KINETIC STUDIES IN THE FIELD OF ACTIVE HALOESTERS

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Kinetic STUDIES IN THE FIELD OF ACTIVE HALOESTERS

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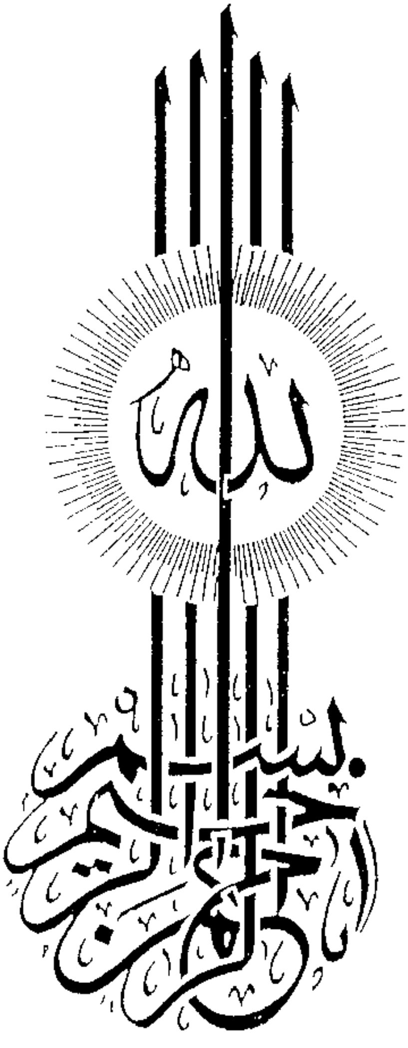
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بسم الله الرحمن الرحيم

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Object of Investigation

A simple, senstive and selective potentiometric method for determination of haloester is developed in the light of kinetic study of the interaction between amines and haloester.

A comperhensive systematic study of the various factors affecting the rate of the reaction was investigated viz., concentration, temperature, and nature of the reaction products in order to illustrate the mechanism of reaction.

SUMMARY

The thesis deals with a comperhensive kinetic study for the reaction of aliphatic amines with ethylhaloester by a simple, senstive and selective potentiometric method.

Chapter I : Comprises a survey on the literature relevant to the kinetics and mechanism of the reactions of haloesters, particularly with amines.

Chapter II : Comprises the expermintal potentiometric procedures adopted in both kinetic and determination studies.

Chapter III : Includes the results obtained in the effect of different factors on electrode response and the kinetic study on the reaction of tested aliphatic amines with ethylhaloester in ethylalcohol as a solvent. The rate of reaction was determined at different temperatures to allow calculation of the thermodynamic activation parameters $\Delta E^{\neq}$, $\Delta H^{\neq}$ $\Delta S^{\neq}$ $\Delta G^{\neq}$.

Chapter IV : Includes a comperhensive general discussion on the aliphhatic amines–haloester reaction. The order of reaction is found to be of first order with respect to ethylhhaloester and the overall order of reaction is found to be pseudo first order due to excess amine used.

The reactivity of amines towards ethylhaloester as measured by k values is found to obey the following order.

piperidine > ethylamine > n–butylamine > benzylamine

The change of halogen atom from chloro to bromo in haloester for the reaction with the same amine, showed marked increase in the rate of reaction.

Linear relationships are obtained on plotting the values of log k vs. pk_a for the reaction of the tested amines with haloester, indicating a more bond formation between the nucleophile and the reaction center at the transition state.

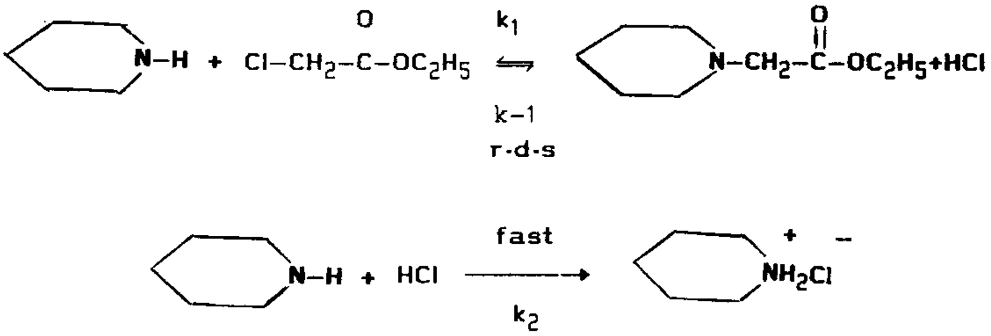
Another linear correlation is also obbained between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ indicating one and same mechanism for the tested series of reactions.

The suggested mechanism involves two steps.

The first step involves interaction between one molecule of each of the two reactants ethylhaloester and amine, and is considered the slow step (rate determining step).

The second step is fast, which involves addition of the halogen acid produced in the first step to another molecule of amine.

Structure of the products is proved by elemental analysis & infrared spectroscopy, and confirm the suggested mechanism, e.g :



The same mechanism is considered to hold for the reaction of other tested amines with haloester.

Chapter I
Introduction

INTRODUCTION

The Kinetic Study

Mishra etal (1) studied the rate of reaction of phenacyl bromide with various substituted benzoate ions in 90% acetone – water mixture, and the activation parameters were computed. The kinetic data, plotted in a Brönsted fashion against pka of the nucleophiles yield linear relationship characterized by $\alpha N = 0.50$ for benzoate ions. The rate data have also been correlated with Hammett equation and the more sophisticated multi parameter Yukawa–Tsuno equation. The linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ indicates the same mechanism. The rate constant was found to decrease with increasing the ionizing power of the solvent.

George etal (2) studied the alkylation of benzene and toluene with alkyl chlorosulfites, arene sulfinates, chloro–and fluorosulfates, arenesulfonates, triflates, penta fluorobenzene sulfonates, and tri fluoroacetates as alkylation agents using $AlCl_3$ or SbF_5 as a catalyst in nitromethane, methylene chloride, carbondisulfide, 1,1,2 tri chlorotrifluoro methane. The inter and intermolecular selectivities of the alkylations was studied based on competitive toluene/benzene rate ratio and isomer distribution. The mechanism of the alkylation reaction has been discussed.

In (1981) Srinivasan etal (3) determined the second order rate constants for the reaction of phenacyl bromide with substituted cinnamate & acrylate ions in 90% (v/v) acetone–water mixture at three temperatures and the activation parameters evaluated.

The electron–releasing groups increase the rate of reaction while electron–withdrawing groups retard it. A satisfactory Hammett correlation with ρ value of –0.208 was obtained.

Srinivasan etal (4) studied the second order rate constant for the reaction of ethyl bromoacetate with several meta and para substituted benzoate ions in 90% (v/v) acetone–water mixture at 303, 308 and 313^{o} K. Electron releasing groups were found to facilitate the rate of reaction while electron withdrawing groups retard it.

Application of Hammett equation gave a good linear free energy relationship with ρ value = 0.38. Potassium benzoate reacts faster than sodium benzoate.

Addition of K^+, Na^+ and Li^+ ions showed a negative salt effect and the magnitude of the effect at similar concentrations increased in the following order $K^+ < Na^+ < Li^+$.

Ananthakrishna etal (5) studied the rate of reaction of phenacyl bromide with various α-substituted benzoate ions in 90% (v/v) acetone-water mixture at 30°, 35° and 40°C and the activation parameters were readily evaluated. The reaction was shown not obey the Brönsted relationship.

The isokinetic temperature unexpectedly is found to be well below the experimental temperature, though the behaviour of α-substituted benzoate is correlated with their polar effects by the Taft equation. It appears that some substituents behave quite unexpectedly.

The polar substituent constants, σ_0, for SCH_3 and SO_2CH_3 groups were evaluated by interpolation in the Taft plot. Variation in $\Delta S^{\neq}$ values was explained in terms of the bulk effect of the groups.

In 1967 MOHANTY R.K. etal (6) determined the rate constant and the activation energy for the reaction of substituted phenacyl bromides with aniline and of m-nitrophenacyl bromide with different substituted anilines. A linear relationship between the dissociation constants of anilines and velocity constants was obtained. Hammett's equation was found to be valid for the reaction with ρ value -1.97, indicating that the reaction rate is retarded with electron withdrawing substituents.

The probable mechanism for the reaction of phenacyl bromides involves a direct SN_2 displacement process.

ANANTHAKRISHNA etal (7) studied the rate constant for the reaction of phenacyl bromide with 6-Substituted 2-Naphthoate ions in 92% (v/v) acetone-water. Arrhenius parameters as well as the enthalpies and the entropies of activation were evaluated. The Hammett equation was found to apply well to this reaction.

BALIAH, and ANANTHAKRISHNA (8) determined the rate constants for the reaction of phenacyl bromide with 4-substituted 1-Naphthoate and 3-Substituted 2-Naphthoate ions in 90% (v/v) acetone-water. Arrhenius parameters as well as the enthalpies and entropies of activation were evaluated. The Hammett equation was found to applys very well to the reaction of phenacyl bromide with 4-substituted 1-Naphthoate ions. A plot of the rate constants against Pka of the corresponding conjugate acids was linear with Brönsted coefficient, $\alpha=0.36$. The behaviour of 3-substituents did not conform to the Taft linear polar and steric relationships.

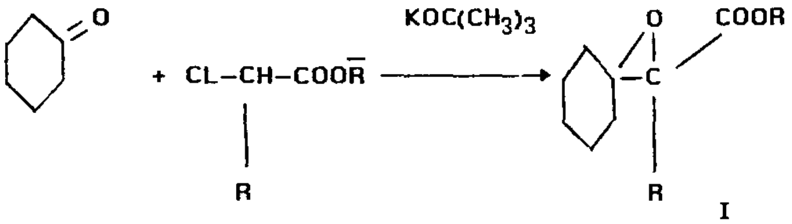
Johnson etal (9) studied the reaction of cyclohexanone and ethyl chloro acetate in presence of potasium t-butoxide in t-butanol. The glycidic ester (Ia) was obtained. Other condensations carried out were :

(1) Cyclohexanone and t-butyl chloro acetate to give (Ib),

(2) Cyclohexanone and ethyl-α chloro propionate to give (Ic),

(3) Cyclohexanone and t-butyl-α-chloropropionate to give (Id),

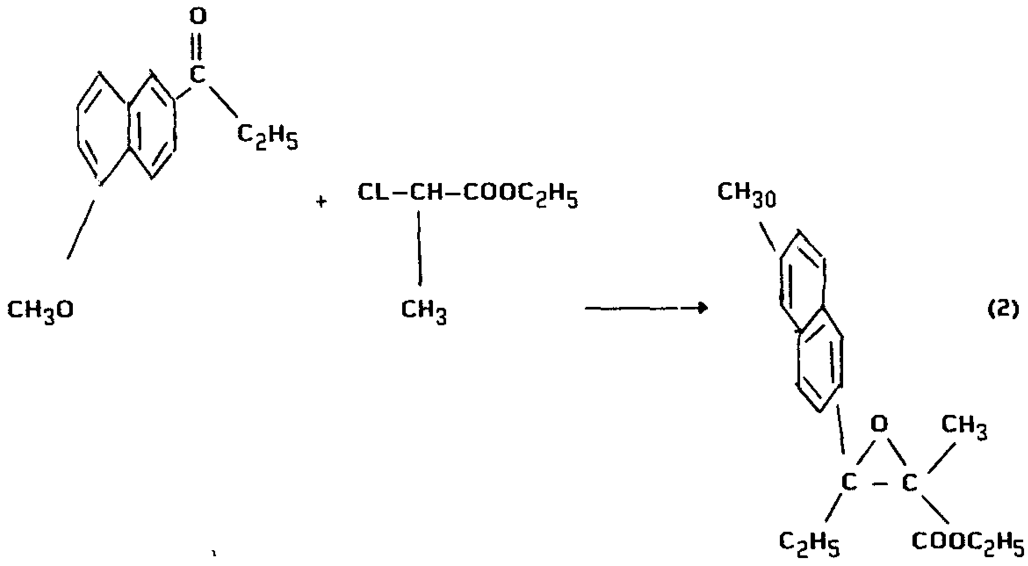
(4) 2-propionyl-6 methoxy naphthalene and ethyl -α- chloro propionate to give (II); 3-phenyl- cyclohexanone and ethyl-α- chloropropionate to give (III)



(1)

I

	R	$\bar{R}$
a :	H	C_2H_5
b :	H	$t-C_4H_9$
c :	CH_3	C_2H_5
d :	CH_3	$t-C_4H_9$



(2)

II