# A THESIS ENTITLED

# RATE OF REACTIONS OF SOME AROMATIC AMINES WITH p-CHLORANIL & p-BROMANIL

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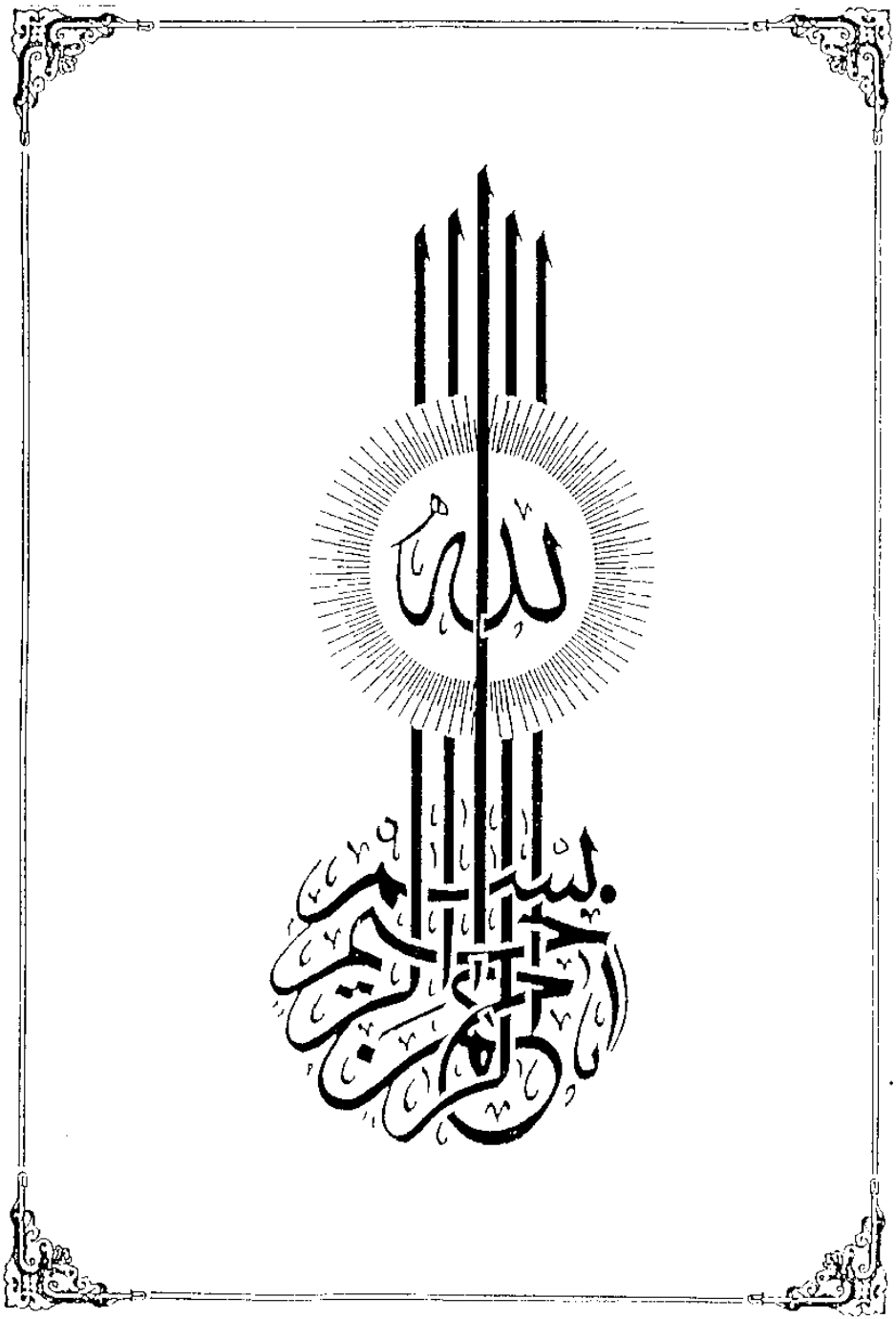

# SUMMARY


a) Reaction Between Isoquinoline or Pyridine with p-Chloranil or p-Bromanil:

The experimental results obtained for the interaction between p-chloranil or p-bromanil and isoquinoline or pyridine in aqueons dioxane show that the reaction takes place in two successive stages, The kinetics of the overall rate is third order, first order with respect to p-chloranil or p-bromanil and second order with repect to isoquinoline or pyridine and the rate is found to be proportional to $C^2_{H_2O}$ .

The dependancy of the reaction rate on water concentration is represented by plots of $k_{obs.}/[D]^2$ against several powers of $[H_2O]$ where the best linear plots with definit intercepts are obtained with $[H_2O]^2$ .

Moreover plots of log $k_{obs.}/[D]^2$ against log $[H_2O]$ give linear plots with slopes equal 2.

The potentiometric kinetic studies which show the liberation of the four halide ions, the elemental analysis, infrared and mass spectra indicate that two halgen atoms are substituted by two amine molecules and the final

product formed has no halogen atoms, this lead us to postulate a mechanism consists of two successive stages. In each one, a termolecular reaction takes place in which one molecule of p-chloranil reacts with two molecules of the electron donor which is isoquinoline (or pyridine) or water.

In the first stage an intermediate specimen S is formed with the liberation of two chloride ions which in turn undergoes further substitution with the liberation of the other two halide ions to form the product P.

However, the problem of such a reaction is substantially resolved by postulating a mechanism of two consecutive bimolecular steps for these two-stages termolecular processes.

In first stage, in the first step, which is fast and reversible, the heterocyclic molecule with its n- and $\pi$- electorons acts as a donor and forms a 1:1 species through the inner ( $\sigma$ ) and outer ($\pi$) complex as an intermediate I of heterocycle-p-chloranil or p-bromanil system.[123-125].

In the second step further nucleophilic substitution of the intermediate takes place by a water molecule to give an intermediate specimen $S_{II}$ which in turn is attacked either by an isoquinoline molecule followed by a water molecule or vice versa to give product $P_{II}$.

Structural Effect:

The higher reactivity of isoquinoline ($K_b$ $1.1 \times 10^{-9}$) than pyridine ( $K_b$ $1.7 \times 10^{-4}$) towards nucleophilic substitution reaction may be due to the difference in their structures where isoquinoline is considered to have both the properties of pyridine and naphthalene and hence its resonance energy is lesser than twice that of pyridine, i.e., it has less aromatic character than for pyridine and thus its $\pi$-electons are much more loosely held than that in pyridine so that it becomes more susceptible towards charge transfer interaction.

The unreactivity of quinoline ( $K_b$ $3 \times 10^{-10}$) towards nucleophilic substitution although its basicity does not greatly differ than that of isoquinoline is explained on the basis of their structure where in isoquinoline the nitrogen

atom which is one atom removed from the benzene ring exhibits aliphatic reactivity. Moreover, in isoquinoline the fusion of the benzene ring at 3,4-positions with pyridine destabilises the pyridine ring so that its resonance energy becomes much less than that in quinoline and thus is much more reactive towards charge transfer interaction than quinoline.

b) Reaction of p-Chloranil and p-Bromanil with Aniline and Anisidines.

The experimental results obtained for the reaction of aniline and its methoxy derivatives with p-chloranil or p-bromanil in aqueous dioxane show that the rate follows a third order kinetic overall, first order with respect to the tetrahalogenated p-benzoquinone and second order with respect to amine, with the liberation of only two halide ions.

The order of reactivity of amines towards charge transfer interaction with p-chloranil in aqueous dioxane falls in the order :

P-anisidine > aniline > o-anisidine > m-anisidine.

This order of reactivity is in harmony with the order of the basicity $K_b$ of the amines.

Thus the higher rate of interaction of p-anisidine with p-chloranil than that of aniline is due to the lower ionisation energy of p-anisidine and also is ascribed to its higher electron-donating ability ( +R) -I).

The low reactivity of o-anisidine is attributed to the ortho-effect.

The lowest rate of interaction of m-anisidine than the other amines is due to the presence of the methoxy group in the meta position where it acts only by its -I effect which results in a decrease in the electron donating ability of the amino group so that its ionisation potential becomes not suffeciently low to form the charge transfer complexes as fast as the other amines.

The effect of structural changes of amines upon their rate of interaction with p-chloranil is attributed either to variation in $E^*$ or in P or in both in the kinetic equation $k = Pze^{-E^*/RT}$, where Z does not change seriously and "P" represents the proportion of the suffeciently energised collisions which actually lead to the formation of the

ireaction product.

m Plots of logk values against $E^{\neq}$ with slopes not equal to 2.303 RT indicate that changes in $E^{\neq}$ are not alone respon-
p sible for changes in reaction velocities but also P factor has an effect on the velocity of the interaction.
a
t The linear relationships between $E^{\neq}$ and log A for the
: interaction between isoquinoline, pyridine , aniline or
1 anisidines with slopes equal to 1.5 in average establish
] the close correlation between the two parameters $E^{\neq}$ and PZ where PZ = A.

The linear relationships between $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ for the reactionof all the amines studied with p-chloranil with slopes equal to unity indicate that there is no variation in $\Delta G^{\neq}$ due largely to the general compensation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

This is in agreement with the experimental results where the calculated $\Delta G^{\neq}$ values vary much less with change in structure of the amines.

The linear plots between logk and $\frac{D-1}{2D+1}$ with positive slopes give further support for the proposed mechanism where

# INTRODUCTION

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Nucleophilic substitution reactions can be illustrated by considering the familiar reactions of alkyl halides where halogen is displaced as halide ion by bases. The mechanism of nucleophilic substitution in aliphatic compounds may occur by two mechanisms, designated $S_N1$ and $S_N2$ [1].

The $S_N1$ mechanism involves slow dissociation of the aliphatic compound into an alkyl cation followed by fast combination of the carbonium ion with any available nucleophilic reagent.

The $S_N1$ substitution is favoured by release of electrons in the aliphatic compound to the site of substitution, whereas the $S_N2$ mechanism involves the rate-determining attack of the nucleophilic reagent on the aliphatic carbon atom with the simultaneous departure of the displaced group.

It is usually but not always that $S_N2$ substitution is favoured by (a) electron withdrawals from the site of substitution, (b) the ambiguity resulting from the different electronic requirements for reagent approach and (c) substituent expulsion.

However, the aryl halides are characterized by low reactivity towards nucleophilic substitution. This low reactivity of aryl halides towards displacement has been

attributed to two different factors :-

a) Delocalisation of electrons by resonance,

b) Difference in($\sigma$) bond energies due to difference in hybridisation of carbons.

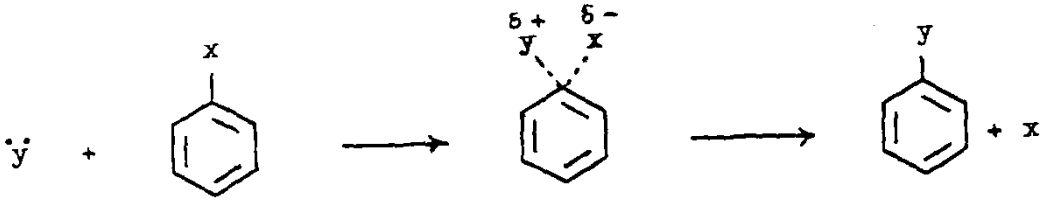
In nucleophilic aromatic substitution electron release causes deactivation, whereas the presence of electron withdrawals like $-NO_2$, -NO, $>C=O$, $\overset{+}{N}_3R$ or $-C\equiv N$ located at ortho or para to the halogen activate the aryl halide towards nucleophilic reagents like $\bar{O}H$, $\bar{O}R$ and $NH_3$, and makes the reaction proceeds quite readily. As the number of these ortho and para substituted groups on the ring increases, the reactivity increases so that trinitrophenol is obtained from 2,4,6-trinitrochlorobenzene by simple treatment with water.

These electron withdrawing substituents activate many groups other than halogen toward nucleophilic substitution except hydrogen which is generally not displaced from the aromatic ring, since this would require the separation of the very strongly basic hydride ion, $\bar{H}$.

In the nucleophilic aromatic substitution the mechanism appears to be in a parallel duality to that for the nucleophilic substitution in aliphatic compounds. Most nucleophilic aromatic substitutions are bimolecular $S_N2$ except for the $S_N1$ decomposition of diazonium cations[2].

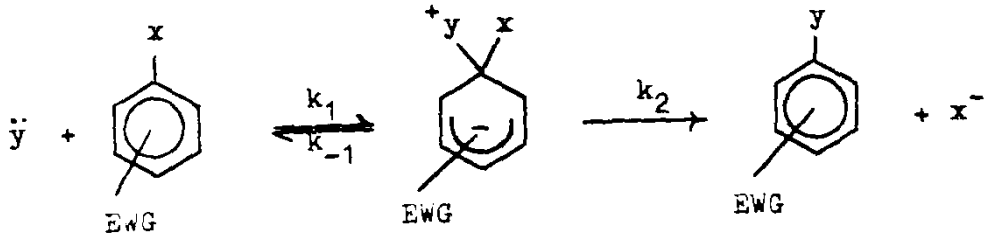
The mechanism of nucleophilic aromatic substitution ($S_NAr$) reactions involving activated substrates and good

leaving groups has been a subject of active discussions in recent years. Chapman et al.[3] have advocated a one-step, $S_N2$-like mechanism in which the intermediate stage I is a true transition state and is represented as follows:



I

Research in this area was strongly stimulated by Bunnett and Zahler[4] who proposed that this reaction should proceed by the two-step mechanism, where the intermediate complex II is formed. The intermediate complex mechanism is represented by the following equation :



II

Aromatic tetravalent carbon, (A compound)

(EWG = Electron-withdrawing group).

This mechanism involves two essential steps: attack of nucleophilic reagent upon the ring to form a carbanion II, followed by the expulsion of halide ion from this carbanion to yield the product. The intermediate carbanion II is a

hybrid of three structures and is an actual compound. Structure II which contains a tetrahedral carbon and the negative charge distributed about the ring, is comparatively stable and corresponds to an energy valley in the energy diagram, i.e., an intermediate complex.

This intermediate complex mechanism predicts second-order kinetics as commonly observed, and the overall second-order rate coefficient depends on the rate of the individual steps.

$$k_{exp} = k_1 k_2/(k_{-1} + k_2) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Reaction occurring by this mechanism may be classified according to the relative magnitudes of $k_{-1}$ and $k_2$:

Class (A): If $k_2 \gg k_{-1}$, i.e., if x is expelled from the intermediate complex much faster than y, equation (1) simplifies to $k_{exp} = k_1$ and the rate is determined by the rate of formation of the intermediate complex.

Class (B): If $k_{-1} \gg k_2$, equation (1) becomes $k_{exp} = k_1 k_2/k_{-1}$ and the rate is equal to the equilibrium concentration of the intermediate complex times the rate coefficient ($k_2$) for its transformation into product.

Class (C): If $k_2$ and $k_{-1}$ are of comparable magnitude, equation (1) cannot be simplified and the overall rate is affected by both the rates of bond making ($k_1$) and of bond-breaking ($k_2$) as well as by $k_{-1}$.

Bunnett and Zahler[4] proposed that the reaction by the intermediate complex mechanism comprises the following principle arguments:

1- The transition state for the one-step, $S_N2$-like mechanism is difficult to rationalize quantum mechanically, whereas the transition state and the intermediate for the intermediate complex mechanism are easily rationalized.

2- In reactions known to involve breaking of a carbon-halogen bond in the rate-determining step, the carbon-fluorine bond should be broken very much slower than other carbon-halogen bonds, but Bunnett and his co-workers[5] proved that in such reaction series the C-X bond was not broken in rate-determining steps. This result is incompatible with the $S_N2$-like mechanism[5], but is agreeably explained in terms of the intermediate complex mechanism (class A), in which the rate is determined by the rate of formation of the intermediate.

In the reaction of piperidine with several 1-substituted 2,4-dinitrobenzenes, six substituents with different five elements were displaced at nearly the same rate[6]. The equality of the rates observed led them to propose that little or no breaking of the old bond had occurred at the rate-determining transition state. Their result is also incompatible with the $S_N2$-like mechanism, but is readily interpreted in terms of the intermediate complex mechanism with $k_2 \gg k_{-1}$ (class A).

Bunnett and Randall[7] established the intermediate complex mechanism for the reaction of N-methylaniline with 2,4-dinitrofluorobenzene and for a large group of aromatic nucleophilic substitution reactions and make this mechanism