuryl chloride with some substituted m-dimethoxybenzenes[73] in chlorobenzene.

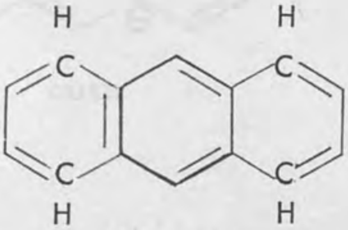
Table 28

Substance	k_2 ($l\ mol^{-1} s^{-1}$)	log k_2	σ_p^{18}	$\sigma_p^{+\ 18}$
Anthracene	2.3×10^{-3}	-2.64	-	-
9-Nitroanthracene	4.24×10^{-5}	-4.37	+0.778	+0.79
9-Methoxyanthracene	8.3×10^{-3}	-2.08	-0.268	-0.778
9-Cyanoanthracene	4.5×10^{-4}	-3.35	+0.66	+0.659
9-Methylanthracene	4.1×10^{-3}	-2.39	-0.17	-0.311
9-Benzoylanthracene	5.6×10^{-4}	-3.25	+0.459	-0.459
9-Bromoanthracene	7.79×10^{-4}	-3.1	+0.232	+0.15
9-Aldehyde anthracene	2.69×10^{-4}	-3.578	+0.22	+0.22

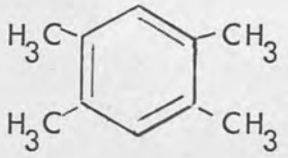
Fig.12 Hammett L.F.E.R. for the reaction of sulphuryl chloride with some anthracenes (C_6H_5Cl, 25°)



This shows that in comparison, the effect of substituents on the rate of substitution of anthracene is not great. Bolton, in the study of steric hindrance to activation by the methoxy group, showed[129] that the steric requirements of sulphuryl chloride and molecular chlorine are similar and that the only steric effects observed in some substituted ethers arose from loss of conjugation by the methoxy group. From this observation it may be concluded that the lower value of reaction constant in the attack of anthracene does not arise from a primary steric effect of sulphuryl chloride. If the steric requirements of anthracene and durene are similar,


CXXXV

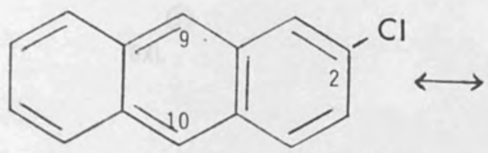
Anthracene


CXXXVI

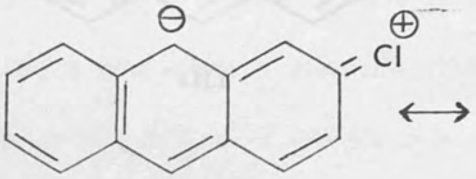
Durene

then by considering Illuminati's observation[130], that the reaction constant for molecular chlorination of $\underline{p}$ X C_6Me_4H is about the same, $\rho = -7.68$, as that for chlorination[128] of $\underline{p}$- X C_6H_4H ($\underline{p}$-substituted benzene), $\rho = -9.8$, we may conclude that the decrease in reaction constant, ρ, cannot come from steric effects at the reaction site, and might result from (i) a decrease in the magnitude of the substituent effect which gets into the ring (e.g. loss of mesomeric effect) or (ii) some of the substituent effect gets delocalised in the two benzene rings not under attack. The methyl and chlorine substituents at C-2 of anthracene show rates of reaction consistent with $\rho = -1.9$, (using σ_p values), similar in magnitude to the figure found for attack on the 9-substituted anthracenes, although there is no steric congestion at C-2 of the anthracene system.

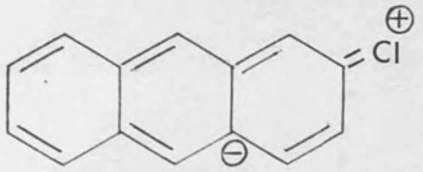
For 2-substituted anthracenes we can write the structures:



CXXXVII

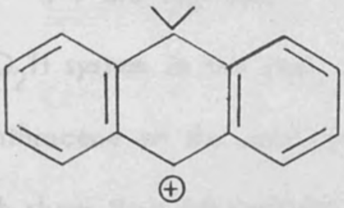


CXXXVIII

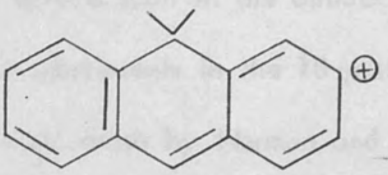


CXXXIX

If we presume that the chlorination occurs at C-10 through structure CXXXIX then we can say that the electronic effect of the substituents is weaker because direct conjugation between C-2 and C-10 is impossible CXXXIX. But because structure CXXXVIII is less quinonoid than CXXXIX it is more stable and the possibility of chlorination at C-9 is more than that at C-10. The lower reactivity of these substituted compounds (2-CH_3- and 2-chloro-), as shown by rate constants smaller than those of anthracene, can be understood since substituents in the 10- position react directly with positive charge CXL from the attack at C-9, but substituents in the 1-8 positions react only indirectly as in CXLI

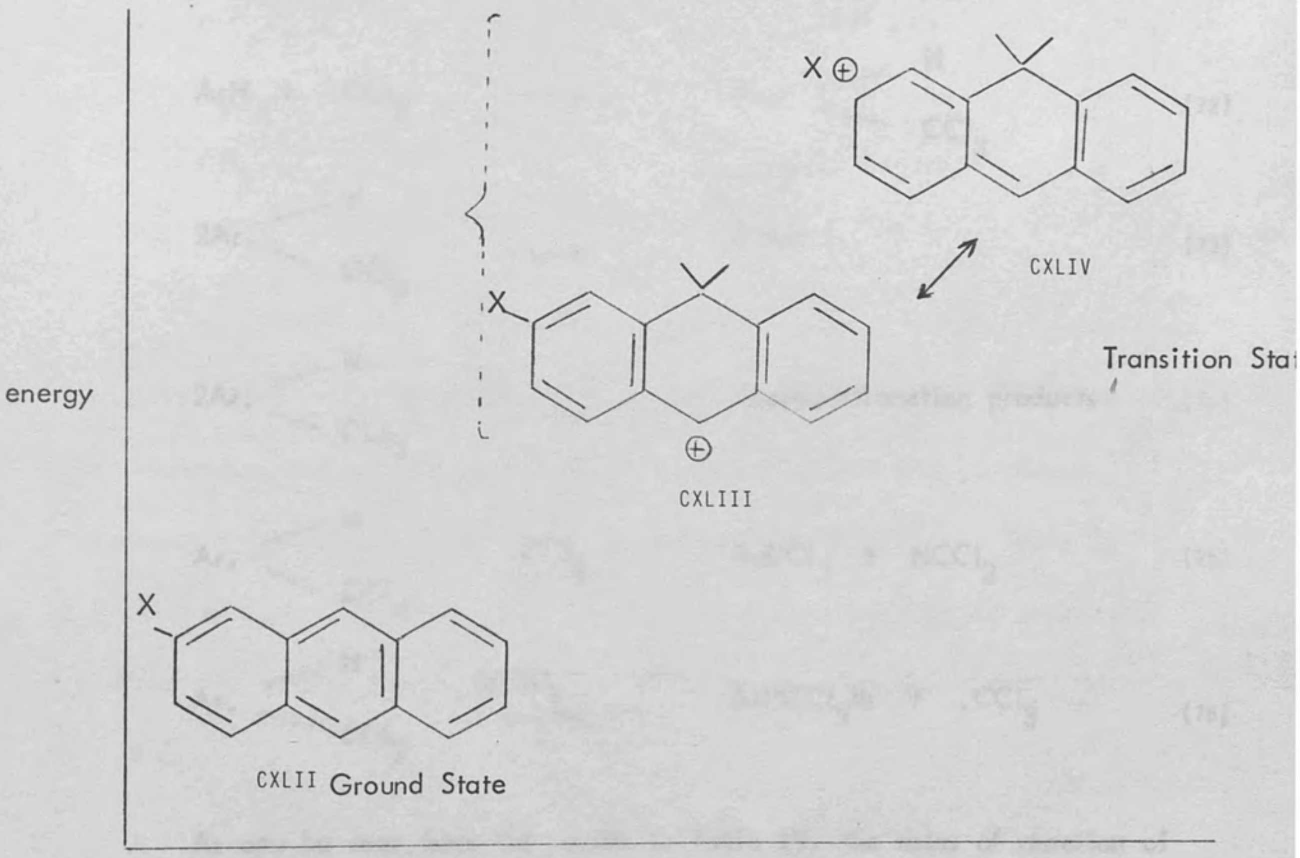


CXL

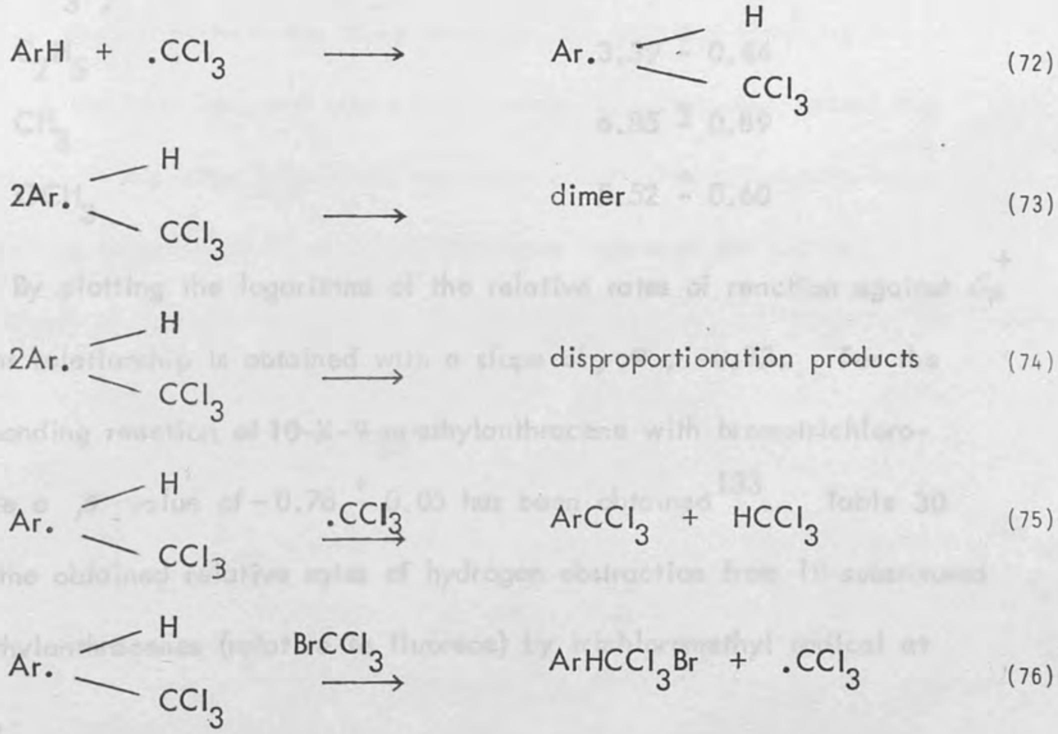


CXLI

which, because a second benzene ring is made quinonoid, has a greater energy requirement and so is destabilised:



Therefore we have kinetic evidence that the electronic effects of groups at C-9 are impeded. It looks like the effects seen in the anthracene-9-CO_2H system in the study of the effects of substituents in the 10-position of anthracene on the acid strengths of 9-anthroic acids by Norman and Ralph[131] which show that the carbonyl group in the acids and esters is precluded from interaction with the aromatic ring. The rates of addition of the trichloromethyl radical to a series of 9-substituted anthracenes, relative to that of trans stilbene, have been determined at 70° in a benzene-bromotrichloromethane mixture[132].



$$\mathrm{ArH} + .\mathrm{CCl_3} \longrightarrow \mathrm{Ar.}\!\begin{array}{l}\mathrm{H}\\ \mathrm{CCl_3}\end{array} \qquad (72)$$

$$2\mathrm{Ar.}\!\begin{array}{l}\mathrm{H}\\ \mathrm{CCl_3}\end{array} \longrightarrow \text{dimer} \qquad (73)$$

$$2\mathrm{Ar.}\!\begin{array}{l}\mathrm{H}\\ \mathrm{CCl_3}\end{array} \longrightarrow \text{disproportionation products} \qquad (74)$$

$$\mathrm{Ar.}\!\begin{array}{l}\mathrm{H}\\ \mathrm{CCl_3}\end{array} \xrightarrow{.\mathrm{CCl_3}} \mathrm{ArCCl_3} + \mathrm{HCCl_3} \qquad (75)$$

$$\mathrm{Ar.}\!\begin{array}{l}\mathrm{H}\\ \mathrm{CCl_3}\end{array} \xrightarrow{\mathrm{BrCCl_3}} \mathrm{ArHCCl_3Br} + .\mathrm{CCl_3} \qquad (76)$$

As can be seen from the results in Table 29, the rates of reaction of anthracene toward trichloromethyl radical are affected by the nature of the substituent. Anthracenes with electron-donating substituents show higher rates than those with electron-withdrawing substituents.

Table 29

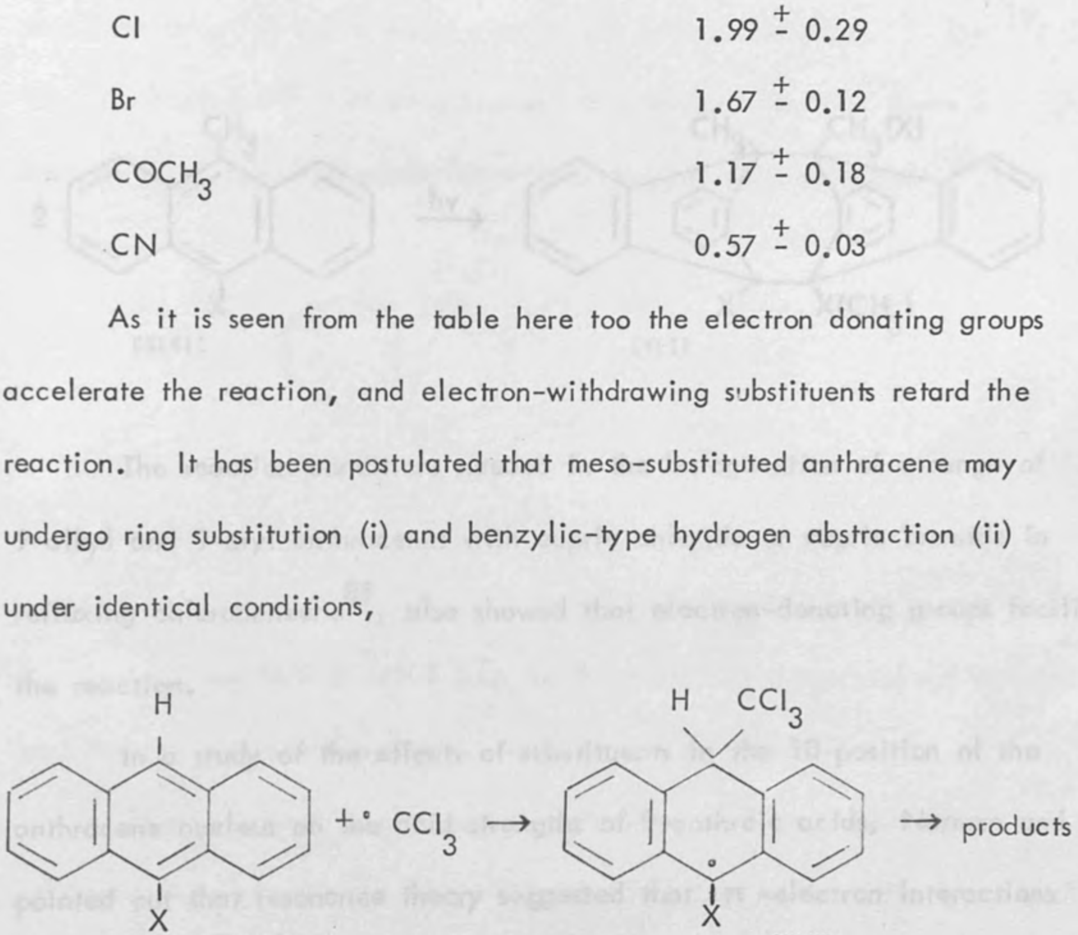
Substituent	k_2 / k_H (relative to stilbene)
NO_2	0.71 ± 0.1
CN	0.34 ± 0.04
CO_2CH_3	0.74 ± 0.07
Br	1.00 ± 0.04
Cl	1.02 ± 0.04
H	1.00
C_6H_5	2.28 ± 0.43
i-C_3H_7	2.38 ± 0.3
C_2H_5	3.39 ± 0.44
CH_3	6.85 ± 0.89
OCH_3	5.52 ± 0.60

By plotting the logarithms of the relative rates of reaction against σ_p^+ a linear relationship is obtained with a slope of, ρ, -0.83. For the corresponding reaction of 10-X-9-methylanthracene with bromotrichloromethane a ρ value of -0.78 ± 0.05 has been obtained[133]. Table 30 shows the obtained relative rates of hydrogen abstraction from 10-substituted -9-methylanthracenes (relative to fluorene) by trichloromethyl radical at 70°C.

Table 30

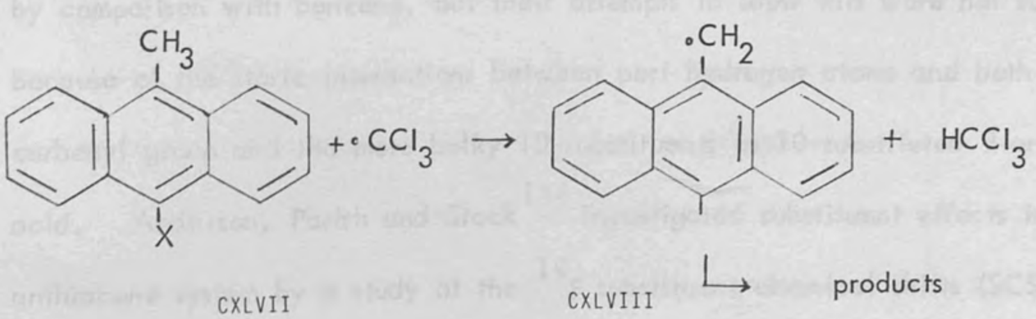
Substituent	k (relative to fluorene)
OCH_3	9.00 ± 0.52
CH_3	4.03 ± 0.55
C_6H_5	1.92 ± 0.11
H	2.75 ± 0.32
Cl	1.99 ± 0.29
Br	1.67 ± 0.12
$COCH_3$	1.17 ± 0.18
CN	0.57 ± 0.03

As it is seen from the table here too the electron donating groups accelerate the reaction, and electron-withdrawing substituents retard the reaction. It has been postulated that meso-substituted anthracene may undergo ring substitution (i) and benzylic-type hydrogen abstraction (ii) under identical conditions,



CXLV CXLVI (77)

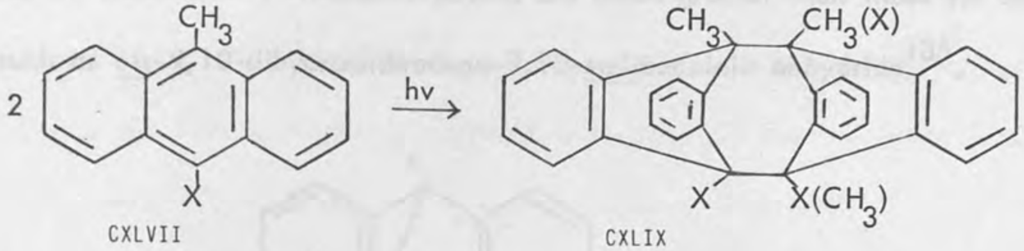
(i)



CXLVII CXLVIII (78)

(ii)

ring substitution at α or β positions of 10-substituted-9-methylanthracenes as a side reaction is low, only in the case of parent-9-methylanthracene ring substitution might be competitive with benzylic hydrogen abstraction although still the latter is favoured process. Dimerisation reaction although rapid for anthracene, is greatly diminished for meso-substituted anthracenes and by using bromobenzene as a co-solvent no dimer could be detected.



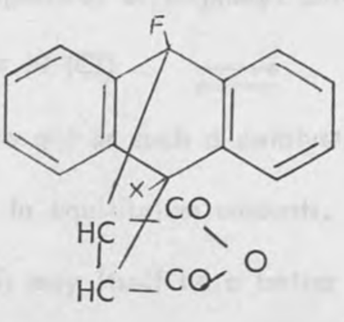
CXLVII CXLIX

(79)

The reaction conditions needed in the halogenation of a range of 9-alkyl and 9-aryl anthracenes with cupric chloride or cupric bromide in refluxing chlorobenzene[88], also showed that electron-donating groups facilitate the reaction.

In a study of the effects of substituents in the 10-position of the anthracene nucleus on the acid strengths of 9-anthroic acids, Norman and Ralph[131] pointed out that resonance theory suggested that π-electron interactions between substituents in the two meso positions of anthracene should be large by comparison with benzene, but their attempts to show this were not successful because of the steric interactions between peri hydrogen atoms and both the carbonyl group and the more bulky 10-substituents in 10-substituted 9-anthroic acid. Anderson, Parish and Stock[134] investigated substituent effects in the anthracene system by a study of the ^{19}F substituent chemical shifts (SCS) in the

10-substituted-9-fluoroanthracenes, and showed that π-electron interactions are enhanced for the *meso*-substituted anthracenes. In this study the steric influences of the *peri* hydrogen atoms were identified for ten substituents with spherical or cylindrical symmetry in the ^{19}F-NMR spectrum of 9-fluoroanthracene. From this study they concluded that substituent effects propagated by π-electron interactions are the cause of the SCS seen in these compounds and that π-induction has a major role in the anthracene series. The ^{19}F SCS for 10-substituted-9-fluoroanthracenes are much greater than those for adducts such as *cis*-9,10-dihydroanthracene-9,10-*endo*succinic anhydride[135].



XCVIII

Thus the SCS is -13.5 ppm for 9-cyano-9-fluoroanthracene and -0.4 ppm for the corresponding adduct with maleic anhydride.

This behaviour is also seen in the cases of 4-cyanofluorobenzene and of 4-cyano-1-fluoronaphthalene where the SCS for the aromatic compounds are greater than the SCS for adducts.

The results for these compounds are in accord with the view that substituent effects propagated by π-electron interactions determine the SCS for conjugated substituents as was postulated by Anderson and Stock[135].

If the logarithms of the rate constants of the reaction of sulphuryl chloride with the substituted anthracenes in chlorobenzene at 25°C is plotted against the available ^{19}F SCS data for the corresponding 10-X-9-fluoro anthracenes in 1,4-dioxane, as the solvent, a good straight line is obtained with only the CN- group not on the line, Fig. 13. This correlations suggests that the substituent effects on the reaction of sulphuryl chloride with 9-substituted anthracenes are propagated by π-induction.

The deviation of 9-cyano-anthracene from the line may be because of the presence of a reversible reaction $Ar{-}C{\equiv}N + SO_2Cl_2 \rightleftarrows Ar{-}CCl = NCl + SO_2$ (79) which may accelerate the rate of formation of the ultimate product in either of two ways. Many organic materials may catalyse the decomposition of sulphuryl chloride, and the reversible process

$$Ar.C\ (Cl) = N\ (Cl) \rightleftarrows Ar.C \equiv N + Cl_2 \qquad (80)$$

allows the nitrile to act as such a catalyst, producing the more reactive electrophile, Cl_2, in equilibrium amounts. Alternative, the N-chloroimine Ar.C (Cl) = N (Cl) may itself be a better electrophile than is sulphuryl chloride and may offer a faster route to substitution by the sequence

$$Ar.C\ (Cl) = N\ (Cl) + Ar'H \longrightarrow Ar.C\ (Cl) = N\ (H) + Ar'Cl \qquad (81)$$

$$Ar.C\ (Cl) = N\ (H) \rightleftarrows Ar.C \equiv N + HCl \qquad (82)$$

followed by regeneration of the reagent through equation (79).

The kinetic complexity of such a scheme could not be immediately predicted, since little is known of the relative rates and equilibrium positions of the various postulated steps. However, such anomalous rates of reaction were not found in the corresponding chlorination of 2,4-dimethoxybenzonitrile or of the 3,5-isomer[73] suggesting quite subtle factors to be involved in the anthracene system.

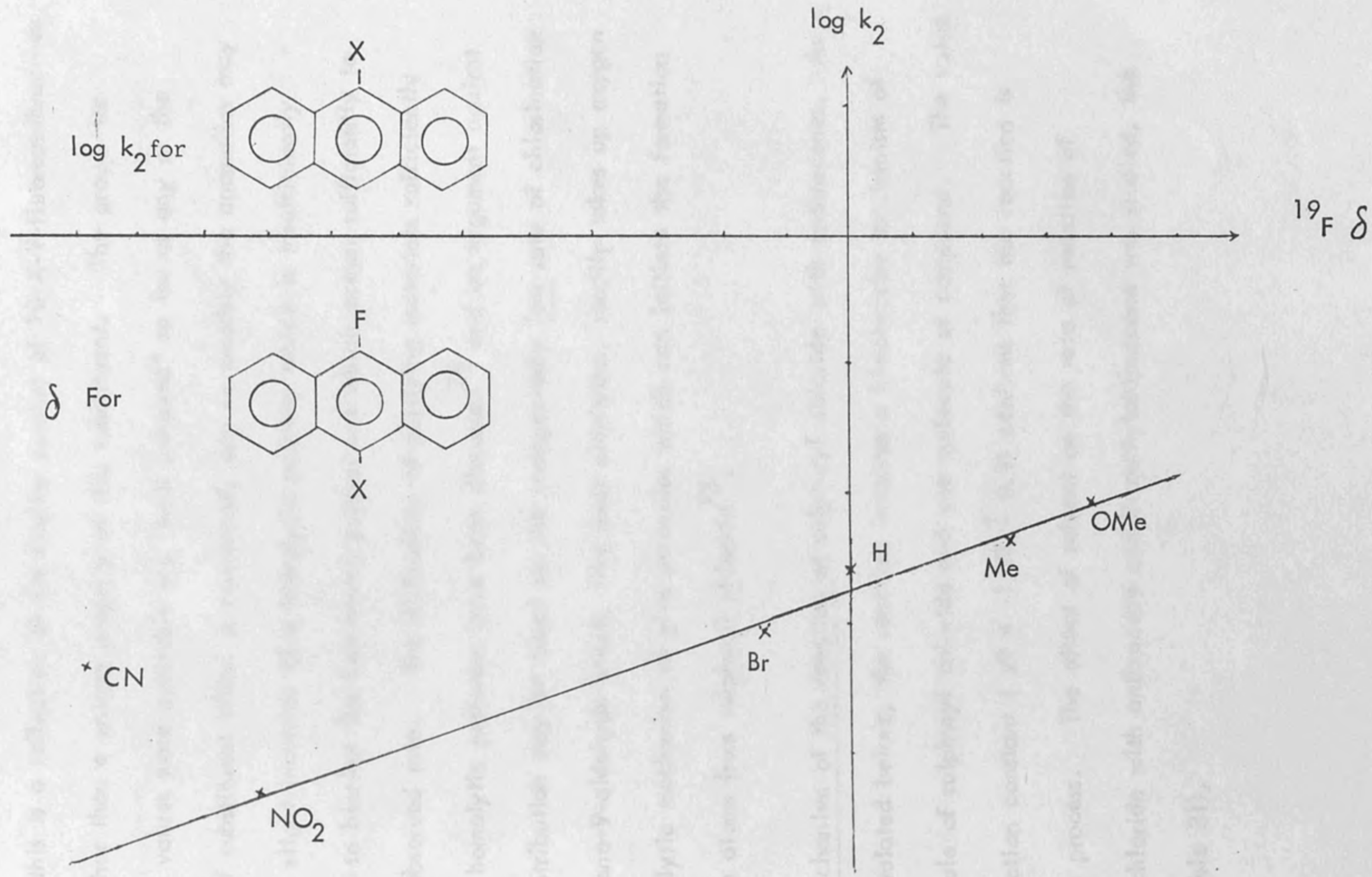


Fig.13 The plot of log k_2 for the reaction of sulphuryl chloride with some anthracenes (C_6H_5Cl, 25°) against ^{19}F SCS from the corresponding 10-X-9-fluoroanthracenes in 1,4-dioxane.

However, the cyano and benzoyl substituents are generally more effective than most measures of the electronic effect (σ , σ^{+} ^{19}F-NMR SCS) would suggest - although the cyano group alone is unusual when SCS values are used, this is a reflection of the smaller number of 10-X-9-fluoroanthracenes studied rather than a unique property of this substituent. The groups for which SCS values were available are "well behaved" so far as any of the measures of substituent effect is concerned, and so possibly the anomalies may reflect the slight incursion of a homolytic pathway which is insufficiently established to blanket the heterolytic process but which occurs sufficiently to raise the observed rate. The difficulties of purifying materials sufficiently to remove homolytic pathways have been discussed[73] and an argument against such a contribution may be based on the unexpectedly low rate of chlorination of anthracene-9-aldehyde which, like most aldehydes, readily takes up oxygen by a homolytic mechanism to give peroxides which can initiate the formation of chlorine atoms from sulphuryl chloride[73].

3.2.3 Mechanism of the reaction of sulphuryl chloride with anthracenes. As it was postulated before, the reaction involves a bimolecular mechanism of one molecule of sulphuryl chloride and one molecule of compound. The value of the reaction constant ($\rho = -1.73 \pm 0.3$) confirms that the reaction is heterolytic process. The effect of solvent on the rate of reaction of sulphuryl chloride with anthracene and 2-methylanthracene was studied, the results (Table 31),

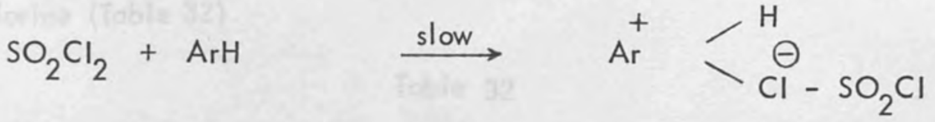
Table 31

The second order rate constants (k_2 l mol^{-1} s^{-1}) of the reaction of anthracene and 2-methylanthracene with sulphuryl chloride in various solvents (at 25°C)

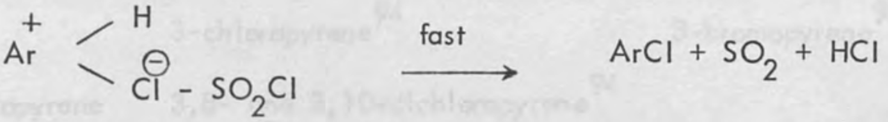
	Solvents		
Substance	chlorobenzene	benzene	o-dichlorobenzene
Anthracene	2.46×10^{-3}	6.7×10^{-4}	2.42×10^{-2}
2-Methyl anthracene	1.35×10^{-3}	3.81×10^{-4}	1.35×10^{-2}

show that the rate of the reaction increases with increasing the polarity of the solvent which is an evidence for a heterolytic mechanism.

The mechanism could be formulated as follows:



(83)



(84)

The evidence for the first step to be slow and rate determining is the absence of isotope effect as the replacement of hydrogen and deuterium by chlorine in the reaction of sulphuryl chloride with some alkylbenzenes in chlorobenzenes by Bolton, both occur at the same rate[136].

3.3.1 Pyrenes

The stoichiometry of the reaction of sulphuryl chloride with pyrenes in chlorobenzene at 25°C is expected to be the same as that for the reaction with anthracenes.

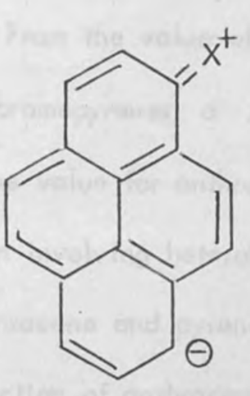
$$ArH + SO_2Cl_2 \longrightarrow ArCl + SO_2 + HCl \qquad (65)$$

The study of the products by t.l.c. and mass spectroscopy shows that only monochloroaromatic compounds are produced. The t.l.c. shows apparently the presence of two different chlorocompounds as well as the starting materials. By considering the products of the reaction of bromination and chlorination of pyrene and 3-substituted pyrenes by bromine and chlorine (Table 32)

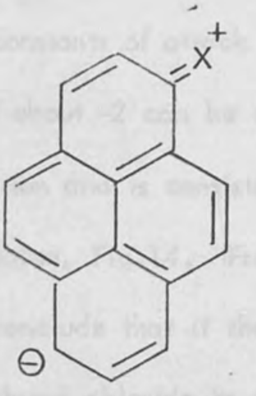
Table 32

Substance	Products of chlorination	Products of bromination
Pyrene	3-chloropyrene[94]	3-bromopyrene[94]
3-chloropyrene	3,8- and 3,10-dichloropyrene[94]	
3-Bromopyrene		3,8- and 3-10-dibromopyrene[94]
3-nitropyrene		3,nitro,8-bromo- and 3-nitro, 10-bromopyrene[137] (ratio 1:4)

it can be concluded that the products of chlorination of 3-substituted pyrenes with sulphuryl chloride are 3-substituted, 8-chloro and 3-substituted, 10-chloropyrene, through the structures such as



CL



CLI

The rate constant of the reaction of sulphurylchloride with pyrene and 3-substituted pyrenes in chlorobenzene at 25°C does not change significantly by changing the concentration of reactants (Table 33). This shows that the reaction is second order, first order with respect to each reactant and that it is a bimolecular process.

Table 33

Second order rate coefficients of reaction of sulphuryl chloride with pyrenes in chlorobenzene at 25° C.

Substance	$[SO_2Cl_2]$M	$[ArH]$M	$k_2 \times 10^{-4}$ l $mol^{-1} s^{-1}$
Pyrene	0.02	0.02	7.35 ± 0.52
	0.04	0.02	7.54 ± 0.50
	0.04	0.02	7.61 ± 0.34
Pyrene-3-aldehyde	0.02	0.02	42.6 ± 0.39
	0.02	0.02	44.4 ± 0.37
	0.02	0.02	41.0 ± 0.45
	0.02	0.04	44.3 ± 0.176
	0.02	0.04	42.4 ± 0.21
3-Chloropyrene	0.02	0.02	1.099 ± 0.32
	0.02	0.02	1.1 ± 0.20
	0.02	0.02	1.0 ± 0.068
3-Bromopyrene	0.02	0.02	1.32 ± 0.123
3-Benzoylpyrene	0.02	0.02	36.45 ± 0.277
	0.02	0.02	38.9 ± 0.29

From the value of the rate constants of attack of pyrene, 3-chloro, and 3-bromopyrenes, a ρ value of about -2 can be obtained which is about the same value for anthracenes reaction and is consistent with electrophilic reaction involving heterolytic mechanism, Fig.14. From the similarity of ρ value for anthracene and pyrene we can conclude that if the substituent effects in the reaction of anthracene with sulphuryl chloride in chlorobenzene is propagated by π-induction, it could be also the case for the reaction of sulphuryl chloride with pyrenes. The rate constant values for the reaction of 3-aldehyde and 3-benzoylpyrene are rather too small to be considered as evidence of homolytic processes, and too high for heterolytic reaction having the same mechanism as pyrene and 3-halopyrenes, for such substituents should deactivate. High rate constant values were also observed for 9-formylanthracene (ca. 2 x 10^{-2}) but these dropped after purifying the aldehyde, free from radical initiators. In the case of pyrene-3-aldehyde which rate is lower than that of anthracene-9-aldehyde, and the possibility of free radical mechanism being involved is not great [illegible] the observation of such high values of the rate constant for attack of both 3-aldehyde and 3-benzoyl pyrene, it might have associated with the carbonyl (C=O) group which is present in both of these compounds. The reaction mechanism might be different from the mechanism of pyrene and 3-halopyrenes with sulphuryl chloride.

$$\mathrm{ArCOX} + \mathrm{SO_2Cl_2} \xrightarrow{\text{slow}} \mathrm{Cl_2} + \mathrm{SO_2} + \mathrm{ArCOX}$$

$$\mathrm{ArCOX} + \mathrm{Cl_2} \xrightarrow{\text{fast}} \text{Products}$$

$(X = H \text{ or } C_6H_5)$

In the case of pyrene and 3-halopyrenes the reaction equation is the same as anthracene.

Table 34

$[\text{Pyrene}] = [SO_2Cl_2] = 0.02M$

Substituent	k_2/l mol^{-1} s^{-1}	log k_2	σ_p
H	7.2×10^{-4}	-3.12	–
Cl	1.0×10^{-4}	-3.96	0.227
Br	1.3×10^{-4}	-3.88	0.232

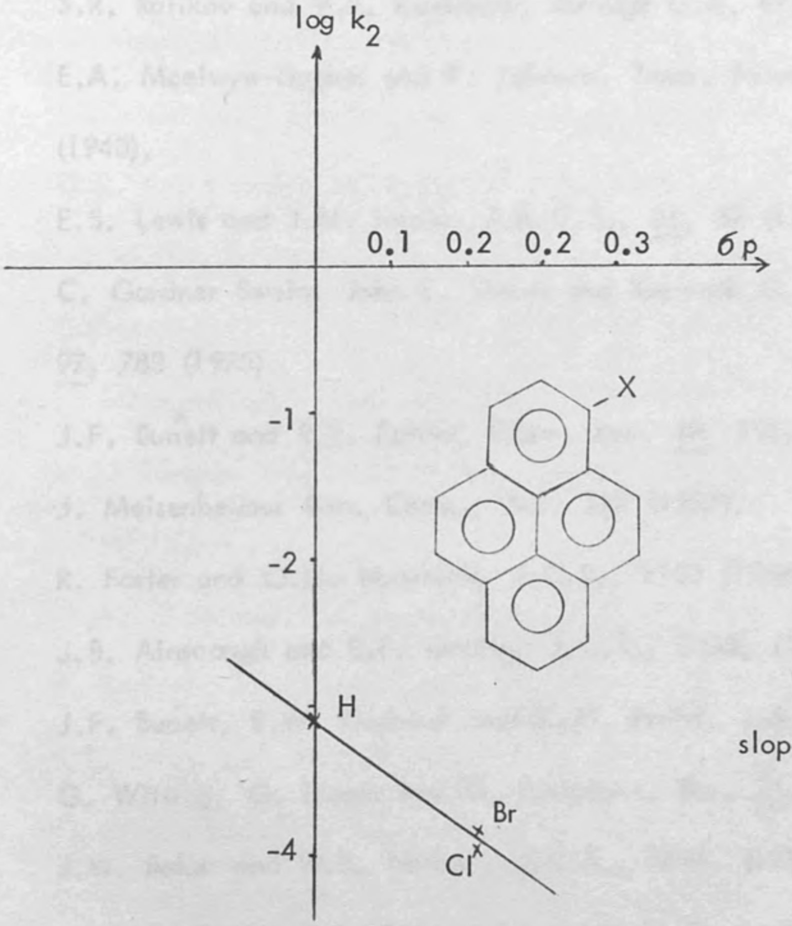


Fig. 14 Hammett L.F.E.R. for the reaction of sulphuryl chloride with pyrenes (C_6H_5Cl, 25°)

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