

Foreword

This book is based on a partial fulfillment of my doctoral thesis, which was finished about 20 years ago.

This book is composed of 7 chapters. In the present work, the author is trying to describe his contribution to the chemistry of a fundamental unit reaction, bimolecular aromatic nucleophilic substitution (S_NAr) reaction, with the hope of leaving something for the welfare of the human being.

Contents of this thesis are as follows:

Chapter 1 gives a short survey of aromatic nucleophilic substitution in general. And Chapter 2 is dedicated to give a slightly deepened introduction to the prevailing reaction mechanisms of bimolecular aromatic nucleophilic substitution.

After the introductory Chapters of 1 and 2, Chapter 3 shows the results of extensive kinetic studies of the reactions of 2,4,6-trinitrohalobenzenes ($PicX$, $X=F$ or Cl) with 2,4-dimethoxyaniline (DMA) at 298K, 308K and 318K, and with aniline at 298K and 318K in cyclohexane. In this solvent, no severe solvation of the reactants and of the intermediate is to be anticipated. These S_NAr reactions, targets of Chapter 3, follow a third-order rate law. A strong acceleration can be observed when a tertiary amine, QN or TEA, as a catalyst is added into the reactions between

PicX and a nucleophilic amine. An inverse temperature effect and a variable element effect are obtained. These kinetic results cannot be explained by the contemporary mechanisms of S_NAr reaction in solvents of low relative permittivity, either steady-state mechanism or dimer nucleophile mechanism. A time-honored mechanism with a concept of SB-GA catalysis is applied to give an acceptable rationalization for these reactions in cyclohexane.

In Chapter 4, the author changes the reaction medium from cyclohexane to benzene, and investigates the reactions of PicX with DMA and with aniline at 298K and 318K. Benzene has been a solvent of choice in the many trials hitherto reported and one has to try this common solvent for the direct comparison of the experimental approach to that of fore-runners. Evidence has been obtained, that is strongly against the currently prevailing steady-state mechanism and dimer nucleophile mechanism, to support SB-GA mechanism in benzene.

Chapter 5 covers the detailed examinations to the results obtained after SB-GA mechanism. Extensive mechanistic studies on the S_NAr reactions of 2,4-dinitrohalobenzenes (DNXB, X=F and Cl) with DMA and with aniline at 298K and 318K in benzene are shown. There is found a third-order dependence of pseudo-first-order rate constant on the concentration of nucleophilic amine. Profound acceleration is substantiated by the addition of QN. The facts require both steady-state mechanism and dimer nucleophile mechanism to be excluded in these “well-studied” reaction systems. Kinetic analyses after SB-GA mechanism are found to give a self-consistent picture of these S_NAr reactions in solvents of low

relative permittivity.

Chapter 6 gives the short conclusion of the present studies and the prospects of this work.

Chapter 7 is an experimental part, and is showing reagents, experimental procedures as well as methods for the analyses of kinetic measurements.