SUMMARY

Kinetic considerations together with DFT calculations can give an insight into the mechanism of a reaction and gives a definite answer concerning the individual steps by which a chemical reaction occurs. Spectrophotometry is a convenient and reliable tool to make a kinetic investigation when a product or reactant is making absorption that follows the Beer-Lamberts law.

This thesis entitled “KINETICS AND MECHANISM OF HALOGEN DISPLACEMENT REACTIONS OF HALONITROBENZENES WITH ALIPHATIC AMINES - A COMPARATIVE STUDY” describes the results of the explorations aimed at investigating the kinetics and mechanism of the reaction of DNCB as well as DNFB with aliphatic amines, n-butylamine, n-propylamine, iso-propylamine, ethylamine and ethanolamine in acetonitrile, Equation 1. Reactions are conducted under pseudo-first order conditions and followed spectrophotometrically by measuring the absorbance of the product at the respective λ_max. In all the cases a clear isosbestic point, indicative of a neat conversion of the reactant into product, is shown by the overlay of the sequential scans of the reaction mixture at definite time intervals. The data from the time course graphs were used to calculate the pseudo-first order constants and second order constants.

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\begin{align*}
\text{Equation 1}
\end{align*}
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Determination of the order of the reactions showed that the reactions follow second order kinetics and comparison of the rate constants for the various amines revealed that the reactivity order is NBA>NPA>EA>EOA>IPA which is in agreement with the order of nucleophilicity among aliphatic amines. The kinetic measurements were conducted in acetonitrile. And a comparison between DNCB and DNFB reactions showed that the rate is always many times higher on the DNFB side. The higher rate of the reaction of amines with DNFB is explained in terms of the mechanism and base catalysis by the amines themselves. The order of the reaction and the higher reactivity of fluoro compound in comparison with the chloro compound suggest that the rate determining step of the reaction is the formation of the Meisenheimer complex. The rate of the reaction between DNFB and EOA in acetonitrile was compared with the rate in toluene and the results show that the reaction is slower in toluene, the less polar solvent. Further, comparison with the rate of reaction for MNFB and EOA revealed that MNFB is much less reactive and the measured activation energies are much higher for the MNFB reaction.

Investigations were done on the displacement of fluorine from DNFB and MNFB and chlorine form DNCB by EOA, a primary amine by molecular modeling by HF and DFT methods. The DFT calculations were conducted in vacuum, acetonitrile, toluene and ethanol to elucidate the mechanism and to establish the effect of polarity of solvent on the activation energy of the reaction. Further, the activation energies were estimated in two more solvents ether and DMF. DFT calculations were utilized to explore the stoichiometry of the reactions of DNFB and DNCB with ethanolamine. The best possible combination of products are HF hydrogen bonded to EOA and N-(2,4-dinitrophenyl)-
ethanolamine so that the reaction involves two molecules of EOA and one molecule of DNFB, **Scheme 1**.

![Scheme 1](image)

The proposed mechanism of the reaction based on the DFT calculations is presented in **Scheme 2**. The mechanism involves the formation of a reactant complex, followed by Meisenheimer complex and the decomposition of the MC is catalyzed by a second molecule of EOA. So the product formed is a mixture of N-(2,4-dinitrophenyl)ethanolamine and HF hydrogen bonded to ethanolamine.

![Scheme 2](image)

A comparison of the calculated activation energies of the reaction in various solvents revealed that Ea decreases with increase in the polarity of the solvent, **Fig 1**. The
activation energy is the maximum in vacuum but decreases progressively from toluene and reaches a minimum in acetonitrile. The Ea for the reaction of MNFB with ethanol amine was determined to be much higher which is attributed to the effect of the absence of the nitro group at para position.

![Activation Energy Graph](image)

**Fig.1.** Variation of activation energy of the reaction between DNFB and EOA in solvents estimated by DFT calculation using B3LYP/6-31G* basis set.

The mechanism of the reaction between DNCB with EOA also was explored by DFT calculations. MO calculations show that the sum of the energies for the product combination P1 and HCl is much lower than that of the reactants confirming that the stoichiometry of the reaction can be represented as in **Scheme 3.**
The basis sets used in the DFT methods failed to optimize the structure for MC formed from DNCB and ethanolamine since it is unstable. The decomposition of the MC takes place spontaneously leading to the product.

This study illustrates that the aromatic nucleophilic substitution reaction of aliphatic amines with chloronitrobenzenes / fluoronitrobenzene follows second order kinetics, first order with respect to each amine and the substrate and the mechanism involves two steps, the formation of Meisenheimer complex and its decomposition where the slow formation of the Meisenheimer complex is rate-determining. In the case of DNFB decomposition of the MC is catalyzed by a second molecule of amine. But the MC formed from DNCB and ethanolamine being unstable decomposes spontaneously.

Moreover, molecular modeling has established that the mechanism of aromatic nucleophilic substitution reaction of ethanolamine with fluoronitrobenzenes involves the formation of Meisenheimer complex and its decomposition catalyzed by a second molecule of ethanolamine. The total and relative energies of the reactants, intermediates, transition states and products were estimated by HF and DFT methods and a possible transition state was explored for the decomposition of MC.