A THESIS

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KINETIC STUDIES ON THE MECHANISM OF SOME NUCLEOPHILIC REACTIONS IN AQUEOUS MEDIA

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KINETIC STUDIES ON THE MECHANISM OF SOME NUCLEOPHILIC REACTIONS IN AQUEOUS MEDIA

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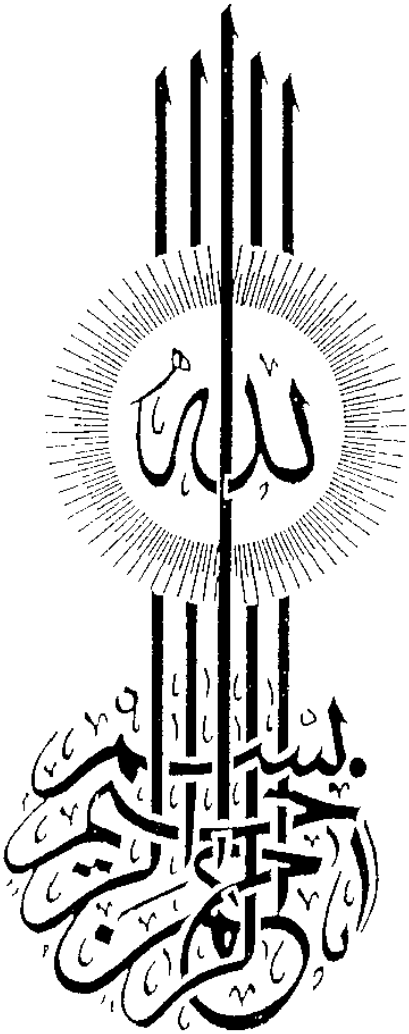
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SUMMARY

Summary

Kinetics Studies on the Mechanism of Some Nucleophilic Reactions in Aqueous Media

The distinct change in colour on mixing the acceptor chloranil solution and donor (amines) solutions indicates the complex formation in the solution . The new absorption bands which are not present in either of the reactants are characterestic of 1 : 1 CT conplexes . The absorption maxima indicate that the transition is of n - π * type .

The 1 : 1 CT complexes formed between equimolecular components are reasonably stable (λ , 564 - 556 nm) , but in excess amine , the CT complexes formation is reasonably fast whereas its transformation to solid products (λ, 314 - 442 nm) is slow . The wave length λ depends on the binary solvent and amine used .

The kinetics of the charge - transfer interaction between p - chloranil as an acceptor with branched and unbranched aliphatic amines , aliphatic heterocyclic and aromatic heterocyclic amines and with toluidines as donors have been followed up spectrophotometrically at 30°c in aqueous non - polar aprotic solvent dioxane , and in dipolaraprotic solvent such as dimethylsulfoxide or dimethylformamide which is miscible with water in all proportions at ordinary temperature in order to study the effect of basicity and change in structure of the donor either sterically or electronically and also in order to gain more insight concerning the pronounced specific solvent effects and polarity of the medium on such a reaction as a typical nucleophilic substitution S_N2 reaction .

Thus , the rates of charge-transfer interaction between p-chloranil with n-propylamine , isobutylamine , diethylamine , pyrrolidine , piperidine , morpholine , pyridine and with o-, m-, and p - toluidines have been studied .

The kinetic data indicate that the rate of formation of CT complex follows the overall second - order equation , first - order with respect to both acceptor and amine , and also the rate of formation of the final product is first - order with respect to CT as well as to the donor .

Thus , reaction follows an overall third order rate equation , first order with respect to p -chloranil and second order with respect to amine .

Since under the experimental conditions, chloranil CA is almost totally consumed, [CA] = [CT] and the rate equation becomes :

$$\frac{d\,[\text{product}\,]}{dt} = k_{obs}\,[\,CA\,]\,[D\,]$$

However , since [CA] is negligible , the band λ 270 - 290 nm is assigned to the monosubstituted product .

The rates increase by increasing the dielectric constant of the medium , the linear plots between log k_{obs} Vs 1/D with negative solpe indicates that the transition state is much more polar than the reactants whereas the linear plots between log k_3 (log k_{obs} / [Amine]^{2}Vs D-1 / 2D+1 with positive slope indicates that the reaction takes place between dipolar molecules . The dependency of reaction rate on $C^2{}_{H_2O}$ together with the Bunnett's linear plot between log k_3Vs log [H_2O] with slope equals to 2 give a good evidence that two water molecules are involved in the rate - determining step . Moreover , the linear plots between k_3Vs$[H_2O]^2$ with definite intercepts indicate that the overall rate splits into two simultaneous mechanistic paths with different rate costants, " true - third order termolecular mechanism k_1" which is water - independent and an " apparent third-order termolecular mechanism k_2 " in, which two water molecules are participants in the rate - determining step . Thus the observed rate constant for the reaction can be written as :

$k_{obs} = k_1 [A] [D]^2 + k_2 [A] [D]^2 [H_2O]^2$

The proportion of the apparent third - order termolecular mechanism becomes more effective by increasing water content of the binary , i.e, by increasing the dielectric constant of the medium .

The difference in rate constants on using different molar ratios of reactants indicates that the product does not form directly from the CT but through an intermediate which is formed in a slow rate - determining step by CT transformation .

The reactivity of solvents which lies in the order :
DMSO > DMF > Dioxane indicates the presence of charge separation in the transformation of the electron donor - acceptor complex (EDA) to the final product , which means that transition state is much more polar than the initial state which is likely to be the monosubstituted procuct.

The increase in the rate by increasing polarity of solvents is attributed to dative structure of the complex (D^+- A^-) which is predominant in the excited state and stabilizes by polar solvents . Thus the higher rate in DMSO than in DMF within the same solvent composition is ascribed to the interaction between its molecules with excited states and such an interaction is very strong in CT systems .
The reactivity of aliphatic amines which falls in the order : n-propylamine > isobutylamine > diethylamine irrespective of their k_b values (4.1×10^{-4}, 3.0×10^{-4} and 10.0×10^{-4} , respectively) indicates that the reaction is highly senstive to the steric factor more than the electronic donation .

The order of reactivity of the aliphatic heterocyclic amines which falls in the order : Pyrrolidine (12.0) > piperidine (11.1) > morpholine (8.5) is in harmony with their pKa values , However the order of reactivity of charge - transfer interaction of toluidines with p - chloranil in aqueous media falls in the order : p-toluidine > m-toluidine > o-toluidine , which obeys both their basicity and electornic effect of substituents .

The higher rate of interaction of p-toluidine is due to the presence of CH_3 group in the para- position where it acts both by its +R and +I effect and thus increases the susceptibility of NH_2 group towards reaction whereas in meta - position it operates only by its +I effect . Thus the ionisation potential of the amino group in the m- toluidine becomes not sufficiently low to form charge transfer complex as fast as p-toluidine . The low reactivity of o-toluidine is attributed to the ortho effect which plays an important rôle in determining the rate constant so that it outweighs the electronic effect . Such a phenomena is frequently expected in the S_N2 reactions . This ortho effect arises from chelation between unshared pairs of electrons of electron-donating nitrogen atom and hydrogens of CH_3 group situated in the ortho position especially when the molecule becomes energised to form the transition state . Thus it leads to a higher p factor and the ionisation potential increases so that electrons on the nitrogen atom become less available for interaction with p-chloranil .

The structures of final products , 2 , 5 - dichloro-3 , 6 - disubstituted p- benzoquinones have been confirmed from their elemental analysis , IR , ^{1}HNMR and mass specteroscopy .

However concerning the heterocyclic aromatic amine , pyridine , $k_b = 2.3 \times 10^{-9}$, the kinetic measurements , elemental analysis of the product and also the IR , ^{1}HNMR , and masss spectroscopy indecate the liberation of the four chlorine atoms and the final product is substitued by only two amine molecules . Thus a two - successive stage mechanism is proposed in which a molecule of p-chloranil reacts with two molecules of electron -donor pyridine followed by two water molecules . In the first stage an intermediate specimen is formed with the liberation of two chloride ions which in turn undergoes further substitution with the liberation of the other two chloride ions to form the product P .

However the wavelength of the products λ_p indicates that the strength of complexes formed from the amines lies in the order :

n- primary aliphatic > secondary aliphatic > secondary alicyclic > branched primary aliphatic > aromatic amines although they possess electron - repelling groups >> heterocyclic aromatic amines.

INTRODUCTION

INTRODUCTION

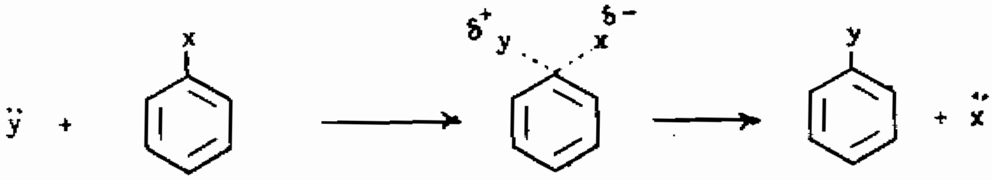
The familiar reactions of alkyl halides are nucleophilic substitution reactions where halogen is displaced as halide ion by bases whereas, the aryl halides are characterized by low reactivity towards nucleophilic substitution. This low reactivity of aryl halides towards displacement has been attributed to delocalisation of electrons by resonance; and difference in (σ) bond energies due to difference in hybridisation of carbons.

In nucleophilic aromatic substitution an electron releasing group causes deactivation, whereas the presence of electron withdrawals such as $-NO_2$,$-NO$, $>C=O$, $\overset{+}{N}_3R$ or $-C\equiv N$ located at ortho or para to the halogen, activate the aryl halide towards nucleophilic reagents such as $\overset{-}{O}H$, $\overset{-}{O}R$ and NH_3, and make 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 ion, $\overset{-}{H}$.

In the nucleophilic aromatic substitution the mechanism appears to be in a parallel duality to that for the nucleophilic substituion in aliphatic compounds. Most nucleophilic aromatic substitutions are bimolecular S_N2 except for the S_N1 decomposition of diazonium cations.[1]

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.[2] 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:



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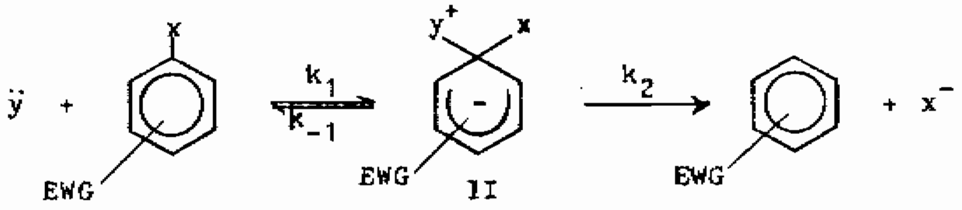
Research in this area was strongly stimulated by Bunnett and Zahaler[3] who proposed that this reaction should proceed by the two-step mechanism, where the intermediate complex II is formed. The intermediate complex mechanism is represented by the following equation:



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 is 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.

$k_{exp.} = k_1k_2/(k_{-1} + k_2)$ .... (1)