# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

**By**

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

*In the name of God,*
*the Compassionate, the Merciful….*

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

**Dr. T.D. Radhakrishanan Nair,**
Professor,
Department of Chemistry

Calicut University
Kerala - 673 635

# CERTIFICATE

The thesis presented herewith embodies the observation on **Kinetic Studies on the Oxidation and Catalysis of Aromatic Aldehydes Using Sodium Hypochlorite**. This is an authentic record of the research work carried out by K.K. Abdu Rahiman under my supervision in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Chemistry of the University of Calicut. This work or part thereof has not been presented for the award of any other degree.

27/03/2002

Dr. T.D. Radhakrishanan Nair

Supervising Teacher

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# DECLARATION

This is to certify that the thesis bound here with is an authentic record of the research work carried out by me under the supervision of **Dr. T.D. Radhakrishanan Nair**, Professor of the Department of Chemistry, University of Calicut, in partial fulfilment of the requirements for the Degree of the Doctor of Philosophy in Chemistry of the University of Calicut, and further that no part thereof has been presented before for any other degree.

K.K. Abdurahiman

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# ACKNOWLEDGEMENT

*This thesis has been prepared under the supervision of Dr. T.D. Radhakrishanan Nair, Prof. of Chemistry, University of Calicut who have generously spent a great deal of his time on this work by encouraging and inspiring me with helpful criticism and efficient guidance. I am indebted to him for giving me considerable freedom of thought, work and expression I enjoyed during this tenure. His deep insight, creative ideas and keen interest in the subject helped me to materialise this work. I place on record my heartfelt gratitude to him.*

*I am thankful to Dr. M.P. Kannan,, Head of the Department of Chemistry for providing the facilities to carry out my work.*

*I am very much grateful to the management, Muslim Educational Society for granting me deputation to complete my research work. I also express my deep sense of gratitude to the Principal and staff of Chemistry Department of M.E.S. Kalladi College, Mannarkkad for their valuable help and encouragement in this venture.*

*I wish to acknowledge my gratitude to all the teaching staff and non teaching staff of the Department of Chemistry, University of Calicut for their help and suggestions in respect of my research work.*

*With pleasure I acknowledge the valuable assistance rendered by my friend and Co-Research Scholar Mr. P. Rajendran, Department Chemistry, Govt. Victoria College Palakkad. I am also thankful to Miss. P.S. Sheeba, Mr. K. Prathap and all other research fellows of the Department for their timely help and encouragement to complete my work.*

*I gratefully acknowledge the financial assistance from U.G.C. by awarding me a research fellowship through faculty improvement programme.*

*I register my gratitude to Microtech Computer Centre, Chenakkal for their timely help in the neat execution of the work processing and laser printing of this thesis in a beautiful way.*

*Finally it would be appropriate to place on record my gratitude to my wife, children and other members of the family who patiently co-operated with my programme during the entire period But for their prayers and support, this work would not have been successful.*

*Above all, I thank God Almighty for all His blessings bestowed on me in my life.*

*K.K.Abdurahiman*

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

2002
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 635
INDIA

# CONTENTS

Chapter I INTRODUCTION Page

1.1 Introduction 1
1.2 Chemistry of Hypochlorite 22
1.3 Chemistry of Cyclodextrins 29
1.4 Phase transfer catalysis 38

Chapter II **REVIEW AND SCOPE OF THE PRESENT WORK**

2.1 **Review of the present work**

2.1.1 Kinetics of oxidation of Benzaldehyde 44
2.1.2 Kinetics of oxidation using Hypochlorite 52
2.1.3 Kinetics of oxidation by Phase Transfer Catalysis 60
2.1.4 Catalysis by Cyclodextrins 63
2.2 **Scope and objective of the present work** 65

Chapter III **EXPERIMENTAL**

3.1 Materials 68
3.2 Kinetic investigation 69
3.3 Stoichiometry of the reaction 70
3.4 Analysis of products of oxidation 71
3.5 Kinetic studies in aqueous acetic acid medium 73
3.6 Catalysis by Cyclodextrins in aqueous acetic acid medium 90

3.7 Kinetic studies in aqueous dioxane medium 101
3.8 Catalysis by Cyclodextrins in aqueous dioxane medium 114
3.9 Kinetic studies in aqueous acetonitrile medium 123
3.10 Oxidation of benzaldehyde in presence of phase transfer catalysts 128

Chapter IV **RESULTS AND DISCUSSION**

4.1 Stoichiometry and product analysis 135
4.2 Kinetic studies 136
4.3 Mechanism and rate law 168
4.4 Conclusion 174
4.5 Summary 175
**REFERENCES** 177
Appendix – Kinetic Data

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| PTC | | Phase Transfer Catalysis |
| $Q^+OCl^-$ | | Tetrabutyl Ammonium Hypochlorite |
| $Q^+$ | | Quaternary Ammonium Cation |
| TBAB | | Tetrabutyl Ammonium bromide |
| CAT | | Chloramine-T |
| BAT | | Bromamine-B |
| ACD | | Alpha cyclodextrin |
| BCD | | Beta cyclodextrin |
| PhCHO | | Benzaldehyde |
| PCB | | Para-chlorobenzaldehyde |
| OCB | | Ortho chloro benzaldehyde |
| PBB | | Para bromo benzaldehyde |
| PNB | | Para nitro benzadehyde |
| Aq.HOAc | | Aqueous acetic acid |

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

**By**

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# PREFACE

Studies on the oxidation of different organic substrates under different conditions have been a subject of great significance both theoretically and practically. Kinetic studies leading to the elucidation of rate laws and mechanism have an important place in such studies. The hypochlorite oxidation of these substrates is one among such studies due to simplicity of operation and commercial importance.

Elucidation of mechanism of the oxidation reactions under various experimental conditions are of academic interest. On the commercial aspect, hypochlorite is an efficient reagent for effecting the oxidation of a large variety of organic compounds. The reagent is readily available, inexpensive non- toxic and causes no environmental pollution. It is a mild and selective oxidant and oxidise specific groups. Commercially it is used as a good chlorinating and oxidizing agent. The fungicidal, the bactericidal, antiseptic and antimicrobial properties of NaOCl make it a very useful reagent for a variety of purposes.

The present work embodied in this thesis deals with the kinetic studies on the oxidation of benzaldehyde and substituted benzaldehydes using sodium hypochlorite in aqueous acetic acid and aqueous dioxane media. The kinetic experiments have been carried out by varying various parameters such as temperature, concentration of substrate, oxidant etc, ionic constant and dielectric constant of the medium. The effect of inclusion catalysts such as cyclodextrins on reaction rates have also been investigated. Attempts were also made to study the rates of oxidation by phase transferred hypochlorite using quaternary ammonium salts.

The thesis is broadly divided in to four chapters.

CHAPTER I contain brief a introduction of the reaction kinetics in solution. The various aspects of chemical kinetics and factors affecting reaction rates are outlined here. The chemistry of sodium hypochlorite , its properties and application in various fields are discussed. A short discussion on the structure, properties and application of inclusion catalyst, viz. cyclodextrins are also given. This chapter highlights, the phase transfer catalysis technique as a new method for the reactions in heterogeneous media.

In CHAPTER 2, a review of the kinetic studies cited in literature related to the present work is included. A brief outline on the scope and objective of the present work are mentioned at the end of the chapter.

CHAPTER 3 is the experimental section. The details of the kinetic investigations including the materials used, their purification and method of kinetic analysis are discussed. The experimental data obtained for the oxidation of benzaldehyde and substituted benzaldehydes in aqueous acetic acid and other solvents in the presence and absence of catalysts, viz. cyclodextrins are given in this chapter. The kinetic studies are also carried out in presence of phase transfer catalyst, quaternary ammonium salts.

CHAPTER 4 is the essence of the thesis where the results of kinetic investigations are co-ordinated and discussed. A suitable mechanism has been suggested for the reaction studied and compared with similar findings in literature.

A list of journals and monographs mentioned in the thesis are given as reference at the end of the thesis. Details of kinetic data of various investigations mentioned in the experimental section are listed in the form of tables at the end.

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

**By**

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# CHAPTER I

# INTRODUCTION

Chemical kinetics deals with the quantitative study of the changes in concentrations of the reactants with time during chemical reactions. The results of such studies can be summarized in the form of rate laws for the elucidation of the mechanistic details of the reaction. Study of reaction kinetics is of utmost importance in chemistry as it gives an insight to the nature and course of reaction. Kinetic studies form the backbone of a thorough mechanistic investigation if carried out in relation to various environmental factors affecting the reaction. The interpretation of the results then lead to an understanding of the mechanism of the reaction. Kinetic data also provide valuable evidence to establish the proposed mechanism and provide viable methods for the successful conduct of chemical processes.

## 1.1.1 Theories of reaction kinetics

The rates of reactions are generally treated on the basis of two well known theories, viz the collision theory[1] and the transition state theory.[2] These are based on two different theoretical approaches.

A close observation of these two theories would reveal that collision theory is a special case of the more rigorous transition state theory for bimolecular reaction between two atoms.

**Collision theory**

The theory suggested by Max Trauz in 1916 is based on the kinetic theory of collisions of gaseous atoms or molecules with the assumption that reactant atoms or molecules act as hard spheres. Later Mec Lewis developed the theory further and gave expression for rates in molecular units. According to this theory the rate of a reaction is equal to the number of activated collision per unit time multiplied by the fraction of molecules having the requisite energy, E given by the Boltzmann factor, $e^{-E/RT}$. Thus

$$k=Ze^{-E/RT} \quad \dots \quad (1\text{-}1)$$

where E is the energy for the reaction to occur and Z is the collision number. Equation (1-1) is modified by including a steric or probability factor P, to account for the deviation in experimental results in relation to the theoretical requirements as

$$k= PZ \exp(-E/RT) \quad \dots \quad (1\text{-}2).$$

For a few reactions P is unity; but for others it varies from 1 to $10^5$. However the theory does not provide any meaningful definition for the factor, P.

**Transition state theory**

Collision theory offers no satisfactory explanation for the rates of reaction in terms of the entropy variation or the changes in the randomness of molecular species involved. The limitations of the theory are rectified in the development of transition theory or the activated complex theory independently by Eyring[3], Evans and Polanyi[4] in 1935. The theory, now being referred to as the conventional transition state theory (CTST) is based on both thermodynamical and statistical mechanical treatment of molecular systems giving due attention to the configration of the transition state on the potential energy surface. The transition state theory is based on the assumption that (i) the activated complex is in equilibrium with the reactants and (ii) that the rate of the reaction is controlled by the slowest process. According to the theory reactants A and B react to produce the product via formation of the transition state $X^{\#}$ as shown,

$$A + B \rightleftharpoons X^{\#} \longrightarrow \text{Products} \ldots\ldots (1\text{-}3)$$

where $K^{\#}$ represents the equilibrium constant for the formation of the activated complex. From statistical thermodynamic consideration the concentration of the activated complex is given by

$[X^{\#}] = [A][B]\ (k_bT/h\nu)\ (Q^{\neq}/Q_AQ_B)\ \exp(-E_a/k_bT)$ ...... (1-4)

Where Q's are the partition functions per unit volume, $k_b$, the Boltzman constant, and $\nu$, the frequency of vibration transition state leading to decomposition. Equation (1-4) can also be rewritten as

$[X^{\neq}] = [A][B]\ (k_bT/h\nu)\ K^{\neq}$ .......... (1-5)

when $K^{\neq} = Q^{\neq}/Q_AQ_B \exp(-Ea/k_bT)$

The velocity or rate of the reaction is given by

$v = \nu\ [X^{\neq}] = [A]\ [B]\ (k_bT/h)K^{\neq}$ .............. (1-6)

In the general case, the equation after the incorporation of the transmission coefficient, $\chi$ becomes

$V = \chi\ [A][B]\ (k_bT/h)\ K^{\neq}$ ......... (1-7)

Since $v = k\ [A][B]$ ............. (1-8)

Equation (1-7) gives

$k = (k_bT/h)\ K^{\neq}$ ............ (1-9)

This general equation predicts that for many elementary reactions the rate constant is an equilibrium constant multiplied by the universal frequency factor $k_bT/h$ which varies only with temperature and has the dimension of reciprocal time.

Analogous to classical thermodynamics $K^{\neq}$ can be related to the free energy of activation $\Delta G^{\neq}$ by the relationship

$\Delta G^{\neq} = -RT \ln K^{\neq}$ or $K^{\neq} = \exp(-\Delta G^{\neq}/|RT)$ ......... (1-10)

$\Delta G^{\neq}$ is composed of two parts, the enthalpy of activation, $\Delta H^{\neq}$ and entropy of activation, $\Delta S^{\neq}$ i.e.

$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ ........... (1-11)

Then equation. (1-10) takes the form

$K^{\neq} = \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/R)$ ......... (1-12)

On substitution of $K^{\neq}$ from equation (1-12), equation (1-9) can be written as

$k = (k_bT/h) \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/R)$ ......... (1-13)

the above equation enables the calculation of the enthalpy of activation $\Delta H^{\#}$ and the entropy of activation $\Delta S^{\#}$. The Transition state theory was applied to the reactions in solution by Wynne-Jones and Eyring[5] and later by Evans, Polanyi and Bell. Since it is difficult to formulate partition function for substance in liquid state, the procedure is to use thermodynamic formulation of transition state theory and to make use of activity coefficients. For unimolecular reactions and reactions in solution the enthalpy of activation is related to activation energy as

$$\Delta H^{\neq} = E_a - RT \qquad \ldots\ldots\ldots \qquad (1\text{-}14)$$

Hence equation (1-13) takes the form

$$k = e^{1}(k_bT/h)\exp(\Delta S^{\neq}/R)\exp(-E_a/RT) \qquad \ldots\ldots\ldots \qquad (1\text{-}15)$$

Equations (1-13) or (1-15) apply to any reaction in solution or unimolecular gaseous reaction.

### 1.1.2 Effect of temperature on Reaction rate

Chemical reactions are sensitive to temperature changes. In the Arrhenius type of reactions the rate constant increases with temperature and the increase is governed by the Arrhenius equation

$$k = A\exp(-E_a/RT) \qquad \ldots\ldots\ldots \qquad (1\text{-}16)$$

The pre-exponential factor A is called Arrhenius factor. The value of A and $E_a$ are calculated graphically from the logarithmic form of the equation, viz

$\log k = \log A - E_a/2.303\,RT$ ……… (1-17)

A plot of log k versus 1/T is linear with slope = $-E_a/2.303R$ and log A as intercept.

The rate constant is related to temperature and various activation parameters by equation (1-13) which may be rearranged as

$\text{Log}\,(k/T) = \log k_b/h + \Delta S^{\neq}/2.303R - \Delta H^{\neq}/2.303RT$ ……

(1-18)

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be evaluated from the plot of log(k/T) versus (1/T) when the slope = $\Delta H^{\neq}/2.303R$ and intercept is

$\log (k_b/h) + \Delta S^{\neq}/2.303R$. Hence $\Delta S^{\neq}$ can be calculated. $\Delta S^{\neq}$ can also be evaluated as follows.

Comparing equation (1-15) with (1-16) we get

$A = e^1(k_bT/h) \exp (\Delta S^{\neq}/R)$ ……… (1-19)

Since the value of $e^1(k_bT/h)$ is ~ $10^{13}$ around 300K, then

$\Delta S^{\neq} = 2.303R \log (A \times 10^{-13})$ ……… (1-20)

Thus $\Delta S^{\neq}$ is positive when $A > 10^{13}$ and negative when $A < 10^{13}$

The activation parameter values give a good indication about the nature of the transition state and is used in the mechanistic interpretation. A negative value of $\Delta S^{\neq}$ indicates that the transition state is more ordered than the reactants. The enthalpy of activation together with the entropy of activation decides the rate of chemical process. When $\Delta G^{\neq}$ remains the same within a series of reaction of related substrates, then it would indicate the operation of similar mechanism in all these reactions. . The enthalpy of activation and the entropy of activation together determine the relative speed.

### 1.1.3 Effect of Solvent

Solvents play an important role in the course of chemical reaction. A unique property of the solvent is its efficiency to bring together the reagents effectively. But a much more significant influence of solvent arise from the relative solvating of the species concerned. The interaction of the solvent and solute molecules may result in the modification of their activities, free energies etc due to the influences of internal pressure of solute and solvent. Solvents are of three general types. The polar protic solvents which posses proton donating functional groups and these include alcohols, amines, carboxylic acids, water, etc. Such solvents posses comparatively high dipole moment and may exhibit hydrogen bonding interactions. Dipolar aprotic solvents posses high dipole moment and electron donor properties; but have no acidic proton in them. Dimethyl sulphoxide (DMS), Dimethyl formamide (DMF), Hexa methyl phosphero triamide (HMPT), Nitrobenzene etc belongs to this class. Non polar aprotic solvents which posses little dipole moment and no acidic proton and have also no donor or acceptor properties. Hydrocarbons, halocarbons etc belong to this class. These solvents are very effective for bringing non polar compounds into solution.

In solution, the solute molecules or ions are not free but are highly solvated. The anion of most of ionic solutes act as necleophiles. Protic solvents like methanol solvate the anion through H-bonding. Thus they stabilize the anion thereby decreasing its necleophilicity and hence the reactivity. In such a situation the role of polar aprotic solvents become significant. They dissolve organic compounds through their lyophilic portion. They also solvate the cationic part of the solute. The anions then become free and more reactive. Thus a change from protic to polar aprotic solvent may increase the reaction rate markedly.

### 1.1.4 Effect of dielectric constant of the medium

The influence of dielectric constant of the solvent medium on reaction rate can be studied by treating reactions as (I) that between two ions (ii) that between an ion and a neutral molecules and (iii) that between two neutral dipolar molecules.

For the reaction between two ions the influence of dielectric constant of the medium on rate is treated on the basis of the equation[7]

$$\text{Log } k = \log k_0 - Z_A Z_B e^2 / r_{AB} k_b T D \qquad \ldots\ldots \qquad (1\text{-}21)$$

where $k_0$ is the value of rate constant in a medium of infinite dielectric constant, $Z_B$ & $Z_B$ are the charge of the two ions and $r_{AB}$ is the distance of closest approach of the two ions A and B for the reaction to take place. According to the above equation plot of log k versus 1/D is linear with slope whose value depends on the charge of ions. For reaction between ions of opposite charge slope is positive and the reaction rate increases with dielectric constant of the medium. Similarly for reaction between ions of same charge slope will be negative and such reactions are facilitated in solvents of lower dielectric constant.

For the reaction between an ion of charge Z and a dipolar molecule with dipole moment $\mu$, Eyring & Laidler[8] based on electrostatic interaction deduced the equation.

$$\log k = \log k_0 + \frac{Z^2 e^2}{2k_b T} \frac{1}{D} \left(\frac{1}{r} - \frac{1}{r_\#}\right) \qquad (1\text{-}22)$$

Where r is the radius the ion and $r_{\neq}$ that of the activated complex. It can be understood from the above equation that the reactions rate will be greater is a medium of lower D if $r_{\neq} > r$

Using coulombic energy approach Amis[9] has deduced the equation

$$\log k = \log k_0 + \frac{Ze\mu}{k_b T\, r_{\neq}^2} \; \frac{1}{D}$$

Equation (1-23) gives a linear plot for log k with 1/D whose slope depends on the charge of the ion. If Z is +ve, the reaction rate decreases with increase of D of the solvent and if Z is –ve the rate increases with D of the medium.

The influence of dielectric constant on free energy of reaction between two dipolar molecules given by Kirkwood[10] by considering electrostatic forces is given as

$$\Delta F = \frac{\mu^2}{r^3} \; \frac{(D-1)}{(2D+1)} \qquad 1\text{-}(24)$$

Applying this to the T.S. theory leads to

$$\ln k = \ln k_0 - \frac{N(D-1)}{RT(2D+1)} \left[ \frac{\mu_A^2}{\overleftarrow{r}_A^3} + \frac{\mu_B^2}{\overleftarrow{r}_B^3} - \frac{\mu_{\#}^2}{\overleftarrow{r}_{\#}^3} \right] \qquad (1.25)$$

Where $\mu$s are the dipole moments. It can be seen that for reactions involving the formation of an activated complex which is more polar than the reactants i.e. $\mu_\#$ is greater than $\mu_A$ and $\mu_B$, the rate of reaction increases with dielectric constant (D) of the medium. In such reactions the plot of log k versus (D-1)/(2D+1) is linear with positive slope . Similarly when the activated complex is less polar than the reactants i.e. $\mu_\#$ is less than $\mu_A$ and $\mu_B$ , the rate decreases with increase of D and the plot of log k versus (D-1)/(2D+1) would be linear with a negative slope.

### 1.1.5 Effect of ionic strength

The influence of ionic strength can be divided into two categories the primary salt effect and secondary salt effect. Primary salt effect refers to the influence of ionic strength on the activity coefficient of the ions in solution, which in turn affect the reaction rate. Bronsted[11] and Bjerrum[12] on the basis of Debye-Huckel theory, deduced the equation for the effect of ionic strength on reaction in aqueous solution, Viz.

$$\log k = \log k_0 + 1.02\, Z_A Z_B \sqrt{I} \quad \ldots\ldots\ldots \qquad (1\text{-}26)$$

Where $k_0$ is the rate constant at zero ionic strength, $Z_A$ and $Z_B$ are the charges of ions and I, the ionic strength which is given by $I = \frac{1}{2}\sum C_i Z_i^{\ 2}$

The above equation predicts that for reaction involving ions of same charge $Z_A Z_B$ is is +ve and hence reaction rate increases with ionic strength of the medium. For reactions involving ions of opposite charge (i.e. $Z_A Z_B$ is -ve) the rate decreases with ionic strength. When the reaction is between an ion and a neutral molecule or between two neutral molecules, $Z_A Z_B$ is zero which means that the reaction rate is unaffected by the ionic strength of the medium.

Secondary salt effect is observed for reactions catalysed by acids or bases specifically. In secondary salt effect there is no direct influence of ionic strength on activity coefficient of the reactants. The degree of dissociation of a weak acid such as acetic acid (or a weak base) change as a result of change in concentration of salt in solution leading to changes in $[H^+]$ obtainable. If the reaction rate depends on $[H^+]$ coming from dissociation of the weak acid, then the rate of reaction will depend on salt concentration and is discussed as secondary salt effect. Based on these concepts the following expression for $[H^+]$ has been deduced.

$$\text{Log}\,[H^+] = \log k_a + \log \frac{[HA]}{[A^-]} + 2Q\sqrt{I} \qquad \ldots\ldots \qquad (1\text{-}27)$$

The charge on the acid HA is zero. Accordingly the concentration of $H^+$ increases with ionic strength.

The existence of salts effects indicates the necessity for the adequate control of ionic strength in kinetic studies. Either the ionic strength is kept low so that the effects are small or a series of measurements have to be made and extrapolated to zero ionic strength. A different technique often used is to keep the ionic strength at some large value which does not change significantly during the course of the reaction.

### 1.1.6 The isokinetic relationship

Lei Liu and Qing-Xiang[13] discussed the isokinetic and iso-equilibrium relationships in chemical reactions. For each series of reactions involving various substituents, there will be a temperature at which all the substituents have the same rate. This is the isokinetic temperature. Exner[14] evaluated the isokinetic temperature using his relationship viz.,

$$\log k_2 = a + b \log k_1 \qquad \ldots\ldots\ldots \qquad (1\text{-}28)$$

Where $k_1$ and $k_2$ are the rate constants at the two extreme temperatures $T_1$ and $T_2$ ($T_2 > T_1$). The plot of log $k_2$ versus log $k_1$ is linear with slope, b. Isokinetic temperature is then evaluated from the expression

$$\beta = \frac{T_1 T_2 (b-1)}{bT_2 - T_1} \qquad \ldots\ldots\ldots \qquad (1\text{-}29)$$

For variation of rate within a reaction series Leffler[15] suggest a linear isokinetic relationship.

$$\Delta H^{\neq} = \Delta H_0^{\neq} + \beta\Delta S^{\neq} \quad \ldots\ldots\ldots \quad (1\text{-}30)$$

where β is the isokinetic temperature evaluated from the slope of linear plot of $\Delta H^{\neq}$ with $\Delta S^{\neq}$. Such a relationships were observed in reaction where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ vary in a parallel fashion.

When the value of $\Delta H^{\neq}$ in equation (1-30) is substituted in equation (1-11) viz., $\Delta G^{\neq} = \Delta H^{\neq} - \Delta S^{\neq}$ and on subsequent differentiation yields

$$\delta(\Delta G) = (\beta - T)\, \delta\Delta S \quad \ldots\ldots\ldots \quad (1\text{-}31)$$

Where T is the experimental temperature. When $\beta = T$, $\delta\Delta G = 0$ and no variation of equilibrium or rate would be expected when substituents or media are changed. Then all members of the series react with the same rate.

When $\beta > T$, the reaction rate or equilibrium is mainly controlled by the enthalpy change. In this region the reaction with lower activation energy will react faster and the interpretations involving potential energy surface can be made. This is the more familiar case where there is an increase of rate as a consequence of decrease of activation energy. At temperatures above β(where $\beta < T$) however the controlling factor is $\delta\Delta S$

and interpretations based on potential energy surfaces would be obviously in error. In such reactions an increase of activation energy leading to enhanced reaction rate are observed.

In general it is found that electronic effects are contained in enthalpy factor and that many solvent effects are due to the entropy factor.

Leffler and Grundwald[16] proved that when a reaction is accelerated by a certain substituent, it does not mean that it will be accelerated at all temperatures or the activation energy is decreased. A large rate difference can exist between two members of an isokinetic series only if the experimental temperature is far from $\beta$. This also mean that for such reactions when the temperature of the system in adjusted to near $\beta$, the rates may be either too fast or too slow to be measured.

Leffler & Grundwald grouped the reactions into two broad categories on the basis of isokinetic and $\rho\sigma$ relationships. In the first category $\Delta H^{\neq}$ shows linear correlation with $\Delta S$. They also show linear correlation with $\sigma$. Such reactions conform to both Hammett & isokinetic relationship. In the second type $\Delta H^{\neq}$ and $\Delta S^{\neq}$ do not show linear correlation either with each other or with σ. Here the fit of Hammett relationship is unlikely.

### 1.1.7 Structural effects

A lot of efforts have been reported for the correlating the structure and reactivity of organic compounds[9,16-23] . The study of structural effects on rate of reaction is one of the important tools to elucidate the mechanism of reactions. The influence of a substituent on reactivity is mainly due to its polar, steric and resonance effects. A number of correlations have been formulated to explain the structural effect on reactivity. In all cases a linear free energy relationship can be observed in a series of related reactions where the free energy of activation or reaction varies linearly with certain property of structural factors. Examples for such linear relationships are Hammett equation,[20] Taft equation[21], Bronsted Catalytic law,[24]. Grundwald – Winstein relationship[25] etc.

### Hammett equation

Hammett[20] in 1937 proposed a quantitative relationship to account for the electronic effect of substituents on molecular reactivity. According to Hammett the rate constants (k) or equilibrium constants

(K) of meta and para substituted benzene derivatives are related with those of unsubstituted compounds in terms two parameters.

$\sigma$ and $\rho$ as

$$\log k = \log k_0 + \sigma\rho . \quad \ldots\ldots\ldots \quad (1\text{-}32)$$

and $$\log K = \log K_0 + \sigma\rho \quad \ldots\ldots\ldots \quad (1\text{-}33)$$

where $\sigma$ is called the substituent constant which is a characteristic of the substituent and is independent of the nature of the reaction. $\rho$ is the reaction constant which is a measure of the susceptibility of the reaction to the electronic effect of the substituent and is reaction dependent. As a standard, an arbitrary value of unity is fixed for $\rho$ for the equilibrium constant of ionisation of benzoic acid and substituted benzoic acid in aqueous solution at $25^0$C under 1 atmosphere pressure. Then substituent constant $\sigma$ becomes equal to the ratio of logarithm of dissociation constant of substituted benzoic acid to that of unsubsituted benzoic acid. It is therefore evident that for electron withdrawing groups which enhance the rate of dissociation, have a +ve value of $\sigma$ and for electron donating groups, which retard ionisation, have a –ve value of $\sigma$. Since the effect of substituent is different when it is in meta and para position, two set of values are assigned for $\sigma$, viz. $\sigma_m$ and $\sigma_{p.}$

The reaction constant ρ is determined from the slope of the plot of log (k/ko) versus σ for the reaction of a series of substituents. A linear correlation for various substituents shows that the same mechanism is operating throughout the reaction series. The value of the reaction constant ρ is a measure of the susceptibility of a reaction to the electronic effect of substituents. When ρ is +ve the reaction is accelerated by electron withdrawing groups and when ρ is –ve it is accelerated by electron donating groups. Similarly a +ve value of ρ indicates a –ve charged centre in the transition state as in nucleophilic substitution and a –ve value of ρ indicates an electron deficient centre in the transition state as in electrophilic aromatic substitution. The absolute magnitude of ρ is a measure of the amount of charge developed at the reaction centre and the extend to which the substituents are able to interact with developing charge.

**Taft equation**

Taft equation[21] was introduced for reactions involving aliphatic compounds in which the steric effects of the substituents were also taken into account;

$$\log (k/k_0) = \rho^*\sigma^* + \delta E_s \qquad \ldots\ldots\ldots \qquad (1\text{-}34)$$

Here $\sigma^*$ is a measure of polar effect of the substituents and $\rho^*$ is the sensitivity of the reaction to the polar effect. $E_s$ is a measure of steric effect of the substituent and $\delta$ is a measure of susceptibility of the reaction to the steric effect. Taft studied the substituent effect on the hydrolysis reaction of ortho substituted benzoate esters catalysed by both acids and bases. The polar substituent constant $\sigma^*$ is related to rate constant of hydrolysis reaction as

$$\sigma^* = \frac{1}{2.48}\left[\log(k/k_0)_B - \log(k/k_0)_A\right] \quad \ldots\ldots\ldots\ldots \quad (1\text{-}35)$$

where A and B represent the acid and base catalysed reactions. This equation can be used to obtain the substituent constant in the ortho position. Assuming that the polar effects of acid catalysed hydrolysis are negligible, then equation (1-34) reduces to

$$\log(k/k_0) = \delta E_s \quad \ldots\ldots \quad (1\text{-}36)$$

The value of $E_s$ can be obtained by setting $\delta = 1$. Taft values for $E_s$ and $\sigma^*$ for some substituents are given in table 1.1. Taft equation is significant as it clearly seperate the steric and polar effect of the substituent, though many criticism were raised against it later.

# Table 1.1

## Hammett substituent constants (σ), polar substituent constants (σ*), and steric substituent constants ($E_s$) for common groups[16,20]

| Substituent | $\sigma_m$ | $\sigma_p$ | Substituent | σ* | $E_s$ |
|---|---|---|---|---|---|
| H | 0.00 | 0.00 | H | 0.49 | 1.24 |
| $CH_3$ | -0.07 | -0.07 | $CH_3$ | 0.00 | 0.00 |
| $C_2H_5$ | -0.04 | -0.15 | $C_2H_5$ | -0.10 | -0.07 |
| $C_6H_5$ | 0.06 | 0.02 | n-$C_3H_7$ | -0.12 | -0.36 |
| COO | 0.36 | 0.73 | n-$C_4H_9$ | -0.13 | -0.93 |
| CHO | 0.36 | 1.13 | t-$C_4H_9$ | -0.30 | -1.54 |
| CN | 0.68 | 1.00 | $C_6H_5CH_2$ | -0.22 | -0.38 |
| $NH_2$ | -0.16 | -0.66 | $(C_6H_5)_2$ CH | 0.41 | -1.76 |
| $NO_2$ | 0.71 | 0.778 | $FCH_2$ | 1.10 | -0.24 |
| OH | -0.01 | -0.36 | $ClCH_2$ | 1.05 | -0.24 |
| $OCH_3$ | 0.12 | -0.27 | $BrCH_2$ | 1.00 | -0.27 |
| F | 0.34 | 0.06 | $ICH_2$ | 0.85 | -0.37 |
| Cl | 0.37 | 0.227 | $Cl_2CH$ | 1.97 | -1.54 |
| Br | 0.39 | 0.232 | $Cl_3C$ | 2.63 | -2.06 |
| I | 0.35 | 0.276 |  |  |  |

## 1.2 Chemistry of hypochlorite

When chlorine is dissolved in water the formation of an array of chlorinating and oxidizing species are predicted[26]. The active oxidizing species are those molecules or ions in which chlorine is in +1 oxidation state. These include $Cl^+$, $OCl^-$, HOCl and $(H_2OCl)^+$. The stability of these species depend on the pH of the solution and temperature of the reaction mixture.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

In strongly acidic medium the equilibrium is forced to the left, when the reaction is largely that of chlorination with some oxidation due to the presence of small amounts of HOCl. As pH rises the equlibrium shifts towards right producing more HOCl, a more oxidative reagent. Hypochlorous acid is weak ($K = 2.8$ to $3.4 \times 10^{-8}$) and dissociate poorly at lower pH (below pH = 6)

$$HOCl \rightleftharpoons H^+ + {}^-OCl$$

As pH reaches 6 to 8, a mixture of hypochlorous acid and hypochlorite ions are largely present and the reaction is mainly that of oxidation. As pH rises above 9, HOCl is completely replaced by $OCl^-$ and the oxidation is maximum. However there is a tendency of the hypochlorite ion to disproportionate in basic solution to produce the corresponding halate ion

$3OCl^- \rightarrow 2Cl^- + ClO_3^-$

The disproportionation of $OCl^-$ is very slow at and below room temperature but very rapid at and above $75^0C$.

Sodium hypochlorite (Liquid bleach or soda bleach liquor) contains 12 to 15% available chlorine. Sodium hypochlorite can be prepared by passing $Cl_2$ gas into a solution of NaOH of suitable strength[27].

$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$

The reaction is accompanied by the rise of temperature which may result in the decomposition of NaOCl forming sodium chlorate. Consequently precaution must be taken to ensure that this temperature is not exceeded. Thus caustic soda solution is cooled before use and usually a bleach solution of low concentration is prepared. Stability of NaOCl can be increased by using gelatin.

G.H. Cady[27] reported the preparation of hypochlorite by electro chemical oxidation of halides in cold dilute solution. The hypochlorite was seperated from chloride by treatment with an amine base or an alcohol when $OCl^-$ form the chloramine (or hypochlorite ester)[29]. The later can be readly seperated and the hypochlorite released by treatment with alkali. Hydrolysis of N-halocompounds (chloramine T, bromamine-T etc.) are often employed for the in site generation of the hypohalite ions[30].

Stability of hypochlorite solution is greatly affected by heat, light, pH and presence of heavy metal cations. Maximum stability is attained with pH close to 11 and with the absence of heavy metal cation. Light decomposes $OCl^-$ faster than heat[31]. Storing in coloured bottles increases the half- life six fold. Storage temperature should not exceed 85⁰F. Above 85⁰F rate of decomposition becomes too high and available $Cl_2$ content is rapidly depleted. At about 100⁰F the formation of sodium chlorate is appreciable. Griffin and [32] Hedallen observed that at least 5% basicity is a favourable condition for the stability of NaOCl where as concentration has very little effect on stability. Presence of substances like carboxy methyl cellulose, gelatin, poly vinyl alcohol, tetra methyl ammonium chloride etc. were found to be effective stabilizers for NaOCl[33]. A fixed proportion of sucrose (0.375 parts), potassium chromate (0.100 parts) and sodium silicate, (10-25 parts) when added to NaOCl serves as good stabilizers[34] Presence of metal ions like cobalt decreases the stability of NaOCl considerably[35]. Generally about 5%

alkaline solution of NaOCl stored in dark bottle kept away from heat and light is fairly stable and used for all practical purposes.

NaOCl is a very good chlorinating and oxidizing agent This property has rendered it an effective reagent in various fields like water-treatment, textile bleaching, laundry, sanitary purpose, photograhic industry, rubber surface treatment, preservatives, antiseptic, biological field and in qualitative analysis.

NaOCl has been used for the oxidation of a variety of organic and inorganic compounds. Oxidation of alcohols, amides, phenanthrene, dithio carbomates, semicarbazide, urea, cyclic ketones, hydrazine and EDTA complexes are reported[36-41] . Cr (III) is converted to Cr(VI) while galenite is oxidised to $PbSO_4$[42] . The conversion of $Pb^{2+}$ to $Pb_3O_4$[43] is achieved with NaOCl which finds use in pigment industry. The oxidation of poisonous $CN^-$ to relatively harmless[44] $CNO^-$ has rendered it a very useful reagent is photography and also in waste water treatment of many plating industries. It is also used for the oxidation of sulphides to polysulphides[45]. In coal industry it is used for desulphurisation and in rubber industry for surface treatment to produce improved wear, resistance and adhesion.

In addition, NaOCl oxidises compounds like amino acids, sugars, starch cellulose[46-50] etc. Oxidation of casava starch by hypochlorite to oxy starch makes it less viscous with improved light transmittance and hence more suited for paper industry. Nylon-60 chlorination is reported to develop fire-proofing quality[51].

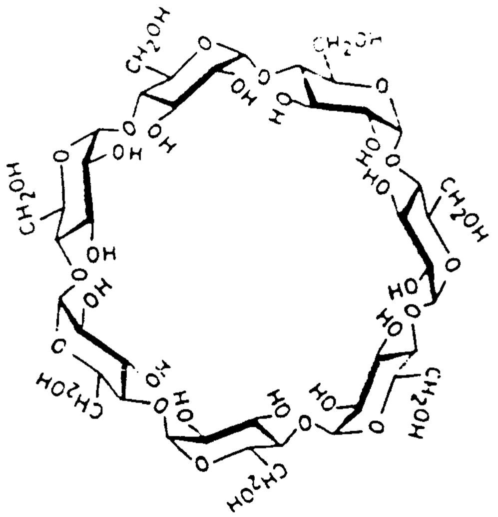
The reaction of NaOCl with hydrazine provides a method for the estimation of hypochlorite. Usually a solution of hydrazine sulphate is used and the end point is detected by a spot-test on KI starch paper. The hydrazine is converted to $N_2$ and some free acid is liberated. However care should be taken to see that the solution is alkaline throughout. A solution of NaOCl at pH = 5 when allowed to react at $21^0C$ for 20 minutes is reported to have brought out an effective seperation of mixtures of Co & Ni[52]. 99% Cobalt is removed by this way. Some colour reactions of NaOCl are also useful in qualitative[53] analysis. Thus compounds which contain $-NH_2$ or $-NH$ group produce a deep blue colouration with phenol and NaOCl. Nitro compounds also show the same colour change. There is the production of nitrophenol which in its oxime form reacts with excess phenol and gets converted to para benzo quinone oxy phenyl imide and hence the colour. HCN, $CN^-$, carbyl amine and $CNS^-$ also answer the same colour reaction. However instead of phenol when quinone reacts with NaOCl, instead of blue colour, a dark yellow crystalline compound (1,4 benzo quinone chlorimide) results. It has to be noted however that some amines like di isobutyl amine, dipropyl amine etc do not answer this colour reaction.

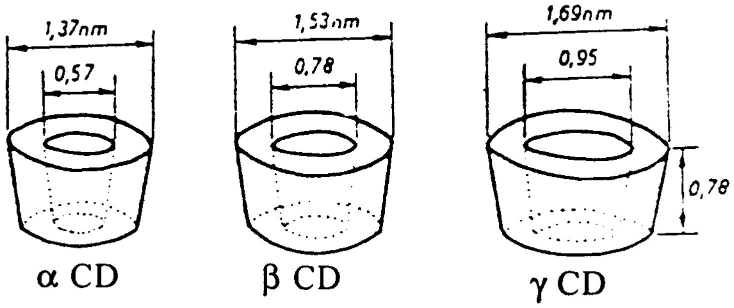
NaOCl function as a preservative. Melon and some fishes could be preserved for longer time when dipped in about 0.6% solution of NaOCl for 5 minutes. When mixed with soap NaOCl in found to be very effective in laundry also. In water and waste water treatment, NaOCl function mainly as a steriliser and $CN^-$ remover. The algae and sulphides present in water can be removed effectively.

NaOCl is widely used in biological field. Boron hypochlorite solution is a very good anticeptic[54]. Its antiseptic action is much greater than that of tincture of $I_2$. It is superior to $I_2$ because $I_2$ has caustic effect on tissues. It is reported that when a solution of NaOCl is added into pus, the bacteria present are weakened, rendered less virulent and the toxins are destroyed by oxidation. It is also reported that NaOCl is very effective in the seperation particles of narcotic tissue[55] (hair, epithelial scarps, coagulated serum etc.). The anticeptic activity of NaOCl last for long and it does not irritate the living tissues. The bacterial activity of NaOCl is reported to be very effective to prevent the growth of bacteria in tuber culosis[56]. Solution of NaOCl containing about 15% available $Cl_2$ when allowed to react for one hour prevented the growth of bacteria completely in the sputum. In addition to its bacterial, fungicidal, anticeptic and anti-microbial activities, it is reported to be a carcinogen in-activator also. Milk and water containing moderate amounts of NaOCl when administered to guinea pigs, an increase in their growth rate is reported[57]. Dental preparations containing N-monochloro glycine at a pH of 9-11 are useful in the prevention of calculus and the dissolution of dental plaque[58,59]. N-monochloroglycine is produced in situ by dissolving 1% glycine hydrochloride in 0.5% NaOCl and adding $Na_2CO_3$ to pH=11. NaOCl is also used for the septoro Nodorum control on wheat.

## 1.3 Chemistry of cyclodextrins

Cyclodextrins or cyclo amlyloses, first prepared and isolated by Schardinger in 1903, are oligosaccharides which can act as host molecules to form inclusion complexes with a large variety of guest moelcules in solid state as well as in solution[60,61]. Cyclodextins are made up of 6,7,8....(D+) glucopyranose units connected through 1,4 linkages to form a large ring and known as α, β, γ ...... cyclodextrins respectively. The three CDs have the shape of a hollow truncated cone (a toroide) of height 7.9 ± $0.1A^0$ which represents the width of the amylose unit [62,63]. The diameter of the cavity depends on the number of amylose units. The inner diameters are $0.57A^0$, $.78A^0$ and $0.96A^0$ respectively for α, β, γ cyclodextrins. The outer diameters are $13.7A^0$, $15.3A^0$ and $16.9A^0$ respectively. All the –OH groups of CDs are projected outwards in such a way that the primary –OH groups projecting from the narrow side of the cones and secondary –OH groups from the wide side. This makes the inside of the cone non- polar and hydrophobic than outside which is [62-65] polar. Just like carbohydrates, CDs are soluble in water and the cavities are generally trapped with water molecules. But since inside of the cones are less polar, the organic guest molecules easily displace water and form inclusion complexes. The primary requirement for inclusion of a guest molecule within the CD cavity is that the size of the molecule fits within the cavity. If the guest molecule is too small it may go through the bottom hole. If the size of the molecule is suitable then hydrogen bond network may be continued within the cavity through the open ends of the toroide and form a hydration sheet around the guest molecule. Thus CD form 1:1 cage complexes with many guest molecules. Since the cavities of α, β & γCDs are of different sizes, a large varieties of guest molecules can form inclusion complexes with CDs. CDs also form channel type complexes in which the host molecules are attached on top of each other like coins in a row[62]. For example α form of CD form cage complexes with acetic, propionic and butyric acids, but channel complexes with valeric and higher carboxylic acids.





CDs can form inclusion complexes with a variety of compounds including polar reagents such as acids, amines, small ions such as $ClO_4^-$ $SCN^-$ and halogen anions,[66] non polar aliphatic hydrocarbons and even rare gases. Inclusion can be formed either in solution or in crystalline state. Water is usually the solvent although other solvents such as DMSO, DMF etc are also used[67].

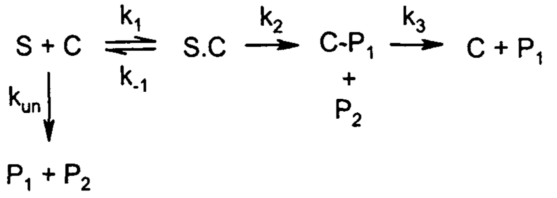
### 1.3.1 Catalysis by cyclodextrins

Many investigations of CD catalysed reactions showed that the reaction rate is not a linear function of CD concentration[68]. But it approaches a maximum value asymptotically with an increase of CD concentration. Competative inhibition was found by the addition of organic compounds which competatively bind in the CD cavity[68,69]. CD catalysed reactions show many of the kinetic features shown by enzymatic reactions including satuaration'[68,70], stereospecificity[68], substrate-catalyst complex formation and competative inhibition. Thus CDs can serve as models of certain enzymes.

CD catalysed reactions can be classified into two categories – covalent catalysis in which the CDs catalyse the reaction via the formation of a covalent intermediate and noncovalent catalysis in which CDs provide their cavities as a polar or sterically restricted reaction fields wihout formation of any covalent intermediate.

### 1.3.2 Covalent catalysis by CD

Covalent catalysis by cyclodextrins proceed as shown in scheme 1, where S and S.C. represent the substrate and the inclusion complex respectively, C-$P_1$ is the covalent intermediate, $P_1$ & $P_2$ are the final products and $k_1$, $k_{-1}$, $k_2$, $k_{-3}$ $k_{un}$, as the rate constants for various processes indicated.



**Scheme I**

Thus the first step of covalent catalysis by CD is the complex formation between CD and the substrate. The second step is the nucleophilic attack by one of the hydroxyl groups of CD on the substrate resulting in a covalent intermediate (C-$P_1$) and $P_2$. This covalent intermediate is converted to the final product $P_1$ and the CD is regenerated. The formation of the covalent C-$P_1$ intermediate has been proved by the spectroscopic detection of acyl-cyclodextrin in the hydrolysis of phenyl benzoate catalysed by CD[70] In the formation of complex (S.C), the phenyl portion of the substrate is included in CD cavity from the wide secondary hydroxyl group side. Then cleavage of phenyl esters proceed through the nucelophilic attack by a secondary hydroxyl group on the carbonyl carbon atom of the substrate. Both α and β CDs accelerate the cleavage of phenyl esters.

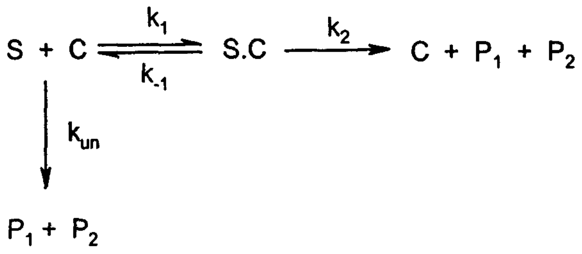
The acceleration factor ($k_2/k_{un}$) vary widely from 300 fold for m-nitrophenyl acetate to 1.1 fold for para t-butyl phenyl acetate.

Studies of covalent catalysis by CDs in the hydrolysis of esters[70,71], amides[72-75] and organo phosphates[69,76-78] led to the following conclusions.

a) Meta substituted phenyl esters show larger acceleration by CDs than corresponding para compounds.
b) Meta/para specificity is larger for esters of more bulky substituents
c) The reactivity of unsubstituted esters is between that of meta and para substituted compounds.

### 1.3.3 Non covalent catalysis by cyclodextrin

In non covalent catalysis CD simply provide an apolar and sterically restricted cavity for the included substrate which can then serve as reaction medium resulting in acceleration of the reaction. The non- covalent catalysis by CD proceeds as in scheme 2.



Scheme 2

The scheme 2 is identical with scheme 1 for covalent catalysis except the de-acylation step

Non covalent catalysis by CDs are attributed to

a) microsolvent effect due to the apolar character of the cyclodextrin cavity

b) Conformational effects due to the geometric requirements of inclusion.

Non covalent catalysis by CDs show the following characteristics

a) The catalytic rate constant $k_2$ (just as the uncatalystic rate constant $k_{un}$) follows the Hammett relationship

b) The rate constant $k_2$ is independent of pH of the medium

c) The position of substituents (ortho, meta, para) hardly affects the acceleration ($k_2/k_{un}$). In covalent catalysis, however, the stereospecificity is marked.

### 1.3.4 Significance of cyclodextrins

CDs are widely used as inclusion catalysts for reactions involving a large vareities of substrate molecule[64]. CDs are also extensively used in the field of pharmaceuticals, food, cosmetics, chemical industry and in analytical field (chromatography). The advantage of CDs over other reagents and catalysts are that the former is soluble in water, non- toxic (although there are exceptions), ecologically friendly, comparatively cheaper in cost, and now easily available. Because of their non toxic nature they are now industrially used to encapsulate foods & drugs[71].CDs are superior to enzymes in their stereospecificity and activity which are unaffected by the change in the acidity of the medium. More than 100 different CD derivatives are now available to suit the requirements in various fields such as food industry, textile industry drug industry, diagnostic field, analytical chemistry etc.

The first observation made in respect of the α-CD catalysed reaction was that of the hydrolysis ethyl para chloromandalate[80]. The addition of $1.32 \times 10^{-3}$M of CD accelerated its hydrolysis by 1.38 fold.

Study of chlorination of aromatic compounds by HOCl showed that CDs exihibit remarkable ortho-para selectivity. Thus in the chlorination of anisole by HOCl,[81] p-.chlorination take place almost exclusively in presence of CD with 5.6 times faster than free anisole. β-CD catalyses the electrophilic allylation of 2-methyl hydro naphthoquinone with allyl or crotyl bromide in aqueous medium giving the corresponding Vit. $K_1$ or Vit.$K_2$ analog in excellent yield. In absence of βCD the yeild was poor and contaminated with considerable amounts of undesired products[82].

In addition to catalysis by CDs, complexes of CDs with drugs, insecticides, dyes[83-87] etc. exhibit many kinds of physiochemical and biochemical features, which are not shown in the absence of CDs. For example the inclusion complex of a drug N-(2,3-dimethyl cyclo hexyl)-N-methyl anthranilic acid with CD formed by heating the drug and CD at $60^0$C is highly soluble in water and thus is suitable for injection[88]. The clatharates of resmethrin with CD is about 1.5 times more effective in killing cockroaches than resmethrin[89] itself. Increase in solubility of guest molecules in water by CDs makes it possible to carry out some reactions using these compounds in aqueous solution. For example the fluorescent labelling of proteins and the plasma membrane by dansyl chloride can be done only by using suspension of an organic solvent-water mixture, because of scant solubility of dansyl chloride in water. However β CD- dansyl chloride complex can effectively label protein and plasma membrane in aqueous solution without any organic solvents[90,91].

## 1.4 Phase Transfer Catalysis

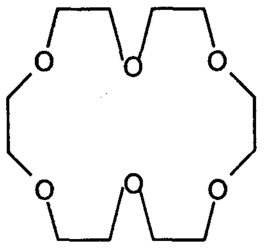
Phase transfer catalysis(PTC)[92-94] has emerged as an excellent technique in the hands of synthetic chemists and physical organic chemists to carry out two phase reactions involving lypophilic organic substrates and hydrophilic reagents. In this method one can select a phase transfer agent that, when used in catalytic quantities, can bring one of the reactants from its normal phase into the normal phase of the other reactant in a more reactive form so that high reaction rates are observed[95]. Such reactions are very slow or not at all take place in the absence of the phase transfer catalyst. For example simply heating and stirring a two phase mixture of an alkyl chloride, 1-chloro octane with aqueous sodium cyanide leads to essentially zero yield of 1-cyano octane even after several days of reaction time. But if a small amount of an appropriate quaternary ammonium salt is added then rapid formation of 1-cyano octane is observed in 100% yield within 2 hours.

The phase transfer catalysts used commonly are quaternary ammonium salts[96], macrocyclic ethers[97] (crown ethers) and macrobicyclic ethers[98] (cryptates). Polyethylene glycols[99,100] are also considered now as PT reagents which can complex with salts of alkali metals and transfer them into organic phase.

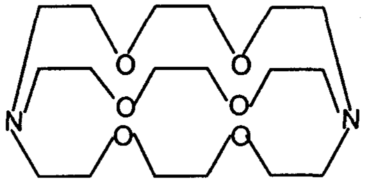
There are some essential requirements for a PT reagent to be used in two phase reactions. The catalyst must be cationic and should have the ability to carry the anion of the reactant from its normal aqueous phase to the organic phase of the other reactant. For a catalyst to be lypophilic and well partitioned in the organic phase, it must have enough organic structure. Moreover the catalyst-anion binding should be loose so that the transferred reagent would be in a more reactive form in the organic phase. Besides these requirements, several additional characteristics of the PT catalyst need to be considered. These include the stability of the catalyst under the reaction conditions, ease of preparation or availability of the catalyst, cost, ease of removal or recovery, selectivity in catalytic activity etc.

Among quaternary salts ammonium, phosphonium, arsonium, antimonium and bismuthonium salts are known to be PT catalysts[101-103]. However quaternary ammonium and phosphonium salts are widely used. Quaternary ammonium salts have the general formula $R_4N^+X^-$ where $X^-$ is usually the halide ion. It has been found that R-groups consisting of alkyl groups with sufficient organic structure are better PT catalysts. Quaternary salts of the type $R(R^1_3)\ N^+X^-$ are frequently used because of their ease of preparation and commercial availability. The important quaternary ammonium salts are tricapryl methyl ammonium bromide, sold under the trade name Aliquat 336, Benzyl triethyl ammonium chloride (BTEAC), Trioctyl methyl ammonium chloride (starks catalyst) and tetrabutyl ammonium hydrogen sulphate (TBAHS).

Among macrocyclic ether the commonly used PT catalytst is 18-crown-6. The macrobicyclic ether [2,2,2] cryptate is most common among these categories.

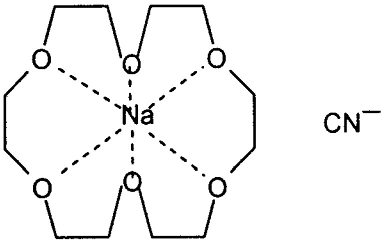


18-crown-6



[2,2,2]cryptate

The cavity of these crown ethers and cryptates can accommodate the cationic part of the reagent of suitable size (especially alkali & alkaline earth metal cations) to form a complex (I) which is organophilic and dissolve homogeneously in organic solvent.

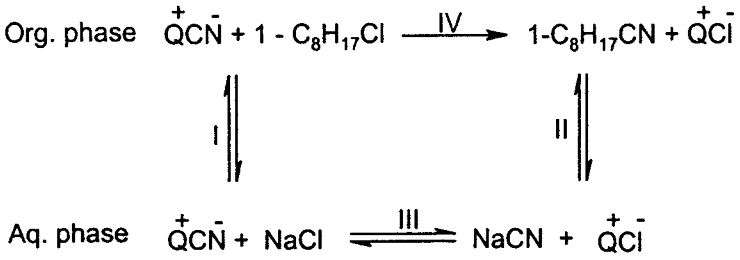


Crown ether complex

The mechanism of PT catalysed reaction using quaternary ammonium salt can be illustrated for the reaction of 1-chlorooctane with NaCN[104]. When the two mixtures are stirred and kept together for days we will not be getting any yield. The $Na^+$ ions are extensively solvated in aqueous phase and cannot cross over into the organic phase with $CN^-$ ions as no such solvation is possible in organic phase. But when a small amount of quaternary ammonium salt is added, the product is quantitatively formed within 2 hours. Here, in contrast to $Na^+$ ion, the quaternary ammonium ion $R_4N^+$, due to the large R group, is poorly solvated in water and prefer organic solvents. Hence $Na^+$ ion will remain in aqueous phase and $Q^+$ ion cross over the inter phase and carry the $CN^-$ ion into the organic phase. Thus an equilibrium is formed in respect of $Q^+CN^-$ in the two phases (equlibrium I). The anion $CN^-$ reacts with 1-chloro octane in organic phase to give the products 1-cyano octane and $Cl^-$ ion. This $Cl^-$

ion get carried to the aqueous phase by $Q^+$ (equilibrium II). The equilibrium III take place entirely in aqueous phase which regenerates $Q^+CN^-$. All equilibria formed are faster than the actual reaction IV which is the rate determining step.

$$1\text{-}C_8H_{17}Cl + NaCN \xrightarrow{Q^+Cl^-} 1\text{-}C_8H_{17}CN + NaCl$$



The $Q^+$ shuttle forth and back till the process is completed.

### Advantages of PTC over conventional method

PT catalysed reaction is superior to conventional procedure due to a number of reasons

1. Expensive anhydrous or aprotic solvents not required
2. Improved reaction rate
3. Lower reaction temperature
4. Easier to work up and easier for purification of products. Since the melting point of quaternary salts are high, the products of the reaction can be distilled off from the quaternary salt.

5. Increased yield of products through the suppression of side reactions.

6. Modification of selectivity

7. Reactions which otherwise never takeplace, can be carried out.

The phase transfer method has been shown to be applicable to awide variety of reactions such as substitution[105-108], elimination[109-111], alkylation[112-115], condensation[116-119], addition[120-124], hydrolysis[125-127], oxidation[128-130], reduction[131-134], esterification[135,136], rearrangement[137,138] etc.

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

## CHAPTER II

# REVIEW AND SCOPE OF THE PRESENT WORK

## 2.1 REVIEW OF THE PRESENT WORK

### 2.1.1 Kinetics of Oxidation of Benzaldehyde

Kinetic and mechanistic studies on the oxidation of benzaldehydes by various oxidants have been cited in literature.

The kinetics of cerium (IV) oxidation benzaldehyde were studied in 85% aqueous acetic acid by Wiberg & Ford[139]. The formation of a 1:1 benzaldehyde-ceric ion complex followed by an acid catalysed decomposition was predicted. A benzoyl radical was formed as the intermediate. The reaction was found to give a kinetic isotope effect. The substituent attached to the phenyl ring retarded the rate irrespective of the sign of the Hammett $\sigma$ value.

Kinetics of the oxidation of para and meta substituted benzaldehydes by pyridinium chlorochromate have been studied in aqueous acetic acid medium[140]. The reaction was first order each in substrate, oxidant and $H^+$ concentrations. Electron releasing substituents retard and electron withdrawing substituents enhance the rate. Addition of monomer to the reaction mixture gave a polymer. Activation parameters have been computed and suitable mechanism has been postulated.

Elango and Karunakaran[141] have reported the kinetics of oxidation of substituted benzaldehydes by quinolinium chlorochromate in aqueous acetic acid medium in presence of perchloric acid. The reaction was $I^{st}$ order w.r.t. the aldehyde, oxidant and $H^+$ concentrations. The validity of Hammett equation was also tested.

Balasubramanian[142] *et al* studied the oxidation of benzaldehydes by imidazolium dichromate in aqueous acetic acid medium. The order w.r.t. the substrate, oxidant and $[H^+]$ were found to be unity. The rate increased with increase of percentage of acetic acid. The reaction doesn't induce polymerisation with acrylonitrile indicating the absence of free radical pathway. The retardation of rate by the addition of $Mn^{2+}$ ions confirm a two electron transfer process involved in the reaction. Electron withdrawing substituents enhance and electron donating substituents retard the rate. Activation parameters have been computed and a mechanism has been proposed.

Oxidation of p-methoxy benzaldehyde and salicylaldehyde by N-sodio N-chlorobenzene sulphonamide (chloramine-B) have been reported in acid medium[143]. The rate shows a first order dependence on [CAB] and fractional order on [aldehyde]. The rate increased with concentration of HCl showing first order dependence in $[H^+]$. Variation of ionic strength and change in dielectric constant of the medium has no significant effect on reaction rate. Thermodynamic parameters were evaluated.

Kalyan Banerji[144] *et al* have reported the kinetics and mechanism of oxidation of substituted benzaldehydes by Bis(2,$2^1$-bipyridylyl) Copper (II) Permanganate (BBCP) in aqueous acetic acid. The reaction is first order w.r.t. BBCP. Michaelis-menten type kinetics were observed w.r.t. aldehyde concentration. The oxidation of PhCDO indicated the presence of substantial kinetic isotope effect. The rates of oxidation of meta & para substituted benzaldehydes were correlated in terms of Charton's triparametric LDR equation where as the oxidation of ortho substituted benzaldehydes were correlated with four parametric LDRS equation. The reaction is subjected to steric acceleration when ortho substituents are present.

Rangappa *et al*[145] investigated the kinetics of chloramine-T(CAT) oxidation of cinnamaldehyde in acid medium and in alkaline medium catalysed by $OsO_4$. In acid medium Michaelis-Menten kinetics is observed with a first order dependence of rate on [CAT] and fractional order in [aldehyde] which becomes zero at higher aldehyde concentrations. Rate dependence on $[H^+]$ varies from inverse fractional to fractional order. In alkaline medium the reaction is first order each in [CAT] and [Os(VIII)] and inverse first order in $[OH^-]$. Solvent isotope effect, effect of added chloride ion and varying ionic strength and dielectric constant of the medium have been investigated. Activation parameters have been computed.

Panigrahi & Misra[146] studied the periodate oxidation of bezaldehydes catalysed by $OsO_4$ in alkaline medium when it was observed that at a particular $[OH^-]$ all the substituted benzaldehydes with electron releasing and electron groups reacted faster than the unsubstituted aldehyde and where the Hammett $\rho\sigma$ relationship showed a break down. However as $[OH^-]$ was increased, a linearity in the plot of $\log k_{obs}$ versus $\sigma$ was noted.

Manikyamba and Raghunatha Rao[147] reported the kinetics of oxidation of benzaldehyde and substituted benzaldehydes by iodate in aq.

methanol in presence of sulphuric acid. The reaction exhibit a first order dependence on [iodate] and [benzaldehyde]. Increase of percentage of methanol increases the rate of oxidation. These is no evidence for stable complex formation between oxidant and the substrate. The plot of log $k_{obs}$ versus Hammett substituent constant is a curve suggesting a continuous change in the transition state. A free radical mechanism consistent with the attack of $HIO_3$ on protonated benzaldehyde to give an adduct in the slow step which further gets oxidised to benzoic acid in the subsequent steps is proposed.

Ru(III) catalysed oxidation of benzaldehydes and substituted benzaldehydes by acid bromate was reported[148] in literature. The reaction was first order each in [substrate], [Ru(III)], independent of acid and zero order w.r.t. [bromate]. The reaction indicates acceleration in rate with increase in percentage of acetic acid in the reaction medium.

Ali and Upadhyay[149] reported the kinetics and mechanism of Ru(III) catalysed and uncatalysed oxidation of hydroxy benzaldehyde by CAT in $HClO_4$ medium containing 20% methanol. The order w.r.t. CAT was found to be unity whereas that in substrate and acid concentrations decreases from unity. The corresponding carboxylic acids were obtained as the product.

Radhakrishnamurthy and Sahu[150] have studied the kinetics of Os(VIII) catalysed oxidation of benzaldehyde and substituted benzaldehydes in alkaline medium and in aqueous ter-butanol medium. The loss of $OH^-$ by single electron transfer in the transition state has been proposed. Lucchi[151] made the first kinetic study of the chromic acid oxidation of a series of aromatic aldehydes in acetic acid solution using $H_2SO_4$ as catalyst. The reaction was first order in aldehyde and Cr(VI) concentrations. The electron withdrawing groups were found to facilitate the reaction.

Kinetic studies on the chromic acid oxidation of benzaldehydes were also reported by Wiberg and Mill[152] and by Graham & Westheimer[153]. In aq. $H_2SO_4$ solution the following rate law has been proposed by them.

$$\nu = K_a[RCHO][HCrO_4]\,[H^+] + K_b\,[RCHO]\,[HCrO_4^-]\,[H^+]^2$$

where as in aq. acetic acid solution the rate of oxidation is proportional to the first power of Hammett acidity function.

$$\nu = k[RHO][HCrO_4]h_o$$

The reaction shows kinetic isotope effect indicating the cleavage of carbon-hydrogen bond in the rate determining step.

Kinetic studies of the oxidation of benzaldehyde with $KMnO_4$ in alkaline medium by Tompkin[154] revealed that the rate increase linearly with increase of $[OH^-]$ over a limited range of concentration.

Wiberg *et al*[155] reported the kinetic studies of the base catalysed $KMnO_4$ oxidation of benzaldehyde. The rate is proportional to the first power of aldehyde and permanganate concentrations and there are terms that are zero order, first order, and second order in hydroxide ion. The reaction shows anisotope effect. The possible mechanism of the reaction was discussed. Both one and two electron processes are possible. The benzaldehyde hydrate dianion has a remarkably small C-H bond energy.

The kinetics of oxidation of benzaldehydes to benzoic acids by quinolinium dichromate in dimethyl formamide containing HCl was reported[156]. Electron releasing groups accelerated the reaction. The reaction constant $\rho$ was $-0.90$. The initial reaction involved a rate determining H-abstraction as suggested by an isotope effect of 5.14 at 333K.

Kinetics of oxidation benzaldehyde and substituted benzaldehydes with ozone in acetic acid medium was also reported[157]. Ozone is shown to react with benzaldehyde attacking both the aromatic ring and the C-H bond of the carbonyl group. Preferential attack on the Carbonyl group was observed for aldehydes containing electron withdrawing groups on the aromatic ring. The oxidation of the Carbonyl group was proposed to be through a radical chain mechanism.

Varsha Benzal *et al*[158] investigated the kinetics & mechanism of oxidation benzaldehydes by oxo(salen) manganese(V) complexes. The oxidation proceed via either a hydride ion transfer or a hydrogen atom transfer from the aldehyde to the Mn(V) complex.

Evidence of an intermediate esterification was reported during the permanganate oxidation of aromatic aldehydes in perchloric acid medium[159]. The reaction was first order w.r.t. permanganate concentration, but of complex order in [aldehyde] as well as [$H^+$]. The influence of substituents on reaction rate and mechanism has also been studied in 40% (V/V) aqueous acetic acid. Thermodynamic values associated with 1:1 intermediate ester formation and the activation parameters associated with the disproportionation steps involved have been evaluated.

### 2.1.2 Review of kinetics of oxidation using hypochlorite

Keith Bowden & T.D. Radhakrishnan Nair[160] reported the kinetic studies on the chlorination of a series of p-substituted acetophenones with hypochlorite in water as well in aq. dioxane medium. The acceleration of rate of p-substituted acetophenones with the use of inclusion catalysts, viz. cyclodextrins were also investigated. The Hammett reaction constants (ρ) were determined both in the absence and presence of cyclodextrins.

Nwaukwa and Keehn[161] reported the use of hypochlorite as a mild oxidant which can be conveniently used to oxidise alcohols to ketones in excellent yield. Ethers are oxidised to esters though only in moderate yield. Kinetics of oxidation of s-butyl alcohol by t-butyl hypochlorite have been investigated by Kudesia & Sharma[162]. The reaction is first order each with respect to the substrate and the oxidant. The activation parameters have been evaluated. The effect of pH and added metal chlorides have also been investigated. A mechanism involving ester formation have been proposed. The solvent isotope effect suggest the removal of a proton in the rate determining step.

Action of aqueous inorganic hypochlorite on several benzyl alcohols has been studied by Cal Y. Meyers.[163] Benzaldehyde and ortho methoxybenzaldehyde were thus obtained in good yield from their respective alcohols. However ortho hydroxy benzyl alcohol under identical conditions provided no aromatic aldehyde but was chlorinated in the nucleus with a concurrent elimination of formaldehyde. Possible mechanisms are considered.

Guthrie and Cossar[164] studied the kinetics of halogenation of ketones by hypochlorite in alkaline medium. The $pk_a$ values of simple ketones were determined from the kinetic data.

Kinetics and mechanism of hypochlorite oxidation of D-xylose and glucoronoxylan in pH range 2-12 was reported by Jain, Singh & Gupta[165]. Xylose and glucoronoxylan isolated from bamboo were allowed to react with NaOCl at pH 2-12. The rate increased with increase of [oxidant], [sub.] and temperature. The highest rate was noted at pH = 7. At the pH of 6-12 all the reactions fitted zero order rate equation. But at pH 2-4 the rate of available chlorine concentration followed a second order rate equation.

Vladimir *et al*[166] have reported the kinetics of reaction involved in the oxidation of free and complexed $CN^-$ by NaOCl. This is suggested as a method for elimination of $CN^-$ from waste water of electroplating industry. Kinetics of oxidation of galenite by NaOCl was studied by Vasilev & Godishnik[167]. Pure galenite ground in the form of parallelopipeds was allowed to react with solutions containing 40 gms. NaOCl per litre and 20gm of NaOH per litre in the temp. range of 20-80$^0$C. The mechanism proposed suggested the adsorption of $OCl^-$ on the galenite. The products are $PbO_2$ and $SO_4^{2-}$.

Vasilev and Godishnik[168] also reported the oxidation of rhenium disulphide by NaOCl. The reaction was carried and at a controlled temperature in glass containers with much stirring. The products of oxidation of $ReS_2$ were $ReO_4$ and $SO_4^{2-}$. The temperature coefficient was reported to be 13.3, and the apparent activation energy was 5.078 kcals/mole. The rate constant decreased with increase of pH. The proposed mechanism involve the adsorption of $OCl^-$ on the activated $ReS_2$. The $ReS_2$ interacts with adsorbed $OCl^-$ with the formation of an activated complex which decompose to give the products.

The oxidation of molybdenite solution to molybdenate by NaOCl in alkaline medium was also reported[169]. The temperature coefficient of the reaction in the range 20-80$^0$C is approximately 1.5.Rate of Oxidation of molybdenite is directly proportional to the concentration of NaOCl.

Kalinina *et al*[170] reported the oxidation of Mn(II) Sulphate to $MnO_4^-$ by $OCl^-$ and $OBr^-$ in presence of Iridium chlorocompounds as catalysts. $K_3IrCl_6$ and $K_2IrCl_6$ catalyse the oxidation. Ir (III) is oxidised to Ir(IV) which form an activated complex with hypohalite ion. The reaction of this activated complex with $MnO(OH)_2$ is the rate determining step. $MnO(OH)_2$ is oxidised to $MnO_4^{2-}$ and finally to $MnO_4^-$. The reaction is very fast. Kinetics of the oxidation of $MnO_4^{2-}$ by $OCl^-$ has been spectrophotometrically studied by Zakarav *et al*[171]. Activation energies with Cu and Co catalysts are also reported.

Kinetics and mechanism of ethanol amine chlorination was investigated[172]. The reaction was carried out at high pH. Variation of ionic strength has no effect on the rate. The rate with respect to the concentration of oxidant, $OH^-$ and amine show different behaviour at different stages. A reaction mechanism compatible with experimental results was suggested.

Stasiak[173] reported the oxidation of phenols by NaOCl. The oxidation of resorcinol was the fastest followed by pyrogallol and pyrocatechol where as those of α and β naphthols are very difficult. α & β naphthols required a very high concentration of the oxidant. This method can be used for the purification of waste water containing phenolic impurities. The final products of oxidation of phenols are the corresponding carboxylic acids.

Karayannis[174] studied the kinetics of the reaction of phenol and NaOCl as a side reaction in a urea-phenol-hypochlorite system. He suggested a kinetic method for determining $OCl^-$ and $Cl^-$ concentrations in commercial bleach. The kinetics of the reaction of phenol and $OCl^-$ with disulformin was reported by Rashkovan *et al*[175]. The reaction was zero order in $[OCl^-]$ and [phenol] but first order is [disulformin]. The oxidation of luminol by NaOCl was studied spectrophotometrically over a range of pH and concentrations[176]. The limiting stage in the stepwise oxidation was bimolecular two electron oxidation by $OCl^-$ to give the diazoquinone. At pH <9 an unstable complex of diazoquinone and NaOCl was formed which rapidly underwent further reactions. Oxidation of luminol by alkaline hypochlorite was studied by stopped flow technique by Isacson *et al*[177]. The rate of decay of light emission was analysed using first order kinetics.

Churganova and Tumanova[178] investigated the kinetics of the reaction between ethanol and sodium hypochlorite at different pH of 2.5, 6 and 7 in phosphate buffer and at temperatures 25, 35 and 50$^0$C. The reaction rate passed through a minimum with increase of pH. Oxidation of primary alcohols[179] with NaOCl was also studied by the same authers at 25$^0$C and at different pH values. Lok and Hall[180] have reported the catalytic oxidation of alcohols and aldehydes by NaOCl in alkaline medium with catalysts $NiCl_2$ $6H_2O$ or $CoCl_26H_2O$. The product was carboxylic acid. The kinetics and mechanism of the oxidation of poly vinyl alcohol by NaOCl have been investigated by Amin, Wadekkar and Mehta[181]. The oxidation was first order in $[OCl^-]$. Maximum rate was observed at pH 8.5. A mechanism based on the –OH group ionisation was proposed to explain the effect of pH on rate of oxidation.

The effect of hypochlorite on cotton was studied by Crossley[182]. Influence of $[H^+]$ on the mercerization, bleaching and some problems of cotton industry are dealt with. Reaction of sodium hypochlorite with cotton cellulose was described by Gregov and Tumanova[183]. The bleaching rates of cotton cellulose, the rates of its molecular weight decrease and the rates of the –COOH group formation showed that the oxidation of cellulose involved participation of both $OCl^-$ and HOCl molecules depending on the solution pH. At lower pH values, the oxidation of secondary –OH group and the ring opening predominated over the oxidation of the $-CH_2OH$ group. At pH = 8 the vicinal secondary –OH groups were oxidised to >CO group which enolised and underwent

1,2 diol cleavage. Kinetics of oxidation of cellulose and glucose by NaOCl have been studied by the same authers. The rate constant, $E_a$ and other thermodynamic constants were evaluated. There is a linear relationship between $E_a$ of oxidation of cellulose and glucose. Kinetics and mechanism of the oxidation of starch and its derivatives by NaOCl and $Cl_2$ are reported[184]. The oxidation of starch in buffered system was highest at pH = 7. The –OH groups of the starch take an active part in the oxidation rate which decreased when C-2 and C-3 hydroxy groups were blocked. Isotope effect is also studied.

Lawless and Searle[185] investigated the kinetics of the reaction between $PH_3$ and NaOCl in alkaline medium. The pH was maintained at 12-13 and the rate expression proposed is $-d(NaOCl)/dt = k[PH_3][NaOCl]/[OH^-]$.

The net reaction is $PH_3 + 2NaOCl \rightarrow H_3PO_2 + 2NaCl$

Reaction between NaOCl and $Na_2SO_3$ was studied by flow thermal method by Srivastava, Nigam and Goyal[186]. The kinetics of the reaction was studied at various temperatures. Reaction rate was 1st order in $[OCl^-]$ and $[SO_3^-]$. A mechanism involving HOCl is proposed. The reaction between NaOCl and some small peptides to study the availability losses of methionine, lysine and tryptophan during technological treatment was reported[184]. The only reaction liable to render methionine residues unavailable in foods would be its oxidation to methionine sulfone. The oxidation of some compounds containing active methylene groups by NaOCl were also reported[187]. The products are identified to be gem diols or gem diketones. Rusin and Roschine[188] have reported the kinetics of reaction between 4-dimethylaminophthalhydrazide and hypochlorite. Rate determining step in the process was suggested to be the reaction of 4-dimethyl aminothalhydrazide anion with HOCl.

Wright[189] reported the action of hypochlorite on amino acids and proteins. The amount of hypochlorite taken up is not equal to the amount of protein present. The behaviour of NaOCl towards α-amino acids was also studied by Kantouch and Abdel Fattah[190]. Glycine, serine, tyrosine, cystein, aspartic acid, lysine and arginine were the different aminoacids studied. The reaction was highly dependent on pH. At pH=2 mono and dichloro derivatives are assumed to be formed. Substitution of one hydrogen of the amino group by an acetyl group decreased the oxidation considerably. The effect of chlorine water and NaOCl on amino acids and proteins were studied by stankovic and Vasatko[191]. Oxidation and chlorination are dependent on pH, temperature and time and also on the ratio of the amount of NaOCl to amino acids. Rausch *et al*[192] have described the kinetics of oxidation of tryptophan by NaOCl. The reaction was studied under pseudo first order condition. The product of oxidation was 3-indole acetaldehyde. A probable mechanism is suggested.

### 2.1.3 Kinetics of Oxidation by Phase Transfer Catalysis

Heterogeneous oxidation of benzyl alcohols using hypochlorite[193] by using phase transfer catalyst, cetyl trimethyl ammonium bromide is carried out in an agitated vessel. The reaction rate is proportional to the interfacial concentration of cetyl trimethyl ammonium hypochlorite in organic phase, which is formed by ion exchange between bromide & hypochlorite ion. The reaction rate constant evaluated by fitting the rate data is $22.7 \times 10^{-3}\ dm^3\ mol^{-1} s^{-1}$ at 303K

Abramovici *et al*[194] reported the oxidation of benzyl alcohol with aqueous sodium hypochlorite catalysed by quaternary ammonium salts as phase transfer catalyst. Two products were obtained, benzaldehyde and benzyl benzoate. The concentration of the organic phase and low pH favoured benzaldehyde as product, where as concentrated organic phase and high pH favoured benzyl benzoate as product.

Kinetics of anodic oxidation of benzyl alcohol in two-phase system involving both, the redox mediator, $OCl^-/Cl^-$ and a phase transfer catalyst were investigated[195]. The reaction order of the anodic oxidation of chloride ion in aqueous phase was unity. The charge transfer parameters $\alpha$, $k^0_2$ and exchange current density $i_0$ of chloride ion oxidised on graphite anode are obtained in the temperature range from 5 to $45^0$C. The model calculation of the anodic oxidation of benzyl alcohol by the theoretical analysis correlates well with the experimental results.

The synergic action of the electron transfer catalyst, meso tetraphenyl porphyrin Mn(III) chloride complex with a common PT catalyst, trioctyl methyl ammonium chloride to promote the oxidation of alcohols has been reported[196]. Direct oxidation of benzyl alcohol with sodium hypochlorite was very slow, but was accelerated by electron-transfer or phase-transfer catalyst. In the presence of both, the oxidation was very fast.

Do and Do have carried out the indirect anodic oxidation of benzyl alcohol[197,198], in the presence of PT catalyst in a continuous stirred tank electrolysis reactor (CSTER). Effect of current density, organic to aqueous volume ratio, concentration of the PT catalyst, flow rate and temperature on current efficiency of producing benzaldehyde were systematically studied in this work. The conversion of benzyl alcohol and the yield of benzaldehyde were increased, and the selectivity of benzaldehyde decreased at a high organic flow rate when both current density and concentration of PT catalyst increased. The power consumption was confirmed by the experimental results as having decreased when the current density decreased and concentration of PT catalyst increased. Rapid spectro scopic assessment of reaction rates in PTC has been carried out by Trifonov & Kuzmanova[199]. The reaction examined include the hypochlorite oxidation of benzyl alcohol. The plot of optical density versus time was found to be linear. The PT catalysts used were Aliquat 336, $Bu_4N^+HSO_4^-$ and $Bu_4PBr$. Amsterdamsky[200] has proposed a procedure for the oxidation of benzhydrol to benzophenone using bleach as oxidant, ethyl acetate as organic phase and tetrabutylammonium hydrogen sulphate as PT catalyst. The oxidation is essentially complete in 30 minutes and the yield range from 70% to 85% after recrystallisation.

Alkyl and aryl substituted hydroquinones are rapidly oxidised to para benzoquinones by stirring their solution in an organic solvent with aqueous sodium hypochlorite in the presence of catalytic amount of tetrabutyl ammonium hydrogensulphate[201]. In the oxidation of monosubstituted hydroquinones, dichloromethane or chloroform is a more suitable solvent than ethyl acetate or benzene whereas the oxidation of di-tri- and tetra-substituted hydroquinones gave comparable results in dichloromethane, chloroform, ethyl acetate or benzene.

Lee and Freeman[202] reported the phase transfer oxidation of alcohols and amines with hypochlorite in presence of quaternary ammonium salts which transfer hypochlorite ion from aqueous to organic media. An interesting and unexpected specific solvent effect has also been discovered with the use of ethyl acetate which greatly expands the synthetic utility of this method. Both the synthetic scope and mechanistic aspects of these reactions are discussed.

Liquid phase oxidation of deactivated methyl benzenes by aqueous NaOCl catalysed by Ruthenium salts under PTC conditions were reported by Sasson *et al*[203]. Quaternary ammonium salts are used as phase transfer catalysts. Kinetic studies show the reaction to be of first order in the substrate, zero order in NaOCl, and combined first order in the catalyst concentrations. The reaction mechanism consists of $RuO_4$ catalysed hydride abstraction and a phase transfer catalysed proton dependent step.

### 2.1.4 Catalysis by Cyclodextrin

Keith Bowden and T.D. Radhakrishnan Nair[160] investigated the kinetics of oxidation of aromatic ketones under alkali condition using hypohalite. It was observed that cyclodextrin catalysed the reaction. This has been explained on the encapsulating effect on reactants of appropriate size by the cyclodextrins in such reaction.

Breslow *et al*[81] reported αCD catalysed chlorination of anisole when para chlorinated product was formed exclusively. The mechanism involves the interaction HOCl with one of the secondary –OH group of the CD to form a hypochlorite group which attacks the sterically favourable para position of anisole molecule included in CD cavity in an intra complex formation.

Trotta[204] *et al* studied the effect of CD on the hydrolysis of carboxylic acid esters when CD and their derivatives act as inverse phase transfer catalysts. The reaction is affected by temperature, choice of CD and also by stirring rate. Lypophilic esters are better hydrolysed under inclusion phase transfer catalytic condition than under classical phase transfer catalytic condition. Some typical features are emphasized and compared with classical phase transfer catalysed reactions.

The hydrolysis of phthalic acid esters catalysed by CDs and their derivatives were reported[205]. Thus a mixture of dimethyl phthalate and methyl β-CD in 10% aqueous NaOH was stirred for 30 minutes at room temperature to give 91.7% phthalic acid. The yield was 32% for the uncatalysed reaction. β-CD catalysed auto-oxidation of benzoin in alkaline medium[206] shows that one mole of benzoin absorbs one mole of oxygen to form one mole each of benzyl and $H_2O_2$ in a first order reaction.

## 2.2 SCOPE AND OBJECTIVE OF THE PRESENT WORK

Sodium hypochlorite is a mild oxidizing agent which can be used to oxidize various organic substrates in good yield without attendant of side reactions. Hypochlorite is superior to other oxidsing agents as it is readily available and is inexpensive. It is non-pollutant and does not cause any environmental problems. Inspite of all these facts, only a few kinetic studies were reported using NaOCl as oxidant. Moreover no fruitful attempt had been made to study the oxidation of carbonyl compounds using NaOCl. Sodium hypochlorite can be used as an effective oxidant for the conversion of aromatic aldehydes to the corresponding acid. Comparative study of the oxidation of aromatic aldehydes using NaOCl in various aqueous protic and aprotic solvents is also relevant.

The present proposed study is on the kinetics and mechanism of the oxidation of benzaldehyde and substituted benzaldehydes using NaOCl in aqueous acetic acid medium. The studies have also been carried out in other protic and aprotic solvents with and without the use of catalysts. Kinetic study has also been conducted using phase transfer catalysts. The main objective of the present work are

1. To study the rate of oxidation of benzaldehyde and some of its ortho and para substituted derivatives using NaOCl in aqueous acetic acid medium and to evaluate the rate constants of the reactions.
2. To find out the stoichiometry of the reaction and to analyse the products of oxidation.
3. To find out the temperature coefficient of the reaction rates for evaluating the Arrhenius parameters and other related thermodynamic parameters.
4. To study the effect varying the concentration of the substrate and the oxidant on the rate of the reaction.
5. To study the primary kinetic salt effect.
6. To study the effect of dielectric constant of the medium on the rate of oxidation.

7. To study the rate of oxidation and evaluation of thermodynamic parameters in aqueous dioxane and in aqueous acetonitrile medium.
8. To compare the reaction rates in various aqueous media containing co-solvents such as acetic acid, dioxane, acetonitrile, DMF and DMSO.
9. To study the effect of substituents on the rate of oxidation of benzaldehyde.
10. To study the catalytic effect of cyclodextrins and some phase transfer catalysts on the rates of hypochlorite oxidation and
11. To evolve a mechanism for the reaction from these kinetic studies.

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

ABDURAHIMAN, K.K

2002
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 635
INDIA

## CHAPTER III

# EXPERIMENTAL

## 3.1 Materials

Aqueous sodium hypochlorite solution (swimming pool reagent) used was of E Merck quality. The benzaldehyde and substituted bezaldehydes were of Analar grade. Solid Analar samples were used as such. Liquid aldehydes were purified before use by distillation at low pressure[207] in an atmosphere of nitrogen. Glacial acetic acid used was of Analar grade. Reductants present, if any, in the acetic acid, were removed by refluxing it with chromic oxide and acetic anhydride for about six hours followed by fractional distillation[208]. Merck analar samples of sulphuric acid, sodium thio sulphate, potassium dichromate and potassium iodide were used. Cyclodextrins used were of Aldrich (USA) make and had a purity of minimum 99%.

The various solvents used such as dioxane, methanol, acetonitrile, benzene etc were purified by standard procedure[208,209].Tetrabutyl ammonium bromide (TBAB) used as phase transfer catalyst was of E. Merck quality. Double distilled water was used for the entire work.

## 3.2 Kinetic investigation

The kinetic experiments were carried out in thermostatic baths fitted with Jackson thermoregulators to maintain the accuracy of temperature of the system within a variation of ± $0.05^0$C. The solutions were prepared either in distilled water or in distilled acetic acid. Ionic strength of the medium was maintained constant by the addition of suitable concentration of sodium chloride.

The kinetic measurement were made under pseudo first order condition by maintaining [substrate]>>[oxidant]. The thermostat was set to the required temperature. A mixture containing appropriate quantities of the substrate, acetic acid. Sodium chloride and water were taken in an amber coloured pyrex glass bottle and thermostated for 20 minutes. A known volume of the oxidant was also thermostated in the same bath separately. The reaction was initiated by adding requisite amount of the above thermally equilibrated solution of the oxidant to the reaction mixture. Aliquots were removed at definite time intervals and the unreacted hypochlorite was estimated by iodometric method. The rate constants were computed using linear regression analysis (by the method of least squares). The least square method is used for fitting the straight line to a set of points that are supposed to be linearly related by the formula.

$$y = mx + c$$

The slope of the straight line is given by

$$m = \frac{\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

and the intercept on the y-axis will be equal to

$$c = \frac{\Sigma y \Sigma x^2 - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

When n is the number of data points and the summations are for all data points of the set.

The values were computed using a CMS computer. The correlation coefficients were determined using the equation

$$r = \frac{n\Sigma xy - \Sigma x \Sigma y}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2]\,[n\Sigma y^2 - (\Sigma y)^2]}}$$

## 3.3 Stoichiometry of the reaction

The stoichiometry of the reaction was determined by the following method. The reaction mixture containing known amount of benzaldehyde in 20%. HOAc with more than two equivalents of the oxidant were mixed at room temperature and kept until the reaction was completed. 5ml of the reaction mixture was pipetted out and the unreacted hypochlorite was estimated iodometrically. The estimation was repeated at different time intervals to get concordant result to make sure that the reaction was complete. From the above data, the stoichiometry of the oxidation reaction is calculated to be 1:1, benzaldehyde: oxidant.

## 3.4 Analysis of products of oxidation

The products of oxidation of benzaldehyde using sodium hypochlorite were isolated and identified as follows. A reaction mixture containing excess of NaOCl over benzaldehyde in 20% acetic acid were refluxed for six hours in a R.B. flask fitted with a reflux condenser. The reaction mixture was then treated with sodium sulphite solution to decompose the excess hypochlorite in the mixture. The resulting solution was shaken several times with ether in a separating funnel. The aqueous layer was driven off and the ether layer was treated with sodium carbonate solution, two or three times. The aqueous layer was collected and on further concentration and cooling, crystals were seperated which were filtered. The product was soluble in hot water and therefore recrystallised from boiling water. The product was identified by qualitative as well as by spectral analysis. It was identified to be benzoic acid from its melting point ($120^0$C) and from the IR spectrum (Fig. 3.4.1)

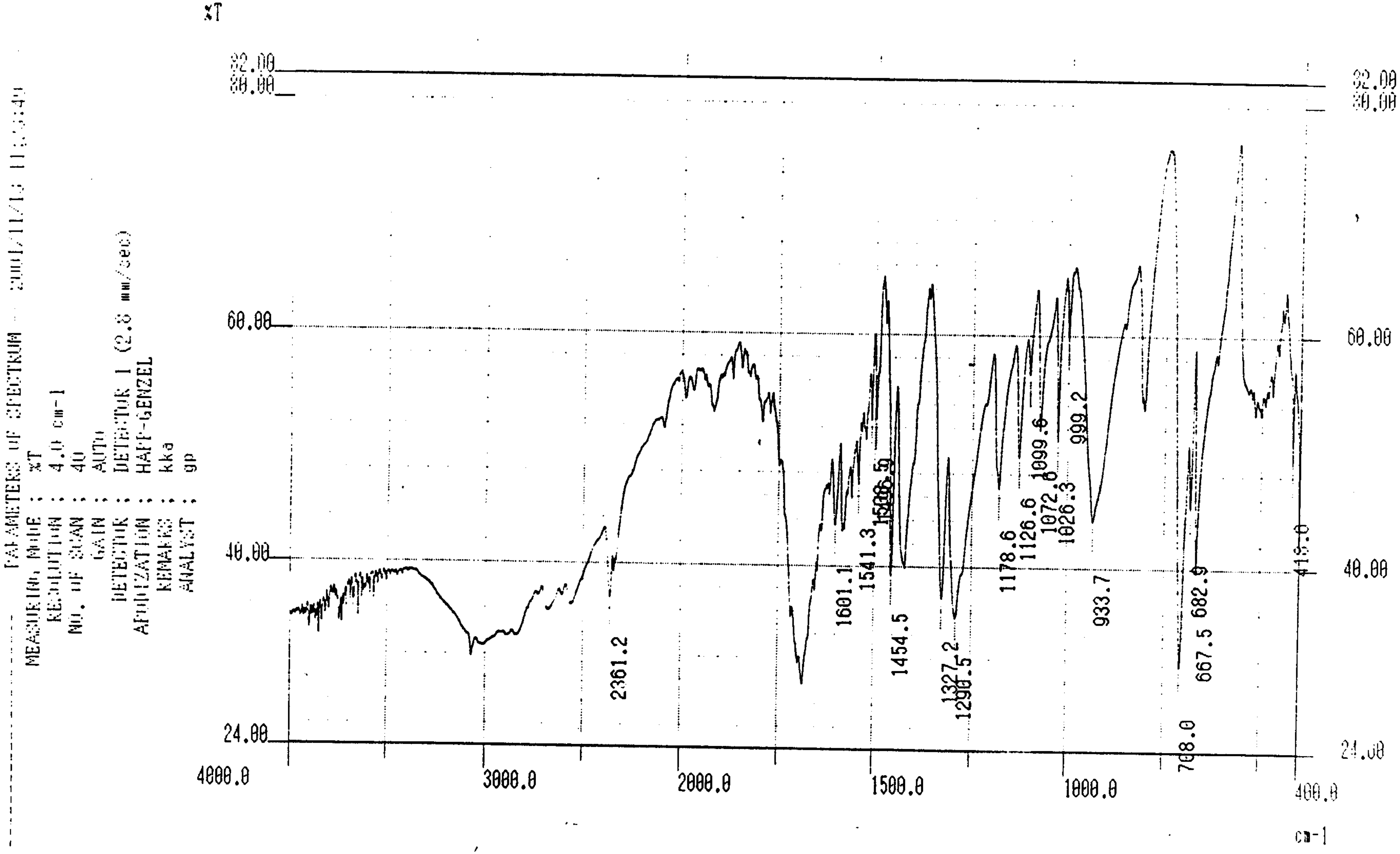


Fig. 3.4.1. IR Spectrum of the product of oxidation of benzaldehyde using NaOCl

## 3.5 Kinetic Studies in Aqueous Acetic Acid Medium

### 3.5.1 Effect [NaOCl] on the rate of oxidation of benzaldehyde

The kinetics of the oxidation of benzaldehyde with NaOCl in 20% aqueous acetic acid medium was followed by taking definite concentration of the substrate ($1.0 \times 10^{-2}$ M) and varying the concentration of the oxidant ($4 \times 10^{-4}$ M – $10 \times 10^{-4}$ M). However the concentration of the substrate in all cases were greater by at least 10 times that of oxidant to ensure pseudo-first order condition. All other kinetic conditions were maintained identical. The plots of log [$OCl^-$] versus time were linear with slopes of identical values indicating a first order dependence of the oxidant concentration on the rate of oxidation. The $k_{obs}$ values are tabulated in Table 3.5.1.

**Table 3.5.1**

**Effect of varying the concentration of NaOCl on the rate of oxidation of benzaldehyde in aq. Acetic acid**

[$C_6H_5CHO$] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

$\mu$ = 0.2 mol dm$^{-3}$ Solvent = 20% HOAc (v/v)

| $10^3$ [NaOCl] moldm$^{-3}$ | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|
| $10^5 k_{obs}$ s$^{-1}$ | 5.03 | 4.95 | 5.18 | 4.98 |
| Correlation coefficient | 0.9998 | 0.9987 | 0.9967 | 0.9907 |

### 3.5.2 Effect of varying the concentration of $C_6H_5CHO$ on the rate of oxidation

The effect of varying the concentration of benzaldehyde on the rate of oxidation was studied in the range 1.0 x $10^{-2}$M to 3.0 x $10^{-2}$ M keeping all other kinetic conditions the same. In all cases the concentration of benzaldehyde was kept in large excess to that of NaOCl. Hence the order obtained ($k_{obs}$) would be that with respect to NaOCl. The pseudo rate constant ($k_{obs}$) = $k_2$ [$C_6H_5CHO$]. The plot of log $k_{obs}$ versus log [$C_6H_5CHO$] is linear (Fig.4.1) with a +ve slope equal to unity (corr. coeff. 0.998) which gives the order with respect to the aldehyde. The second order rate constant ($k_2$) of the overall reaction is obtained by dividing $k_{obs}$ with substrate concentration. Constancy in the value of $k_2$ was observed.

**Table 3.5.2**

**Effect of varying the [$C_6H_5CHO$] on the rate of oxidation in aq.HOAc**

[NaOCl] = 1.0 x $10^{-3}$ mol dm$^{-3}$ T = 303K

$\mu$= 0.2 mol dm$^{-3}$ Solvent: 20% Aq. HOAc (v/v)

| $10^2$ [$C_6H_5CHO$] mol dm$^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ s$^{-1}$ | 5.10 | 7.72 | 10.25 | 13.25 | 15.16 |
| Corr. Coeff. | 0.9975 | 0.9987 | 0.9996 | 0.9974 | 0.9997 |
| $k_{obs}$/($C_6H_5$-CHO] | 5.10 | 5.14 | 5.12 | 5.31 | 5.11 |

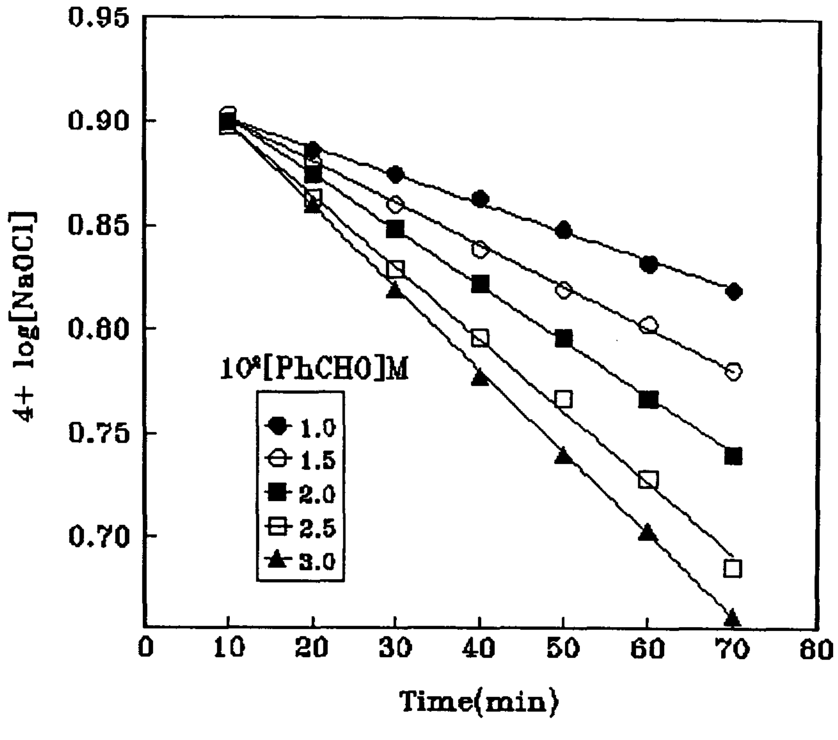


**Fig 3.5.1 Effect of [substrate] on the hypochlorite oxidation of PhCHO in aqueous HOAc**

### 3.5.3 Effect of added mineral acid on the rate of oxidation of benzaldehyde

The effect of mineral acid on rate was studied by adding different concentration of sulphuric acid in the system over a range of $0.25 \times 10^{-2}$ _ $5.0 \times 10^{-2}$ mol $dm^{-3}$. The concentration of the substrate and oxidant and other parameters are kept constant. An increase in specific rate was observed with increase of concentration of $H_2SO_4$. The values are tabulated in table 3.5.3 and (Fig.3.5.2)

## Table 3.5.3

## Effect of added acid on the rate of oxidation of benzaldehyde in aq. acetic acid

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl) =$1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ moldm$^{-3}$

Solvent = 20% HOAc (V/V)

| $10^2$ [H$^+$] moldm$^{-3}$ | 0 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|---|
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 6.53 | 7.41 | 8.44 | 9.90 | 11.32 |
| Corr. Coeff. | .9976 | .9998 | .9994 | .9998 | .9997 | .9958 |

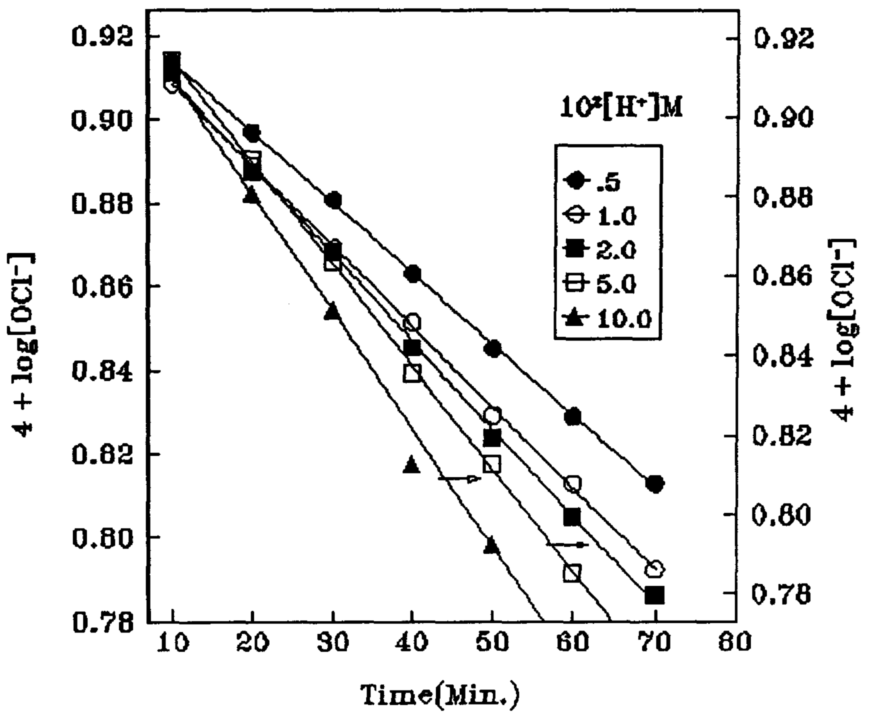


Fig 3.5.2 Effect of mineral acid on the oxidation of PhCHO in aqueous HOAc

The increase of $k_{obs}$ values indicate that the reaction is acid catalysed. A plot of log $k_{obs}$ versus log $[H^+]$ is linear with a positive slope indicating that the reaction is acid catalysed and agreeing with a fractional order dependence on $[H^+]$ (Fig.4.5).

### 3.5.4 Influence of ionic strength on the rate of oxidation

The effect of ionic strength of the medium on the rate of oxidation was studied using calculated amounts of sodium chloride. The $k_{obs}$ values calculated by least square method revealed that ionic strength had negligible effect on the hypochlorite oxidation of benzaldehyde. The data are given in table 3.5.4.

**Table 3.5.4**

**Effect of ionic strength on the rate of oxidation of benzaldehyde using NaOCl in aq. Acetic acid medium.**

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl) =1.0 x $10^{-3}$ mol dm$^{-3}$ Solvent = 20% HOAc (v/v)

| $10^2$[NaCl] mol dm$^{-3}$ | 1.0 | 2.0 | 3.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| $10^5\ k_{obs}\ s^{-1}$ | 5.07 | 4.91 | 5.10 | 4.79 | 5.10 |
| Corr. Coeff. | 0.9972 | 0.9967 | 0.9963 | 0.9973 | 0.9886 |

### 3.5.5 Influence of polarity of the medium on the rate of oxidation

One of the important kinetic investigations which gives an insight into the nature of the interaction taking place in the rate determining step of the reaction is to study the effect of polarity of the medium. Here the oxidation of benzaldehyde using NaOCl was carried out at different percentage of acetic acid and water. The results are presented in table 3.5.5 and fig 3.5.3.

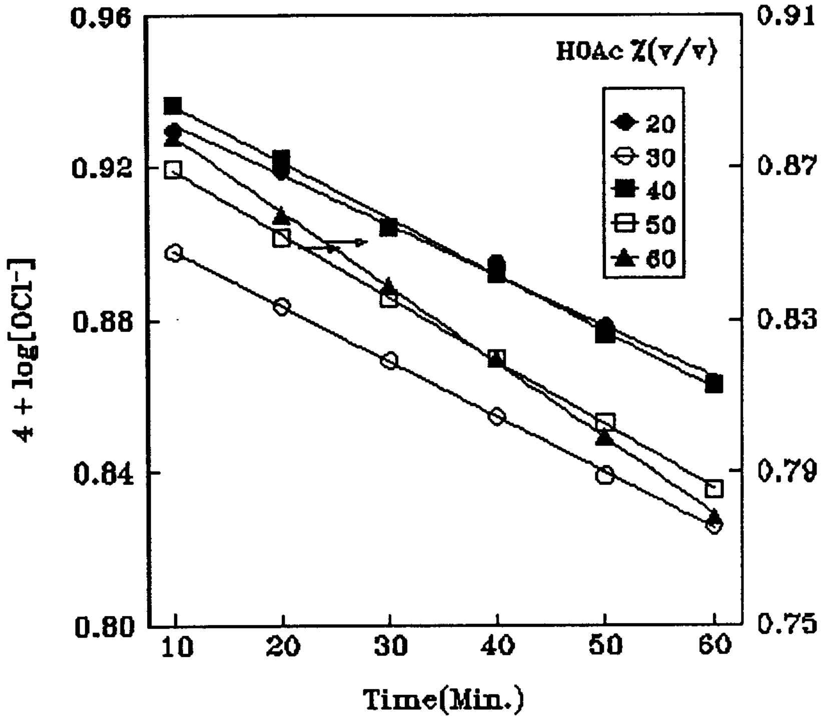


Fig. 3.5.3 Effect of polarity of the medium on the oxidation of PhCHO

### Table 3.5.5 Effect of polarity of the medium on the rate of oxidation of benzaldehyde

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl) $= 1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| Percentage of HOAc | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| Dielectric constant(D) | 61 | 54 | 47 | 39.8 | 32 |
| Corr. | .9936 | .9995 | .9986 | .9996 | .9996 |
| $10^5 k_{obs} s^{-1}$ | 5.10 | 5.49 | 5.87 | 6.64 | 7.6 |

The results show that the rate increases with decrease of dielectric constant of the medium. A plot of log $k_{obs}$ versus D-1/2D+1 gave a linear curve with negative slope (Fig 4.7). The dielectric constant values are obtained from literature. A plot of D versus percentage of acetic acid was drawn with available data and on extrapolation of the straight line, the D values corresponding to other percentages of acetic acid, which are not available in the literature, were calculated.

### 3.5.6 Influence of addition of products on the rate of oxidation

To study the influence of products of the reaction on the rate, one of the products viz benzoic acid was added directly to the reaction system. The results showed that the addition of products have no influence on the rate of oxidation of benzaldehyde.

## Table 3.5.6

## Effect of addition of benzoic acid on the rate of oxidation of benzaldehyde

[NaOCl] =$1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent =20% HOAc(v/v)

T =303K

| $10^2[C_6H_5CHO]$ mol dm$^{-3}$ | 0 | 1.0 | 1.5 | 2.0 |
|---|---|---|---|---|
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 5.07 | 4.91 | 5.03 |
| Corr. Coeff. | .9976 | .9972 | .9968 | .9970 |

### 3.5.7 Effect of radical trapper on the rate of oxidation

To the reaction mixture containing the substrate ($1.0 \times 10^{-3}$mol dm$^{-3}$), oxidant ($1 \times 10^{-3}$mol dm$^{-3}$), sodium chloride (0.2 mol dm$^{-3}$) in 20% aq. HOAc medium, 5ml of acrylonitrile was added and kept overnight. No polymerization was observed indicating the absence of any free radical formation during the course of the reaction.

### 3.5.8 Effect of temperature on the rate oxidation and evaluation of thermodynamic parameters

The influence of temperature on the rate of oxidation of benzaldehyde was studied over the range of 303K– 318K under otherwise identical conditions. The data are given in table 3.5.8(a) and fig.3.5.4.

## Table 3.5.8(a)

### Effect of temperature on the rate of oxidation of benzaldehyde using NaOCl

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ moldm$^{-3}$ T = 303K

[NaOCl) $= 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 5.10 | 6.14 | 7.33 | 8.18 | 10.29 |
| Corr. Coeff. | .9997 | .9953 | .9981 | .9997 | .9992 |

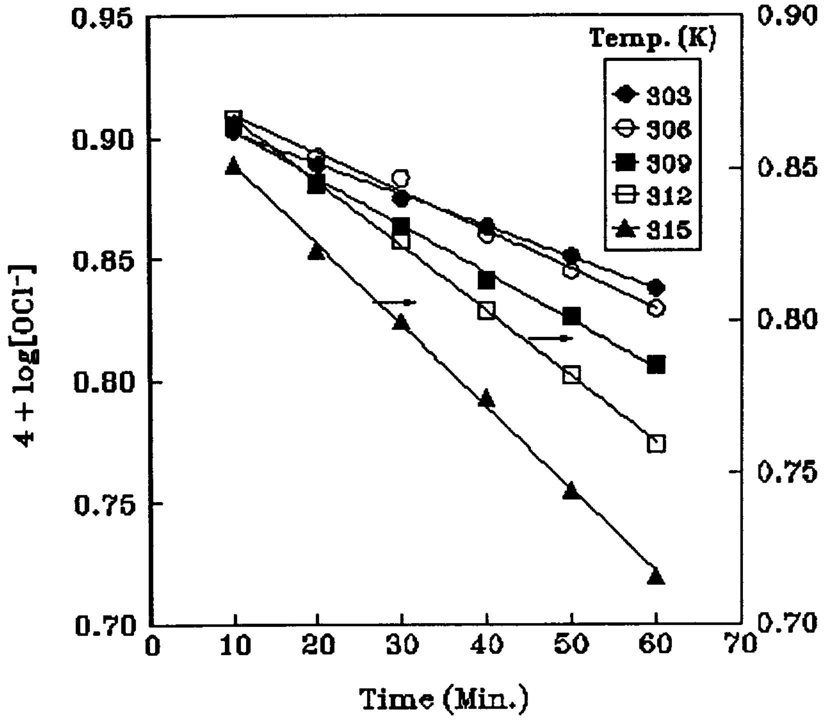


Fig. 3.5.4 Effect of temperature on the oxidation of PhCHO in aq. HOAc

The results show that the specific rate increases appreciably with temperature. The plots of log$k_2$ versus 1/T and log k $_2$/T versus 1/T were drawn (Fig 3.5.5). The various thermodynamic parameters such as energy activation, entropy of activation, enthalpy of activation and free energy of activation were calculated. The results are shown in table 3.5.8(b).

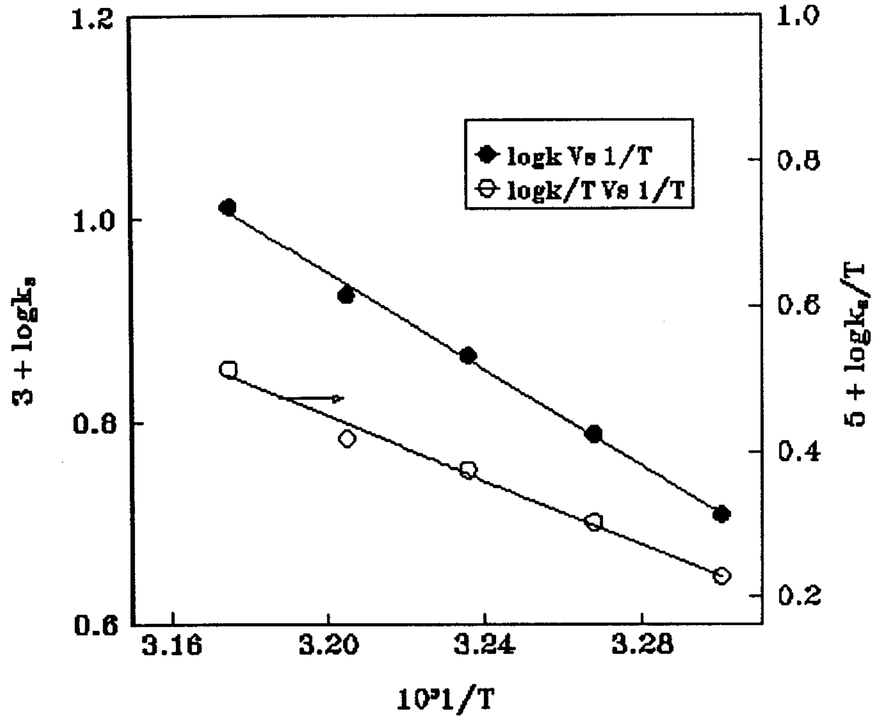


**Fig. 3.5.5 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PhCHO in aq. HOAc**

## Table 3.5.8(b)

## Activation parameters

| Parameters | $E_a$ (kJmol$^{-1}$) | $\Delta H^{\#}$ (kJmol$^{-1}$) | $^{-}\Delta S^{\#}$ (JK$^{-1}$mol$^{-1}$) | $\Delta G^{\#}$ (kJmol$^{-1}$) |
|---|---|---|---|---|
| | 47.05 | 44.45 | 142.28 | 87.5 |

### 3.5.9 Effect of substituents on the rate of oxidation using NaOCl

The effect of substituents on benzene ring of benzaldehyde was studied using p-nitro, p-chloro, o-chloro, p-bromo and p-methyl benzaldehydes (Fig4.8). It was observed that the rate of oxidation increases in the order p-methyl<H<o-chloro<p-chloro<p-bromo <p-nitro. The values are given in table 3.5.9.

**Table 3.5.9**

**Effect of substituents on the rate of oxidation using NaOCl**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[Oxidant] =$1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent = 20% HOAc (v/v)

| Substrate | PMB | PhCHO | PCB | OCB | PBB | PNB |
|---|---|---|---|---|---|---|
| $10^5 k_{obs} s^{-1}$ | 3.88 | 5.10 | 7.02 | 5.76 | 7.18 | 22.42 |
| Corr. Coeff. | .9984 | .9997 | .9992 | .9996 | .9990 | .9995 |

### 3.5.10 Effect of temperature on the rate of oxidation of substituted benzaldehydes

The effect of temperature of temperature on the rate of oxidation of substituted benzaldehydes were studied over temperature range of 303K – 315K. The $k_{obs}$ values are presented in table 3.5.10. From the plots of log k versus 1/T and log k/T versus 1/T, the activation parameters were calculated for each of the substituent (Table 4.2.8b)

**Table 3.5.10 Effect of temperature on the rate of oxidation of substituted benzaldehydes using aq. HOAc**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[Oxidant] =$1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent = 20% HOAc

| Substrate | 303 (K) | | 306 (K) | | 309 (K) | | 312 (K) | | 315 (K) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $10^5k_{obs}$ ($s^{-1}$) | corr. Coeft | $10^5k_{obs}$ ($s^{-1}$) | corr. coeft | $10^5k_{obs}$ ($s^{-1}$) | corr. coeft | $10^5k_{obs}$ ($s^{-1}$) | corr. coeft | $10^5k_{obs}$ ($s^{-1}$) | corr. coeft |
| PMB | 3.88 | .9988 | 4.72 | .9965 | 5.60 | .9981 | 6.33 | .9982 | 7.79 | .9998 |
| PhCHO | 5.10 | .9976 | 6.14 | .9953 | 7.38 | .9981 | 8.18 | .9997 | 10.29 | .9992 |
| OCB | 5.76 | .9940 | 7.18 | .9997 | 9.28 | .9998 | 11.8 | .9995 | 15.22 | .9997 |
| PCB | 7.02 | .9998 | 8.71 | .9998 | 10.98 | .9996 | 14.93 | .9998 | 17.27 | .9998 |
| PBB | 7.18 | .9989 | 9.06 | .9999 | 11.59 | .9993 | 15.05 | .9998 | 17.81 | .9998 |
| PNB | 22.42 | .9998 | 27.98 | .9994 | 37.35 | .9998 | 48.63 | .9997 | 60.68 | .9998 |

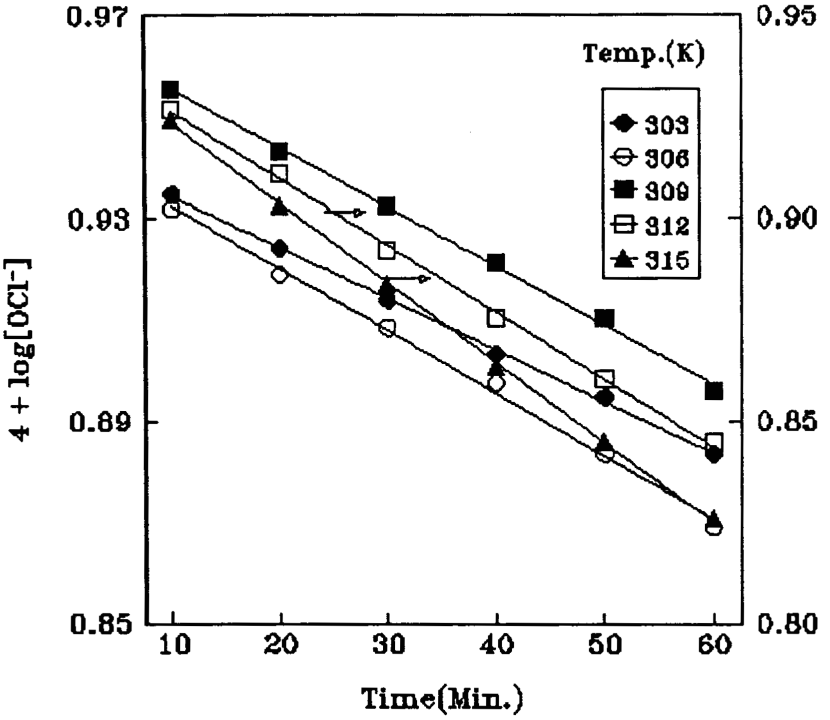


Fig 3.5.6 Effect of temperature on the oxidation of PMB in aq. HOAc

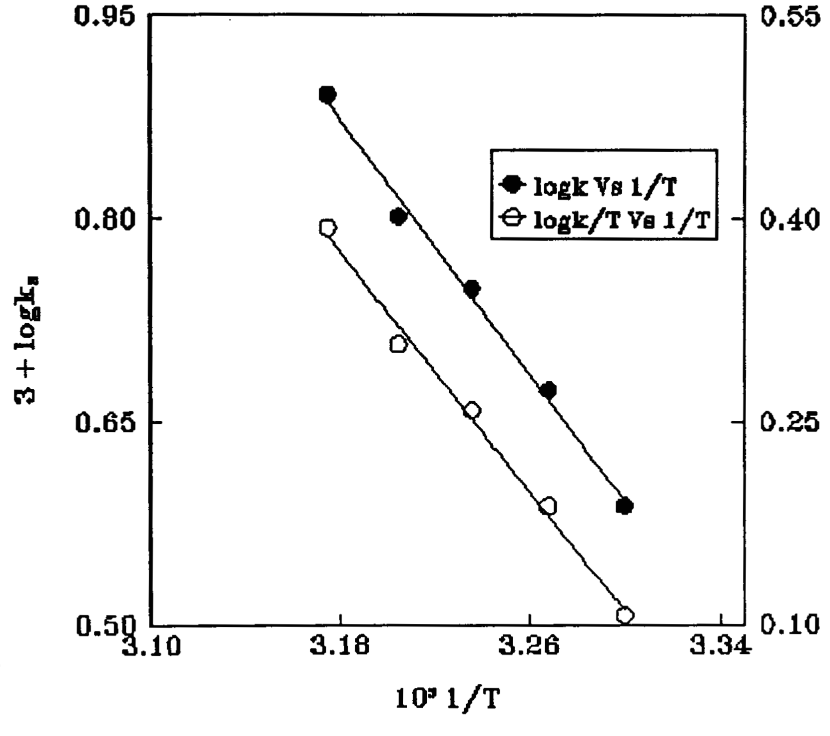


Fig 3.5.7 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PMB

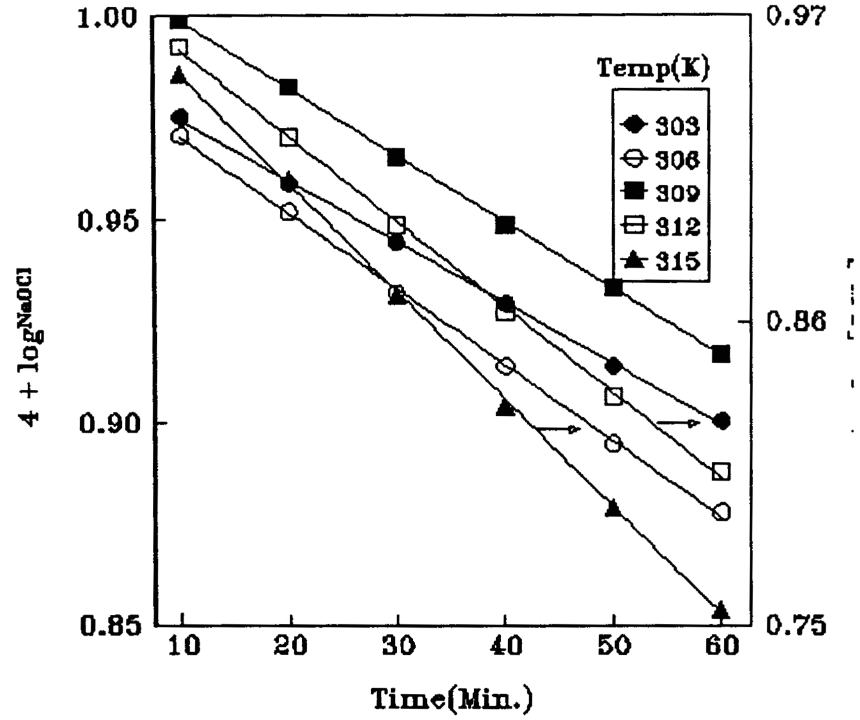


Fig 3.5.8 Effect of temperature on the oxidation of OCB in aq. HOAc

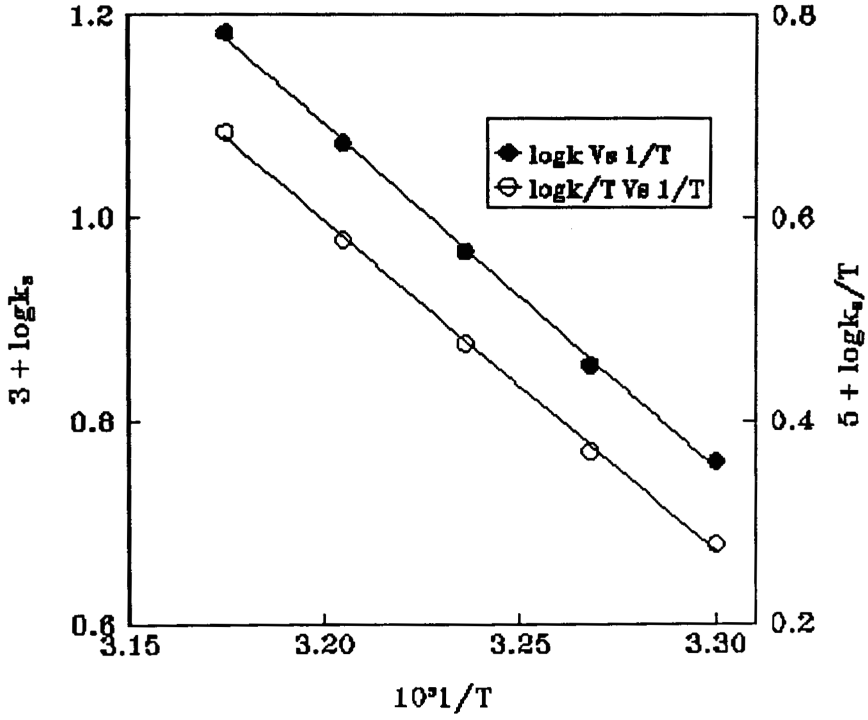


Fig 3.5.9 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of OCB

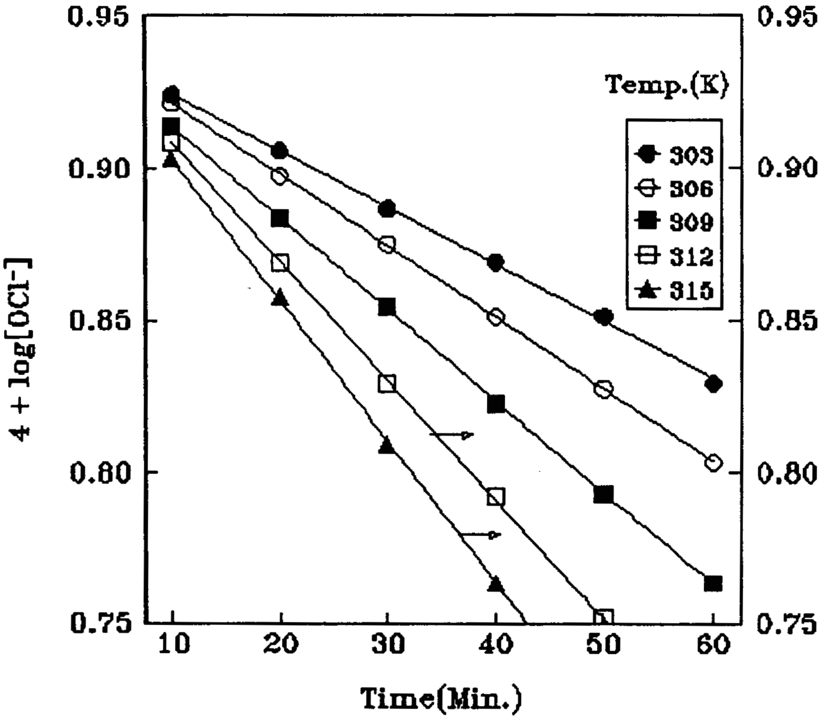


Fig 3.5.10 Effect of temperature on the oxidation of PCB in aq. HOAc

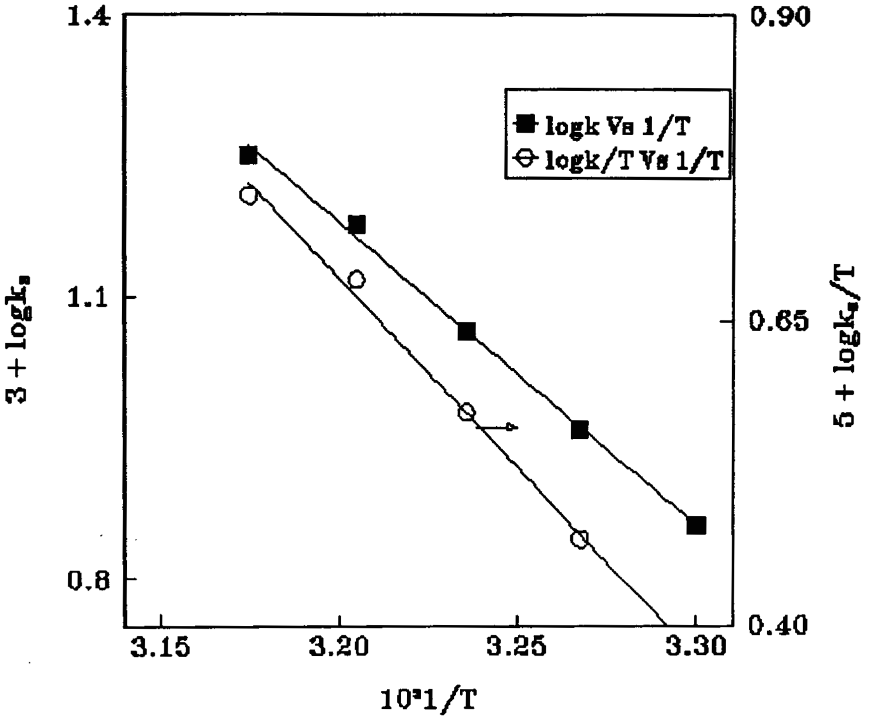


Fig 3.5.11 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PCB

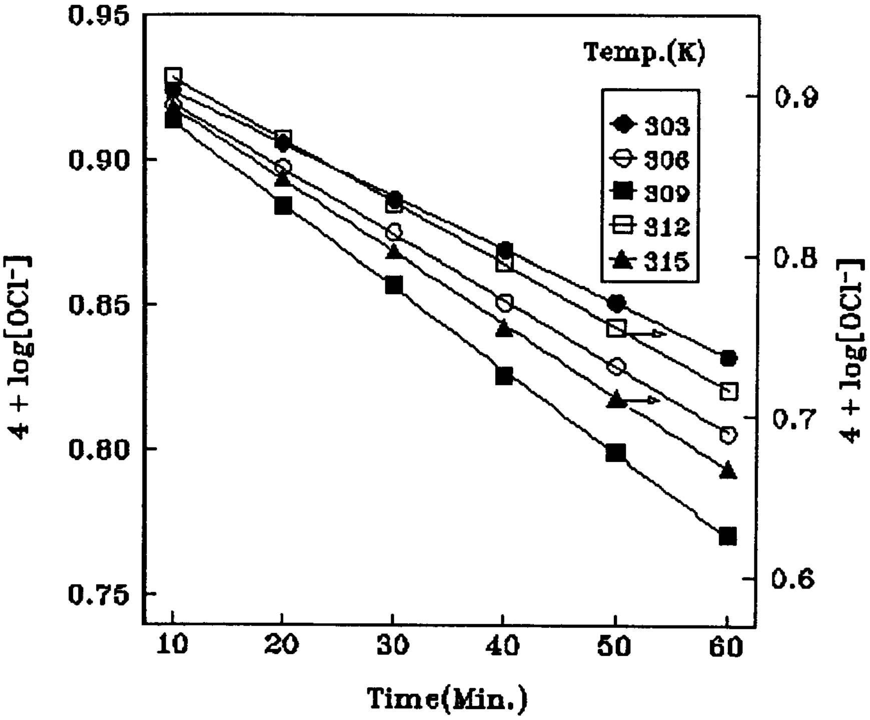


Fig 3.5.12 Effect of temperature on the oxidation of PBB in aq. HOAc

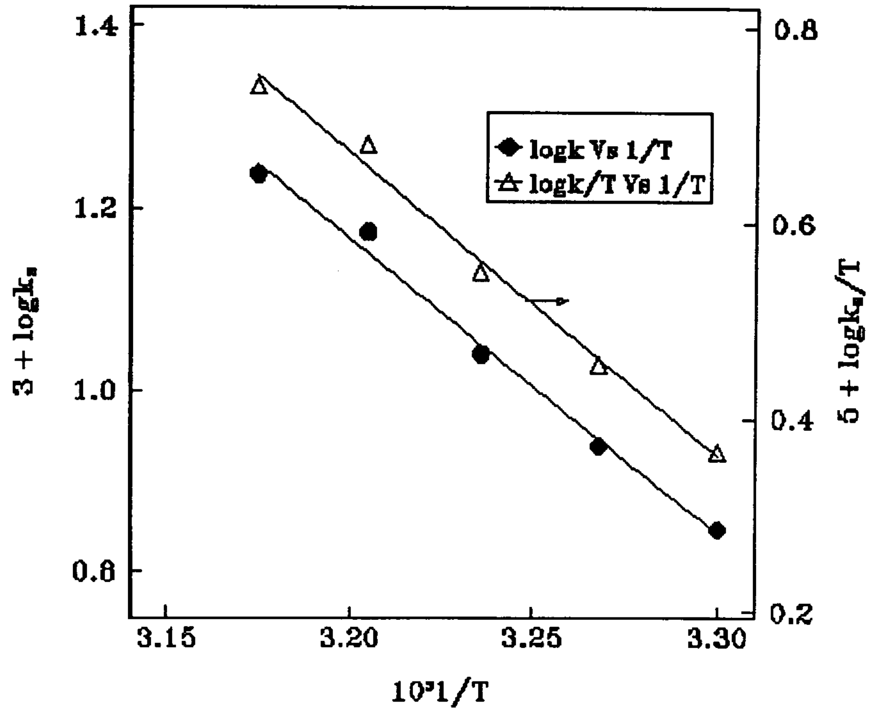


Fig 3.5.13 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PBB

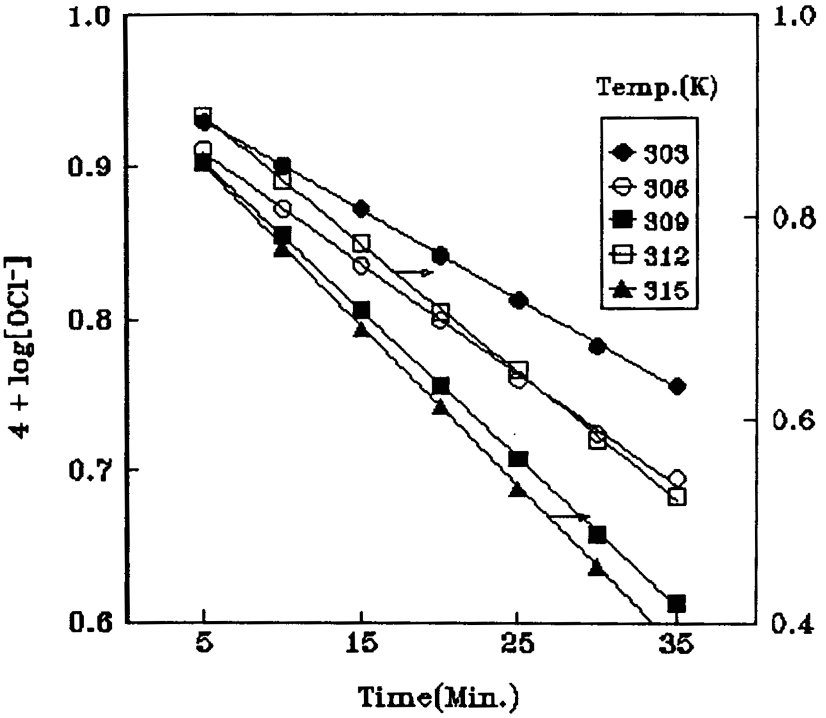


Fig 3.5.14 Effect of temperature on the oxidation of PNB in aq. HOAc

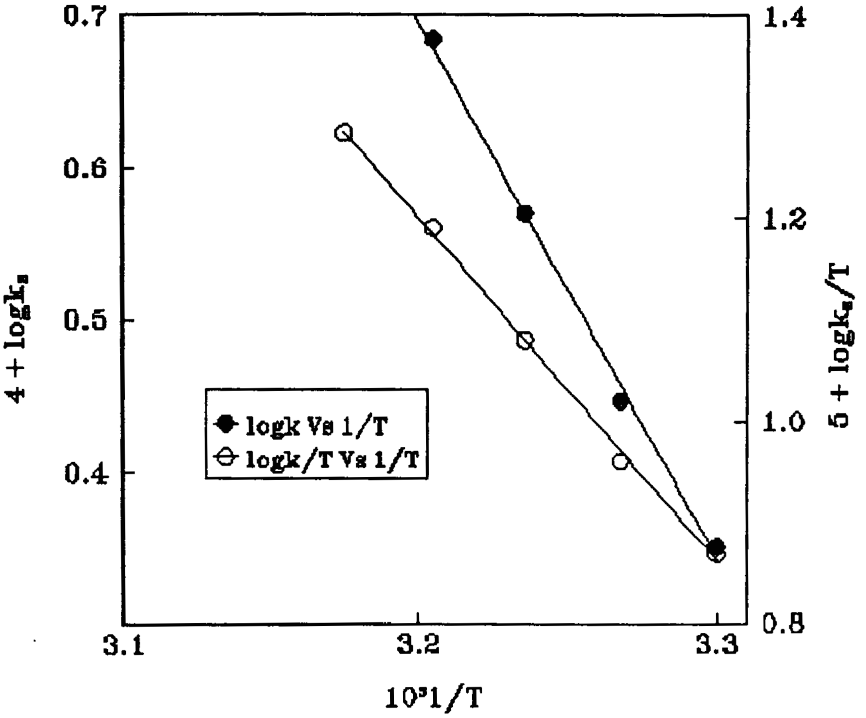


Fig 3.5.15 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PNB

## 3.6 Catalysis by Cyclodextrins in Aqueous Acetic Acid Medium

Cyclodextrins are oligosaccharides which form inclusion complexes with a large variety of guest molecules in solid state as well as in solution. When used in catalytic qualities CD's can accelerate the rate of many organic reactions. In the present kinetic investigation 2 x $10^{-3}$ M of cyclodextrin was used to study the influence of the catalyst. Other kinetic conditions were maintained identical in all measurements.

### 3.6.1 Effect of addition of cyclodextrins on the rate of oxidation benzaldehyde

The influence of α-Cyclodextrin (ACD) and β -Cyclodextrin (BCD) on the rate of oxidation of benzaldehyde were studied in 20% aq. acetic acid medium. The data given in table 3.6.1 showed that addition of CD's accelerated the rate significantly.

## Table 3.6.1

## Effect of addition of ACD and BCD on the oxidation of benzaldehyde in 20% aq. acetic acid.

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ T = 303K,

| | ACD | BCD |
|---|---|---|
| Concentration | 2.05 x $10^{-3}$ mol $dm^{-3}$ | 2.05 x $10^{-3}$ mol $dm^{-3}$ |
| $10^5$ $k_{obs}$ $s^{-1}$ | 6.12 | 6.02 |
| Corr. Coeft. | 0.9975 | 0.9982 |

### 3.6.2 Effect of temperature on the oxidation of benzaldehyde in presence CD's in aq. acetic acid

The effect of temperature on oxidation of benzaldehyde using NaOCl was studied in presence of ACD and BCD. The results are presented in tables 3.6.2(a) & 3.6.2(b) and Fig.3.6.1 &3.6.2

## Table 3.6.2 (a)

## Effect of temperature on the oxidation on benzaldehyde in 20% aq. acetic acid medium in presence of ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ [ACD] = 2.1 x $10^{-3}$ mol $dm^{-3}$

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ T = 303K, $\mu$ = 0.2 mol $dm^{-3}$

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 6.12 | 7.34 | 8.43 | 9.86 | 11.51 |
| Corr. Coeft. | 0.9975 | 0.9982 | 0.9996 | 0.9972 | 0.9952 |

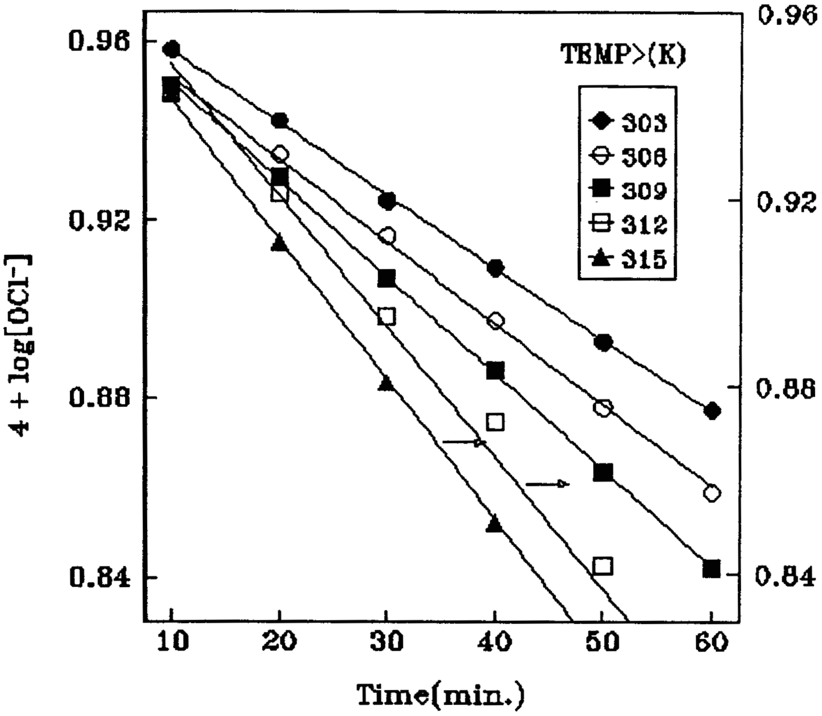


Fig. 3.6.1 Effect of temperature on the oxidation of PhCHO catalysed by ACD

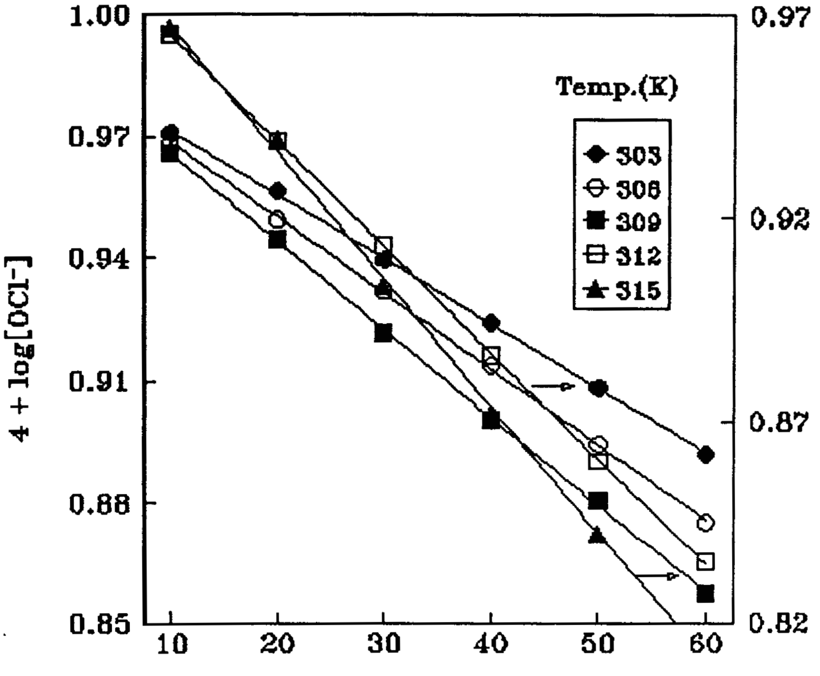


Fig. 3.6.2 Effect of temperature on the oxidation of PhCHO catalysed by BCD

## Table 3.6.2 (b)

## Effect of temperature on the oxidation on benzaldehyde in aq. acetic acid medium in presence of BCD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [BCD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent: 20% aq. acetic acid

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 6.02 | 7.13 | 8.46 | 9.99 | 11.72 |
| Corr. Coeft. | 0.9982 | 0.9973 | 0.9968 | 0.9996 | 0.9970 |

The activation parameters were determined from the plots of log k versus 1/T and log k/T versus 1/T plots. The values are given in table 4.2.9(c) (Fig.3.6.3 & 3.6.4)

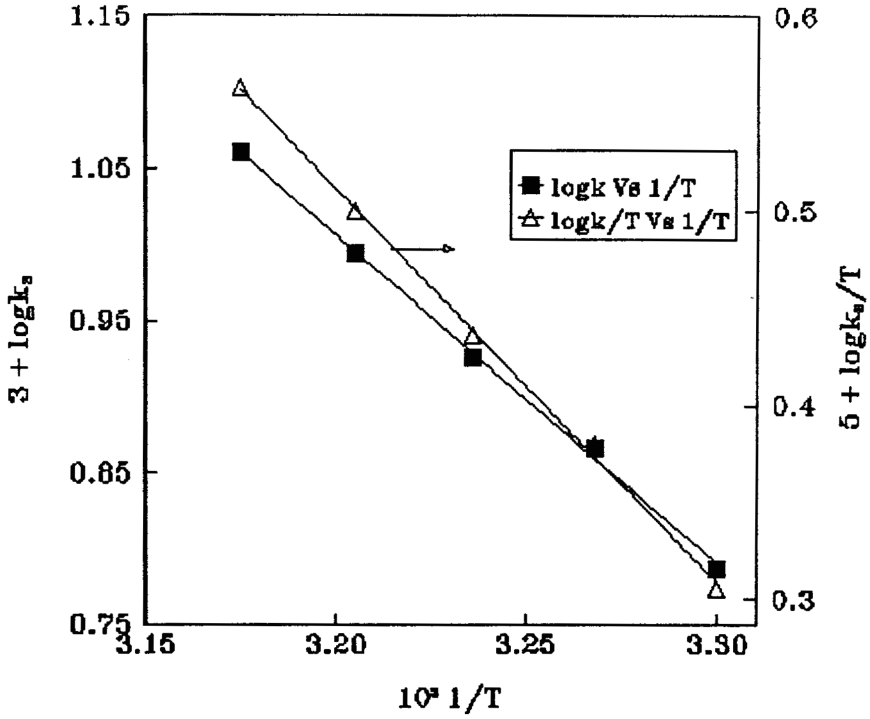


Fig. 3.6.3 Plots of log k vs 1/T and log k/T vs 1/T in presence of ACD

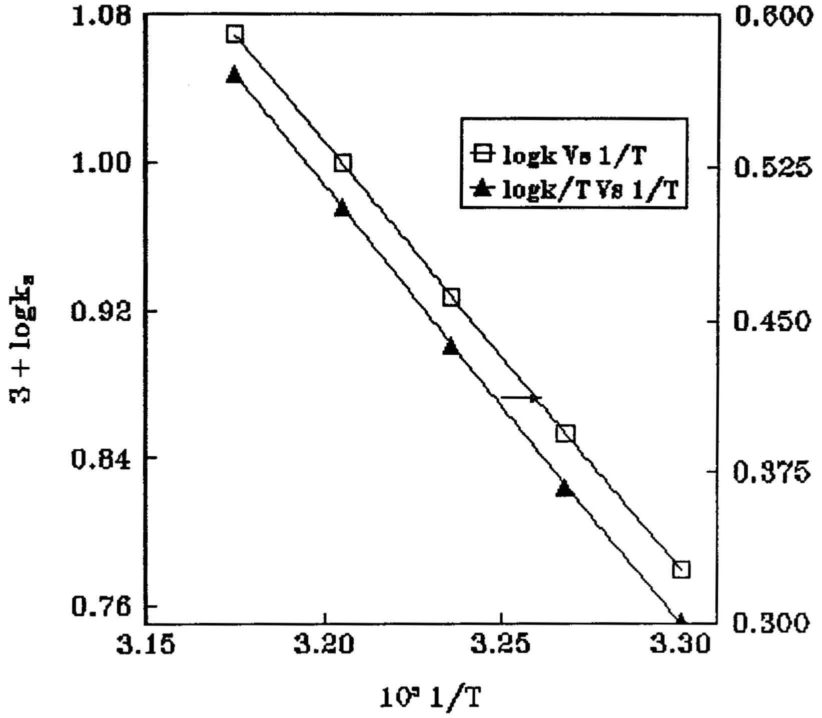


Fig. 3.6.4 Plots of log k vs 1/T and log k/T vs 1/T in presence of BCD

### 3.6.3 Effect of substitutents on the rate oxidation in presence of cyclodextrin.

The effect of various substituents viz. p-methyl, p-chloro, p-bromo and p-nitro groups on the rate of oxidation in presence of ACD were studied in aq. acetic acid medium. For each of the substituents an acceleration in the value of rate constant was observed on the addition of ACD. The results are given in table 3.6.3 and Fig.4.19.

**Table 3.6.3**

**Effect of substituents on the rate of oxidation of benzaldehyde in presence of ACD in aq. HOAc medium**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent: 20% aq. acetic acid T = 303K

| Substituent | p-Methyl | H | p-Chloro | p-Bromo | p-Nitro |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 4.65 | 6.12 | 8.56 | 8.90 | 35.87 |
| Corr. Coeft. | 0.9998 | 0.9975 | 0.9977 | 0.9984 | 0.9980 |

### 3.6.4 Effect of temperature on the oxidation of substituted benzaldehydes in presence of cyclodextrin

The effect of addition of ACD on the oxidation of various substituted benzaldehydes at different temperature were studied are given in table 3.6.4. The activation parameters $E_a$, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were also calculated from Arrhenius plots (Table 4.2.9 c).

**Table 3.6.4**

**Effect of temperature on the rate of oxidation of substituted benzaldehydes in presence of ACD**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent: 20% aq. acetic acid

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Temperature (K) | $10^5 k_{obs}$ s$^{-1}$ | | | | |
| 303 | 4.65 | 6.12 | 8.56 | 8.90 | 35.87 |
| 306 | 5.46 | 7.34 | 10.9 | 11.03 | 44.67 |
| 309 | 6.41 | 8.43 | 13.26 | 13.65 | 55.59 |
| 312 | 7.44 | 9.86 | 16.2 | 16.61 | 68.0 |
| 315 | 8.50 | 11.51 | 19.95 | 20.35 | 83.18 |

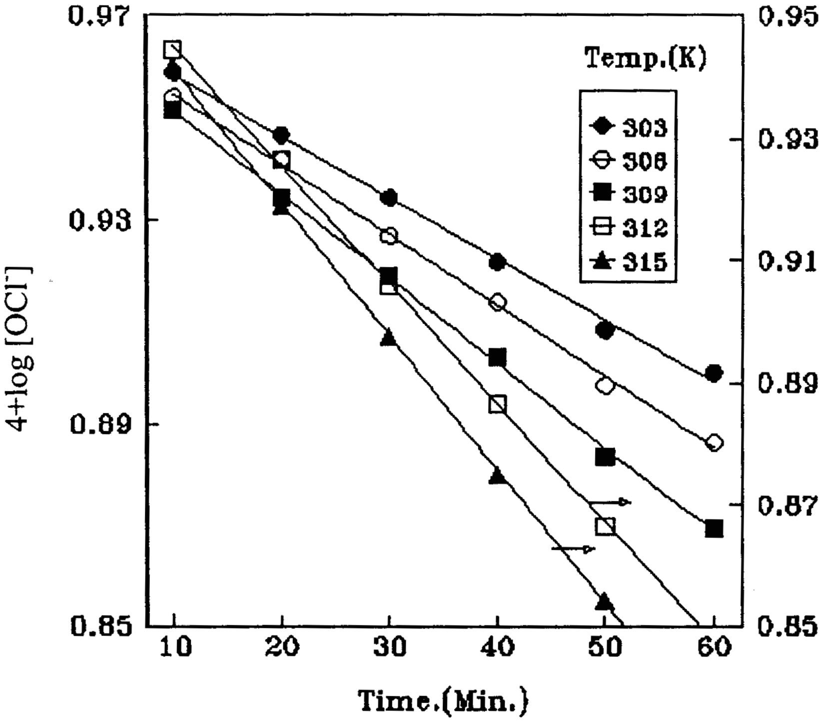


Fig 3.6.5 Effect of temperature on the oxidation of PMB catalysed by ACD

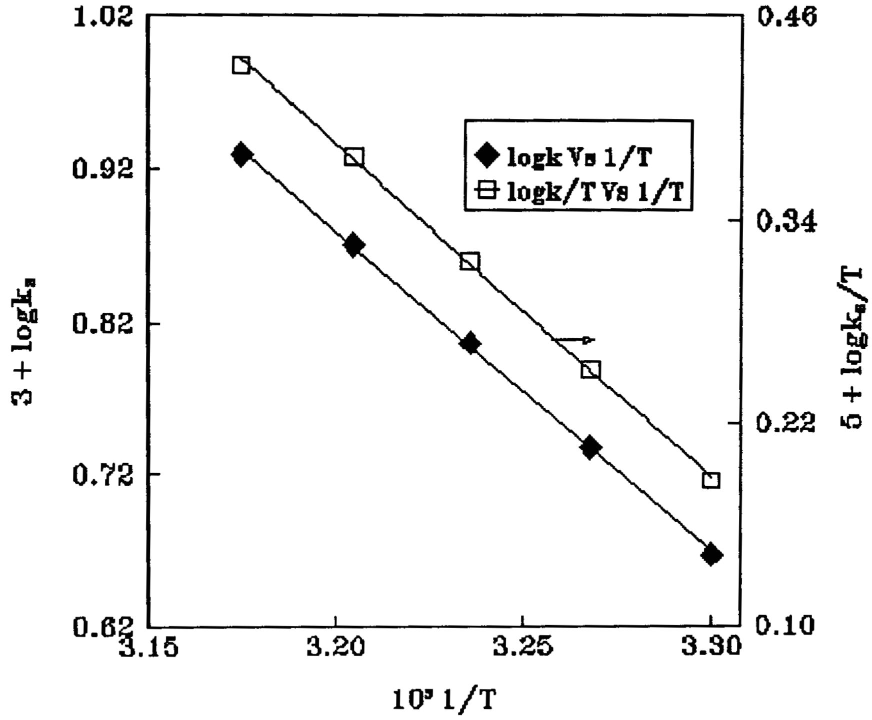


Fig 3.6.6 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PMB catalysed by ACD

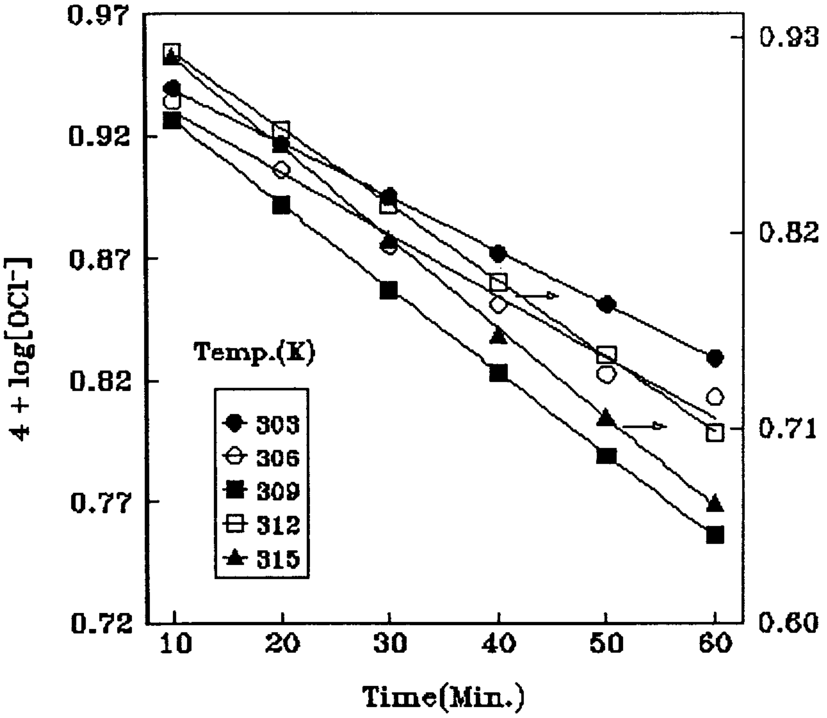


Fig 3.6.7 Effect of temperature on the oxidation of PCB catalysed by ACD

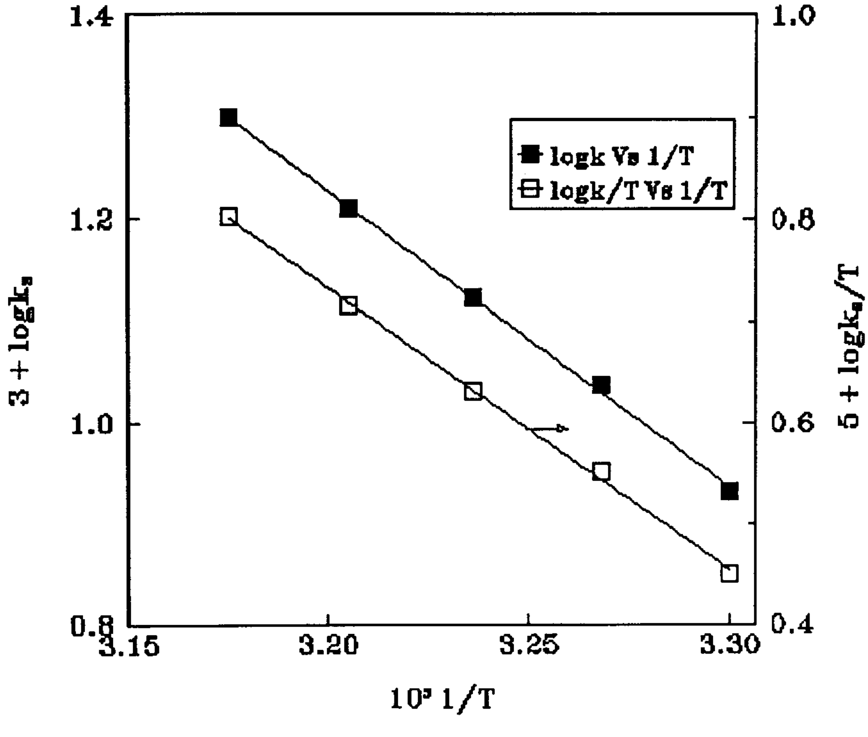


Fig 3.6.8 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PCB catalysed by ACD

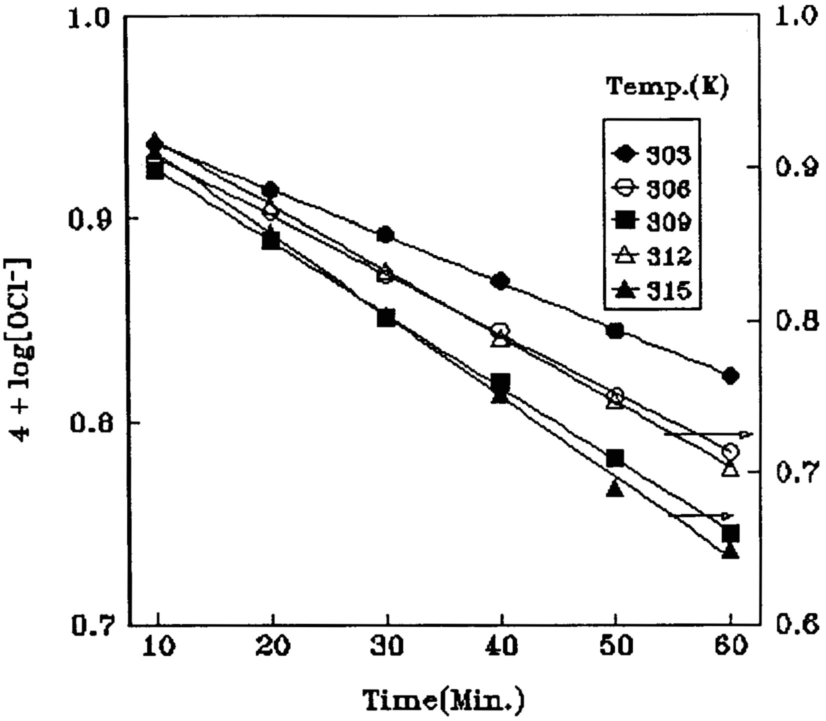


Fig 3.6.9 Effect of temperature on the oxidation of PBB catalysed by ACD

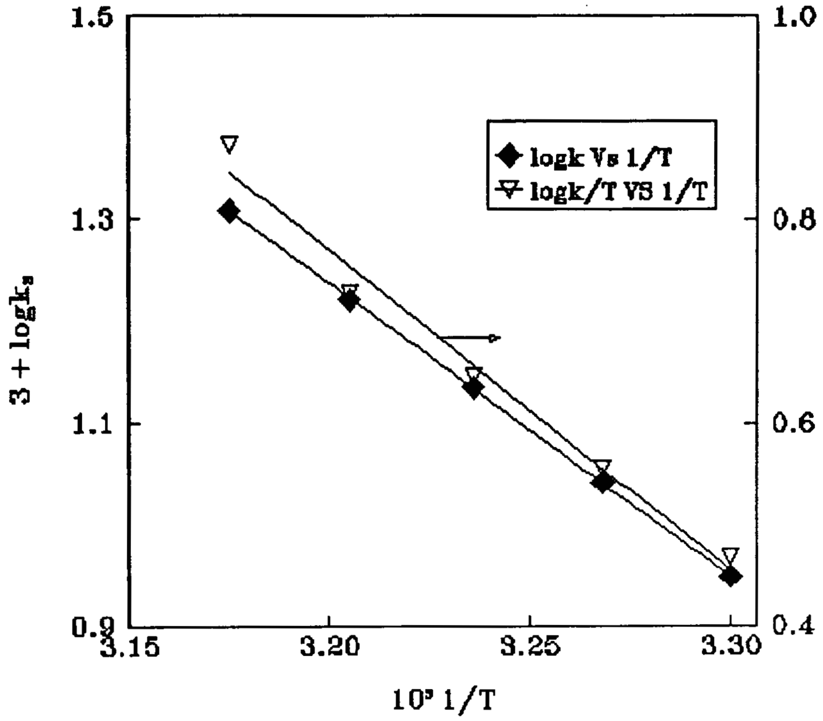


Fig 3.6.10 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PBB catalysed by ACD

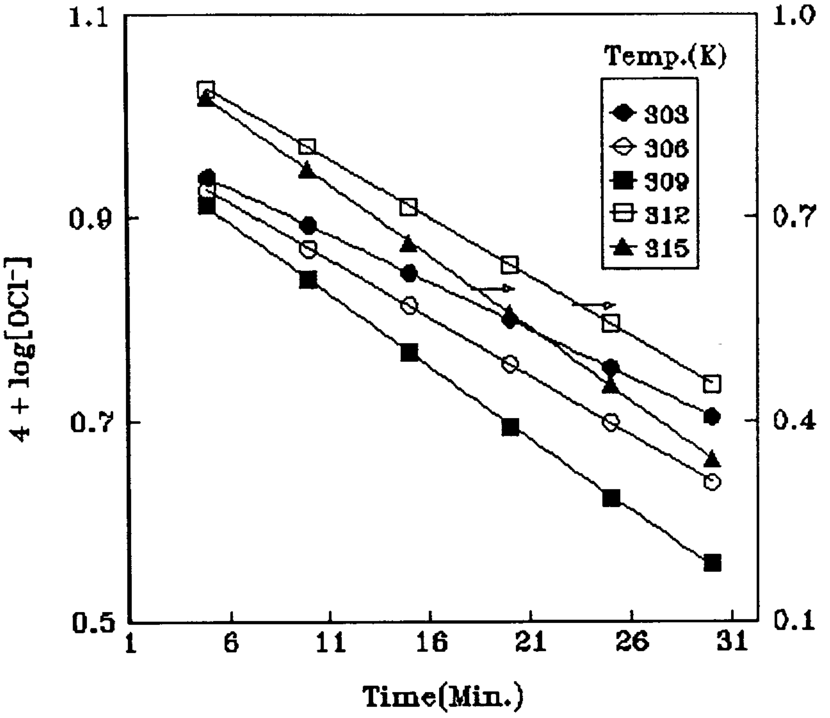


Fig 3.6.11 Effect of temperature on the oxidation of PNB catalysed by ACD

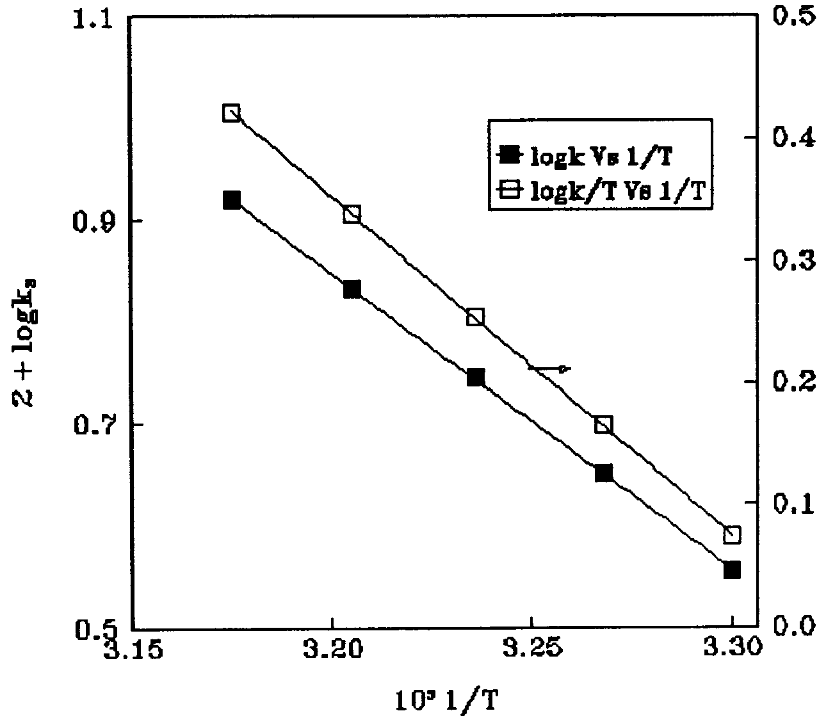


Fig 3.6.12 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PNB catalysed by ACD

## 3.7 Kinetic Studies in Aqueous Dioxane Medium

### 3.7.1 Effect of varying [NaOCl] on rate of oxidation of benzaldehyde

Kinetics of the oxidation of $C_6H_5CHO$ by NaOCl has been carried out in aqueous dioxane medium. The concentration of the substrate was fixed at $1.0 \times 10^{-2}$ M while the oxidant concentration varied from $4 \times 10^{-4}$ M to $10 \times 10^{-4}$ M. Other kinetic conditions were maintained uniform in all measurements. The linear plot of log [$OCl^-$] versus time indicated the first order dependence of the oxidant concentration on the rate of oxidation. The pseudo first order rate constant $k_{obs}$ obtained showed that the rate oxidation is practically unaffected by the change in concentration of the oxidant.

**Table 3.7.1**

**Effect of varying concentration of NaOCl on the rate of oxidation of benzaldehyde in aqueous dioxane medium**

[$C_6H_5CHO$] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

$\mu = 0.2$ mol dm$^{-3}$ Solvent: 20% aq. Dioxane

| $10^4$[NaOCl] mol dm$^{-3}$ | 4.0 | 6.0 | 8.0 | 10.0 |
|---|---|---|---|---|
| $10^5$ $k_{obs}$ s$^{-1}$ | 8.94 | 9.24 | 9.25 | 9.14 |
| Corr. Coeft. | 0.9941 | .09992 | 0.9987 | 0.9982 |

### 3.7.2 Effect of varying [$C_6H_5CHO$] on the oxidation in aq. dioxane

The effect of varying concentration of benzaldehyde was studied in the range 1.0 x $10^{-2}$ to 3 x $10^{-2}$ M All other kinetic conditions were identical. The concentration of the aldehyde was maintained in large excess to that of NaOCl in all cases. From the kinetic data the observed rate constant $k_{obs}$ was calculated which showed an increase with increase in concentration of the aldehyde (table 3.7.2 and fig.3.7.1). From the linear plot of log $k_{obs}$ against log [substrate], the order with respect to the aldehyde was calculated. The second order rate constant ($k_2$) of the overall reaction was obtained by dividing the pseudo order rate constant with substrate concentration. Constancy in the value of $k_2$ was observed.

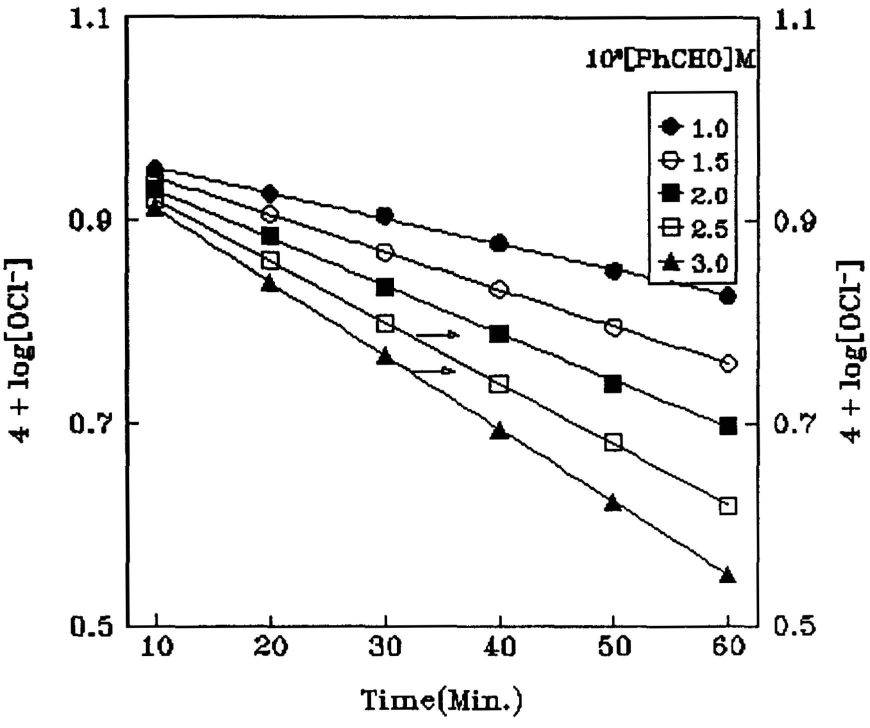


**Fig. 3.7.1 Effect of [substrate] on the oxidation of PhCHO in aq. dioxane**

## Table 3.7.2

## Effect of varying substrate concentration on the rate of oxidation of benzaldehyde using NaOCl in aq. Dioxane medium

$[NaOCl] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

$\mu = 0.2$ mol dm$^{-3}$ Solvent: 20% aq. Dioxane

| $10^2[C_6H_5CHO]$ mol dm $^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 9.14 | 14.0 | 17.85 | 23.03 | 27.69 |
| Corr. Coeft. | 0.9998 | 0.9999 | 0.9998 | 0.9999 | 0.9999 |
| $k_2 = k_{obs}/[C_6H_5CHO]$ ($dm^3mol^{-1}$ $s^{-1}$) | 9.14 | 9.33 | 8.93 | 9.21 | 9.22 |

### 3.7.3 Effect of added mineral acid on the rate of oxidation of benzaldehyde

The effect of $[H^+]$ on the rate of oxidation of benzaldehyde using NaOCl in aq. Dioxane medium was studied by adding different amounts of sulphuric acid in the system ($0.25 \times 10^{-2}$M – $5.0 \times 10^{-2}$M). The concentration of the substrate, oxidant and other parameters of the medium were kept constant in all measurements. An increase in specific rate was observed with an increase of $[H^+]$. The results are presented in table 3.7.3 and fig. 3.7.2

## Table 3.7.3

### Effect of varying substrate concentration on the rate of oxidation of benzaldehyde using NaOCl in aq. Dioxane medium

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent: 20% aq. Dioxane

| $10^2[H^+]$ mol dm$^{-3}$ | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ s$^{-1}$ | 12.66 | 13.17 | 16.54 | 19.77 | 22.95 |
| Corr. Coeft. | .9998 | .9999 | .9995 | .9990 | .9999 |

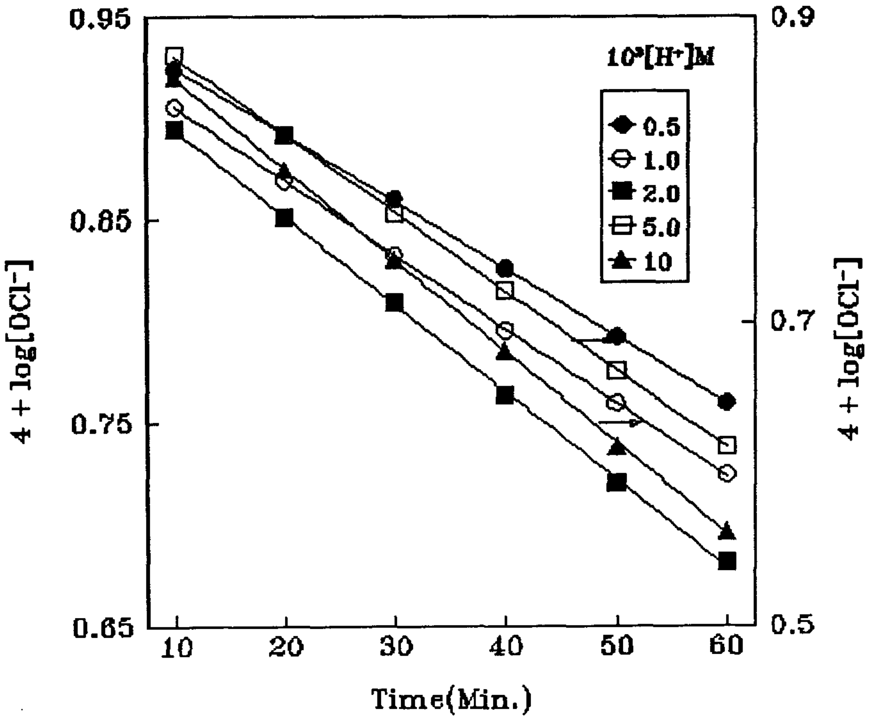


Fig. 3.7.2 Effect of $[H^+]$ on the oxidation of PhCHO in aq. dioxane

The plot of log $k_{obs}$ versus log $[H^+]$ was linear with positive slope indicating that the reaction is acid catalysed and a fractional order dependence on $[H^+]$

### 3.7.4 Influence of ionic strength on the rate of oxidation

The effect of ionic strength on rate was studied by using calculated amount of NaCl. The rate data obtained showed that ionic strength of the medium had only negligible effect on the hypochlorite oxidation of benzaldehyde. The data were tabulated in table 3.7.4.

**Table 3.7.4**

**Effect of ionic strength on the rate of oxidation**
**of $C_6H_5CHO$ using $OCl^-$ in aq. dioxane**

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. Dioxane

| $10^2$[NaCl] mol dm$^{-3}$ | 1.0 | 2.0 | 3.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ s$^{-1}$ | 9.14 | 9.52 | 9.36 | 9.12 | 9.28 |
| Corr. Coeft. | 0.9998 | 0.9997 | 0.9990 | 0.9991 | 0.9920 |

### 3.7.5 Influence of polarity of the medium on the rate of oxidation

Kinetic measurements were carried out to study the effect of polarity of the medium on the hypochlorite oxidation of benzaldehyde by taking different percentage of dioxane and water in the kinetic system (20 – 60% dioxane, v/v). The data presented in table 3.7.5 revealed that the rate of oxidation increased with increase of percentage of dioxane in the medium.

### Table 3.7.5

### Effect of percentage of dioxane on the hypochlorite oxidation of benzaldehyde

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| Dioxane (%) | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| $10^5\ k_{obs}\ s^{-1}$ | 9.09 | 33.12 | 56.57 | 82.29 | 103.32 |
| Corr. Coeft. | 0.9972 | 0.9998 | 0.9999 | 0.9998 | 0.9998 |

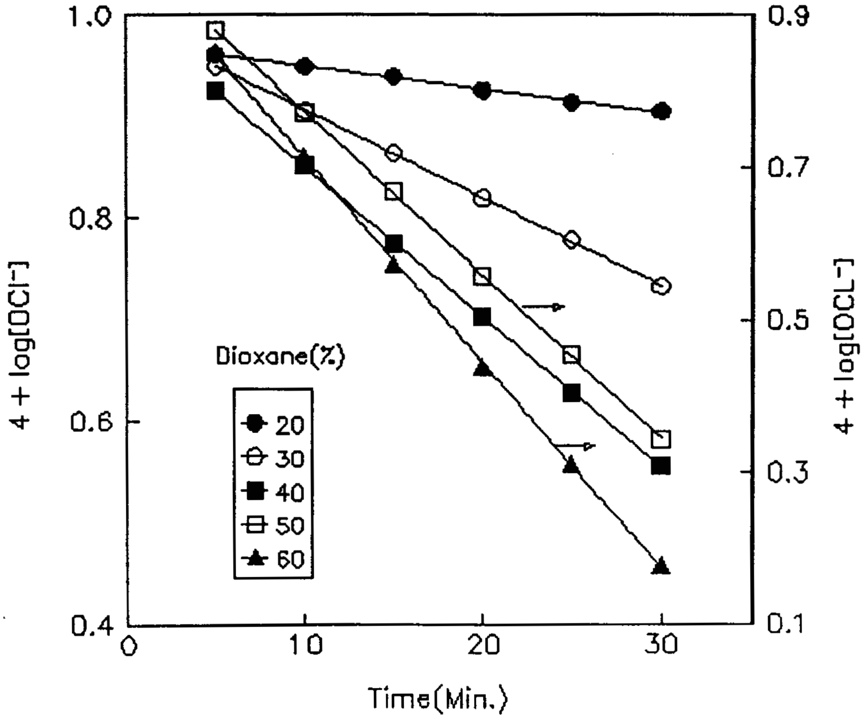


Fig. 3.7.3 Effect of polarity of the medium on the oxidation of PhCHO

## 3.7.6 Effect of temperature on the rate of hypochlorite oxidation of benzaldehyde in dioxane medium

The influence of temperature on the rate of oxidation of benzaldehyde was studied over a temperature range of 303K – 318K under identical condition of [substrate], [oxidant], ionic strength etc in 20% (v/v) aqueous dioxane. The thermodynamic parameters, Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were calculated from the plots of log k vs 1/T and log k/T vs 1/T. The results are given in table 3.7.6(a) and 3.7.6(b) and Fig 3.7.4 and Fig 3.7.5

**Table 3.7.6(a)**

**Effect of temperature on the oxidation of benzaldehyde**

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. dioxane

| Temp. (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 9.14 | 10.94 | 13.43 | 16.27 | 19.15 |
| Corr. Coeft. | 0.9998 | 0.9999 | 0.9999 | 0.9995 | 0.9990 |

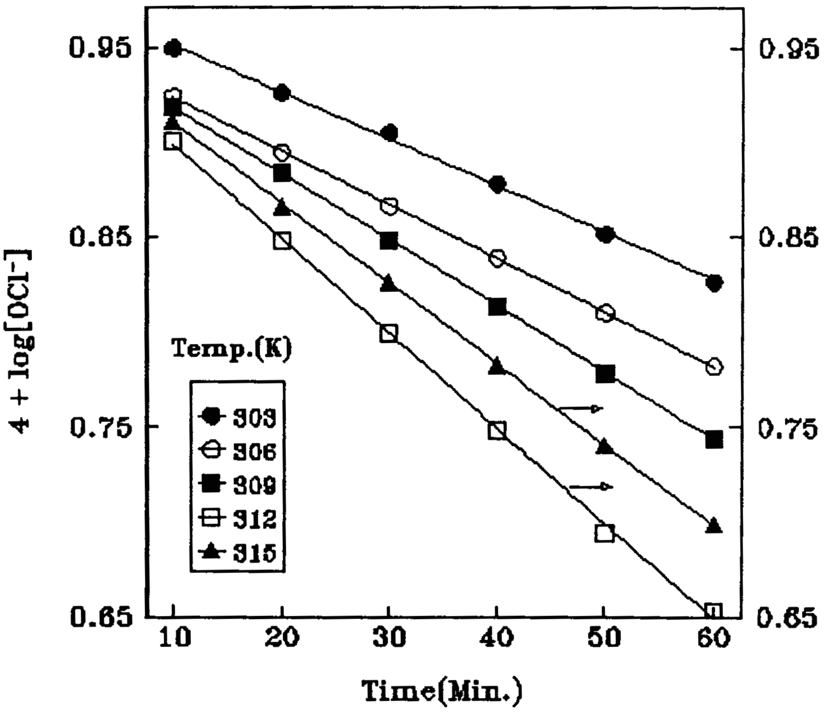


Fig. 3.7.4 Effect of temperature on the oxidation of PhCHO in aq. dioxane

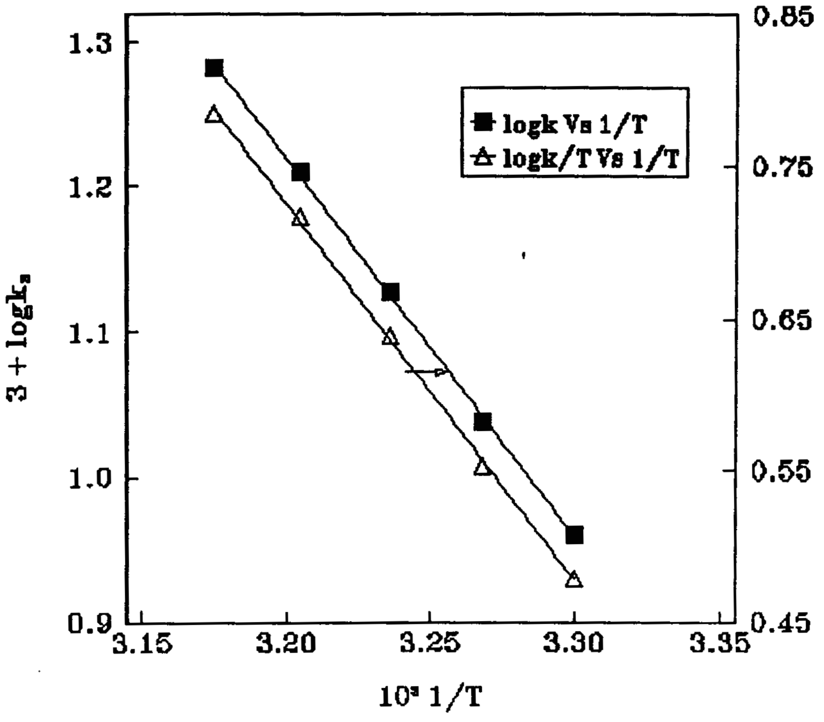


Fig. 3.7.5 Plots of log k vs 1/T and log k/T vs 1/T on the oxidation of PhCHO
Table 3.7.6 (b)

**Activation parameters for the oxidation of PhCHO in aq. dioxane medium**

| Activation parameters | Ea (kJ $mol^{-1}$) | $\Delta H^{\neq}$ (kJ $mol^{-1}$) | $-\Delta S^{\neq}$ ($JK^{-1} mol^{-1}$) | $\Delta G^{\neq}$ (kJ $mol^{-1}$) |
|---|---|---|---|---|
| | 49.75 | 47.28 | 128 | 86.9 |

### 3.7.7 Effect of substituents on the rate of oxidation of benzaldehyde

The influence of various substituents attached on the benzene ring of benzaldehyde on the rate of oxidation in dioxane medium was studied. It was observed that the rate increased in the order of substituents p-methyl<H<p-chloro<p-bromo<p-nitro. The values were given in table 3.7.7.

**Table 3.7.7**

**Effect of substituents on the rate of oxidation of PhCHO in 20% aq. Dioxane medium**

[Substrate] = $1.0 \times 10^{-2}$ mol $dm^{-3}$ T = 303K

[NaOCl] = $1.0 \times 10^{-3}$ mol $dm^{-3}$ $\mu = 0.2$ mol $dm^{-3}$

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| $10^5 k_{obs} s^{-1}$ | 6.87 | 9.14 | 10.28 | 10.86 | 28.47 |
| Corr. Coeft. | 0.9998 | 0.9998 | 0.9996 | 0.9990 | 0.9998 |

### 3.7.8 Effect of temperature on the rate of oxidation of substituted benzaldehydes

The effect of temperature on the rate oxidation of various substituted benzaldehydes were studied over the range 303K – 315K. The data are given in table 3.7.8(a) to 3.7.8(d) in the Appendix. Plots of log k vs 1/T and log k/T vs 1/T were drawn and activation parameters were calculated for each of the substituent.

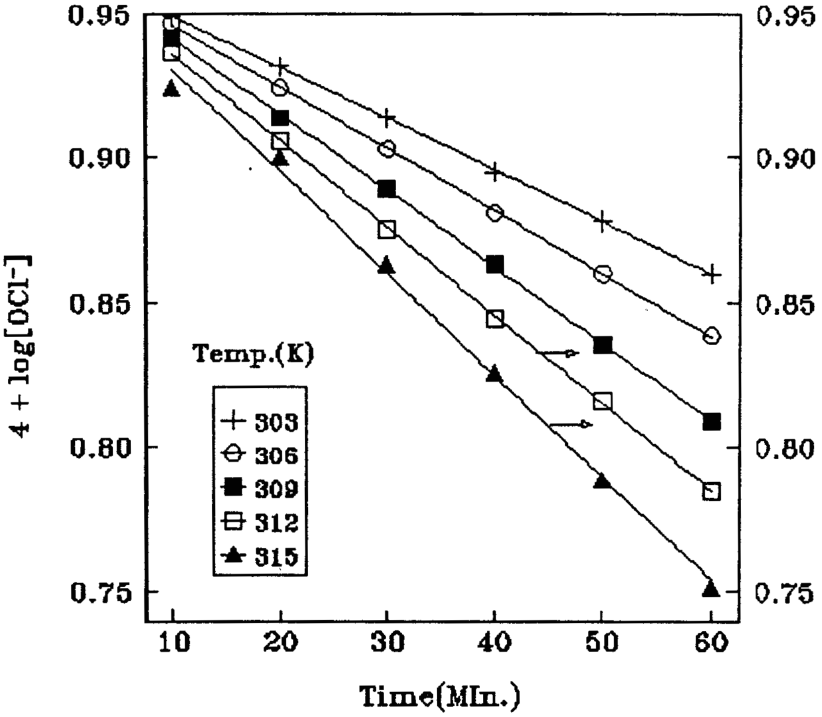


Fig 3.7.6 Effect of temperature on the oxidation of PMB in aq. dioxane

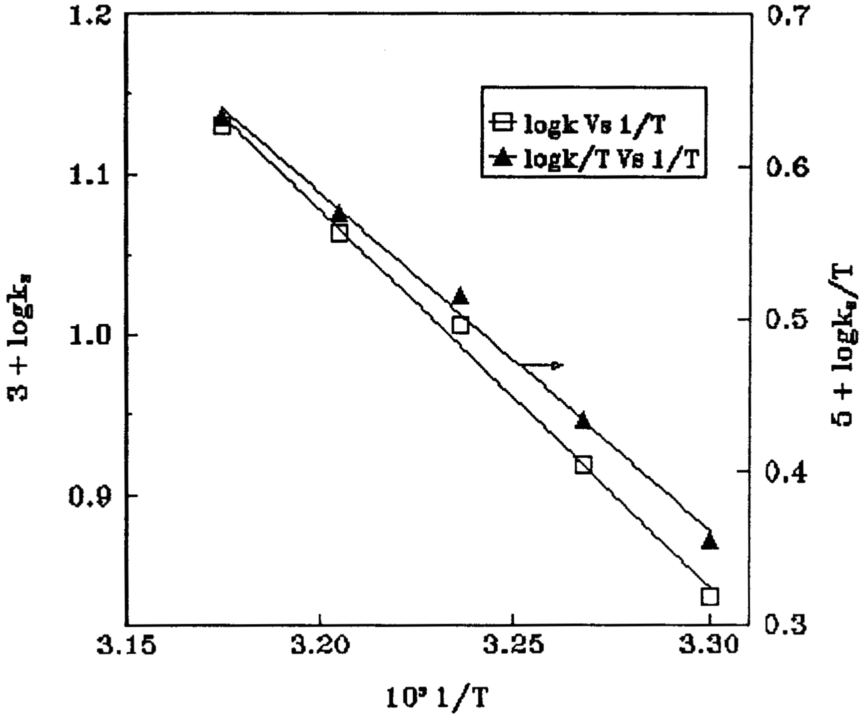


Fig 3.7.7 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PMB

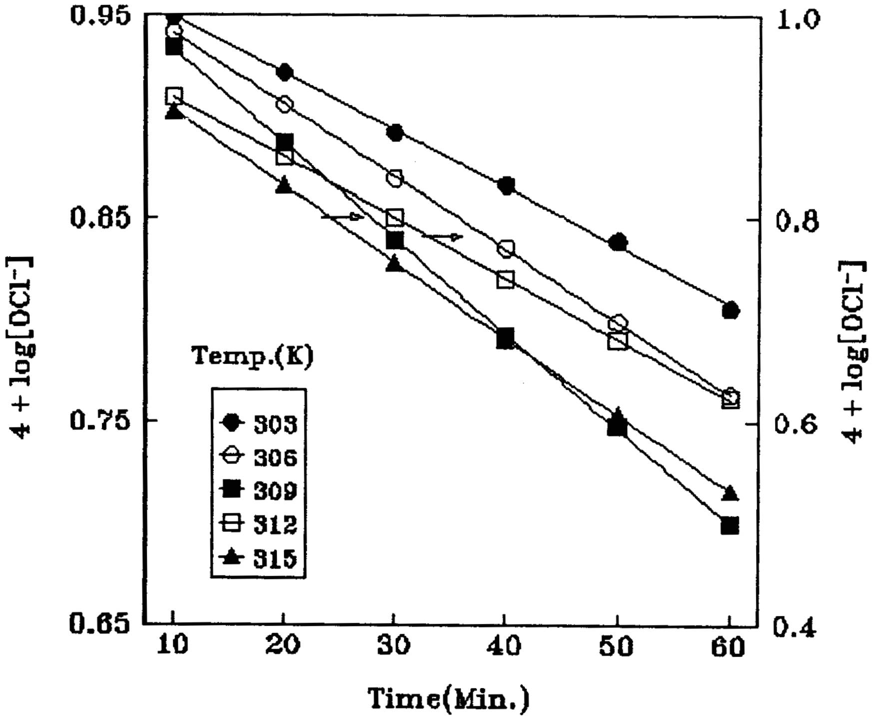


Fig 3.7.8 Effect of temperature on the oxidation of PCB in aq. dioxane

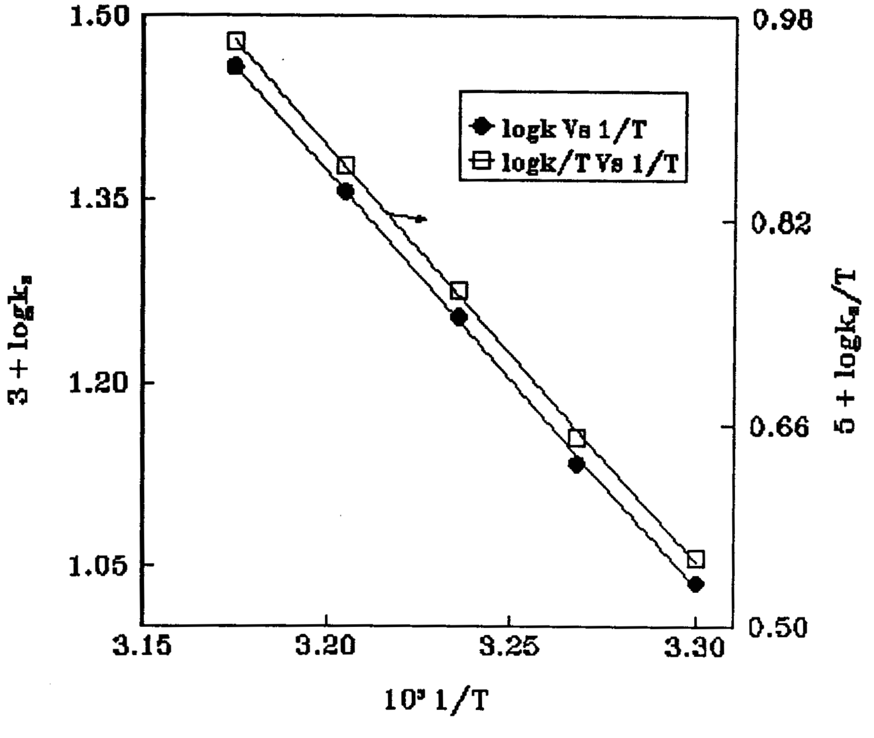


Fig 3.7.9 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PCB

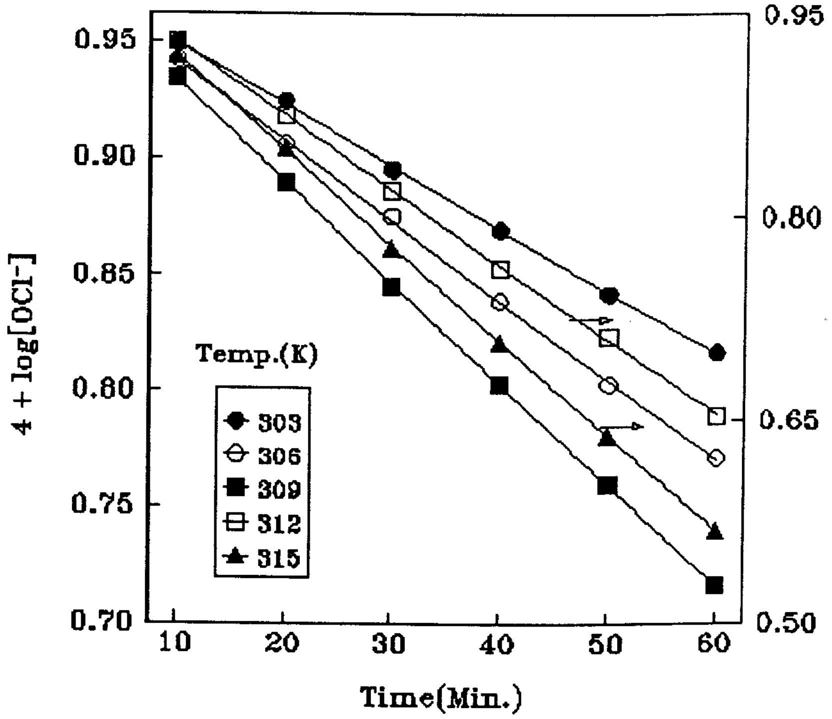


Fig 3.7.10 Effect of temperature on the oxidation of PBB in aq. dioxane

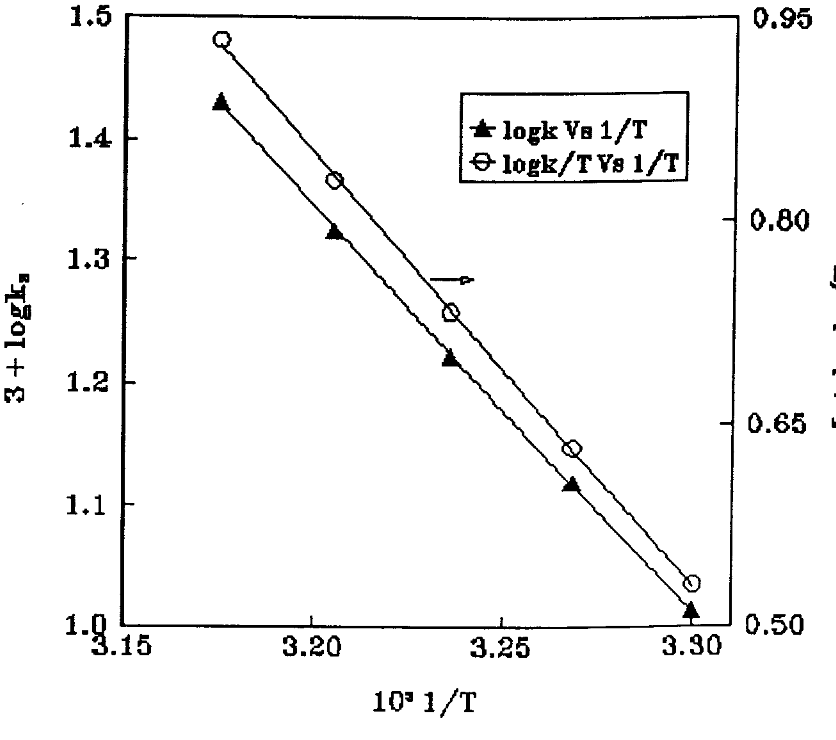


Fig 3.7.11 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PBB

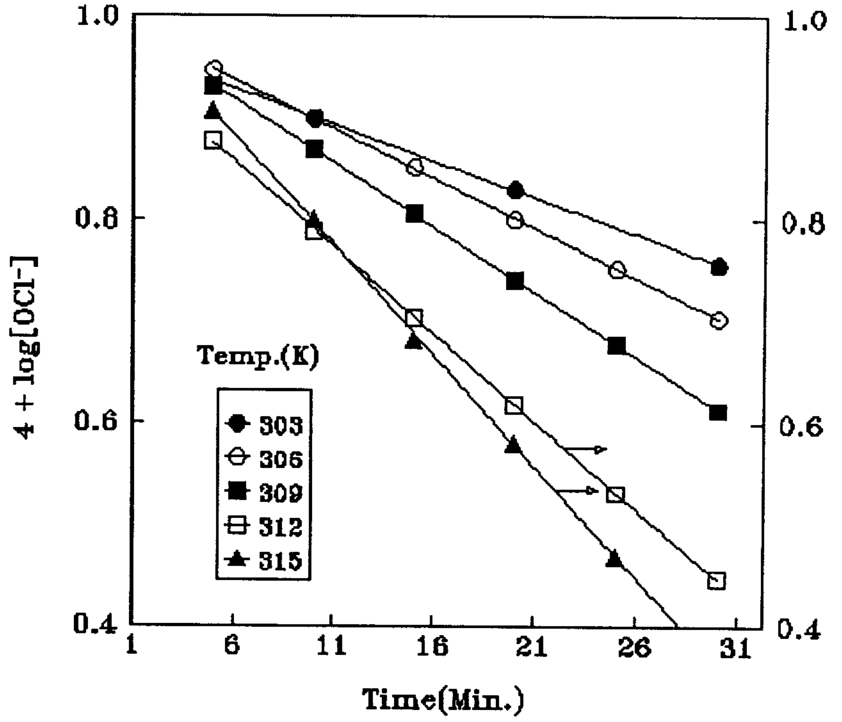


Fig 3.7.12 Effect of temperature on the oxidation of PNB in aq. dioxane

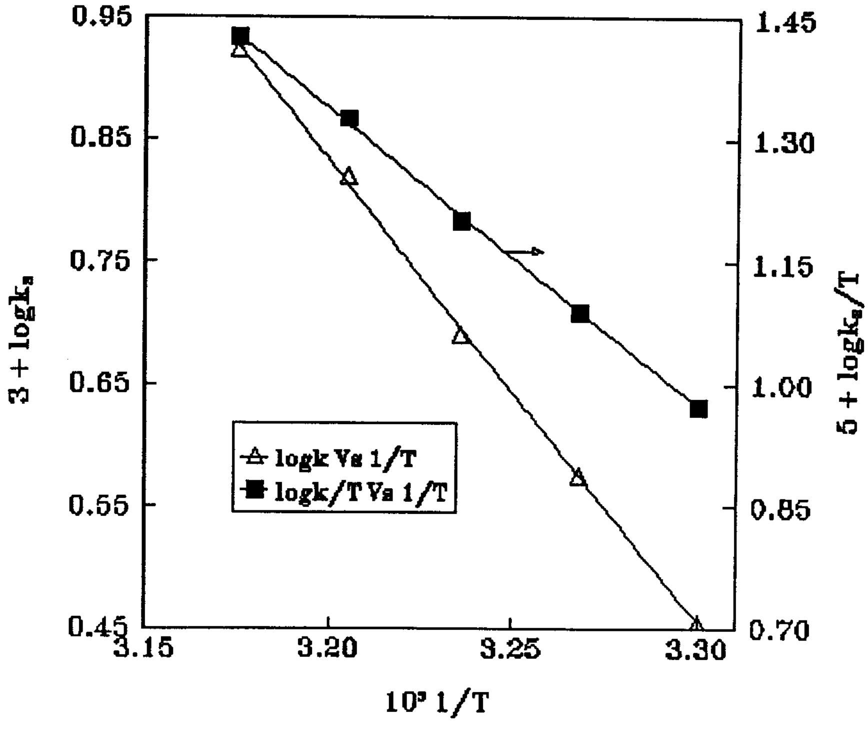


Fig 3.7.13 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PNB

## 3.8 Catalysis by Cyclodextrins in aq. Dioxane Medium

Effects of cyclodextrins were studied by carrying out the kinetic measurements in presence of catalytic amounts of ACD and BCD, keeping all other kinetic conditions unchanged.

### 3.8.1 Effect of addition of cyclodextrins on the oxidation of benzaldehyde in aq. dioxane medium at various temperatures.

The influence of catalysts viz. ACD and BCD on the hypochlorite oxidation of benzaldehyde in aq. dioxane medium, at various temperatures 303–315K. were investigated. The data are given in table 3.8.1(a) and 3.8.1 (b).

**Table 3.8.1 (a)**

**Effect of temperature on the oxidation of benzaldehyde in 20% aq. dioxane medium on presence of ACD**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5\ k_{obs}\ s^{-1}$ | 14.88 | 17.79 | 21.38 | 25.26 | 30.05 |
| Corr. coeft. | 0.9998 | 0.9988 | 0.9987 | 0.9989 | 0.9998 |

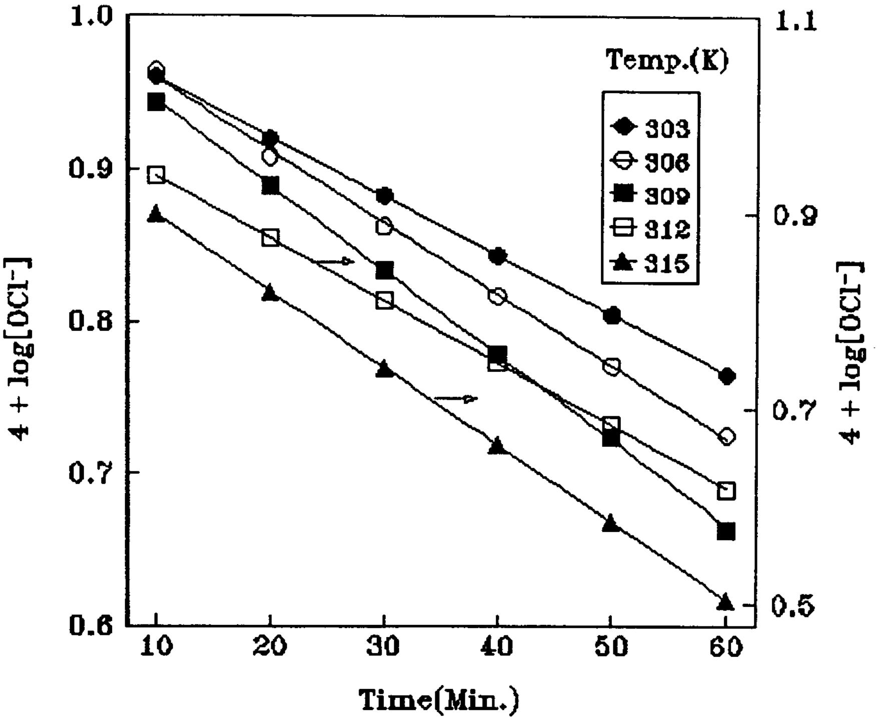


Fig 3.8.1 Effect of temperature on the oxidation of PhCHO catalysed by ACD in aq. dioxane

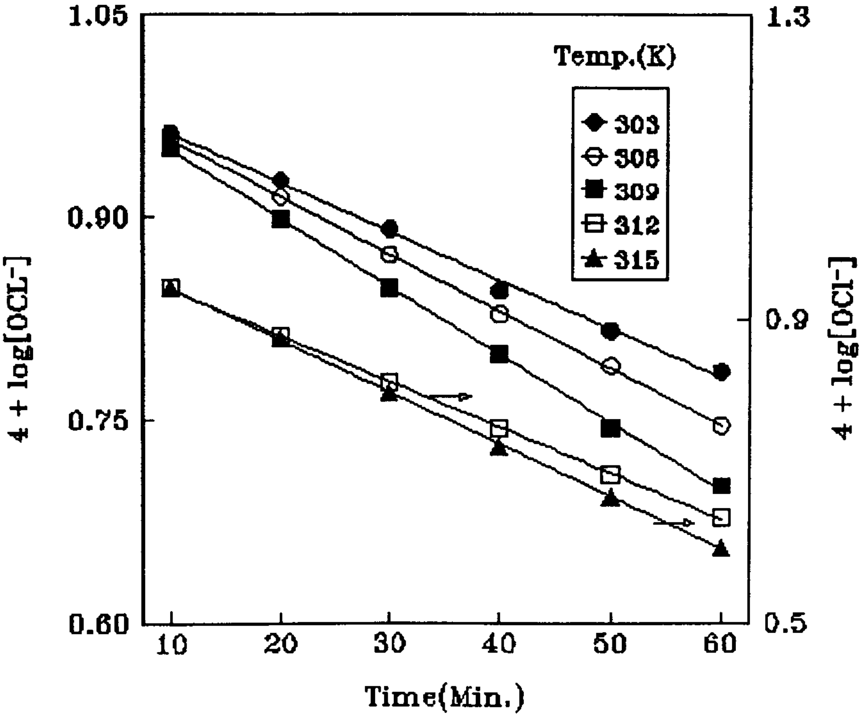


Fig 3.8.2 Effect of temperature on the oxidation of PhCHO catalysed by BCD in aq. dioxane

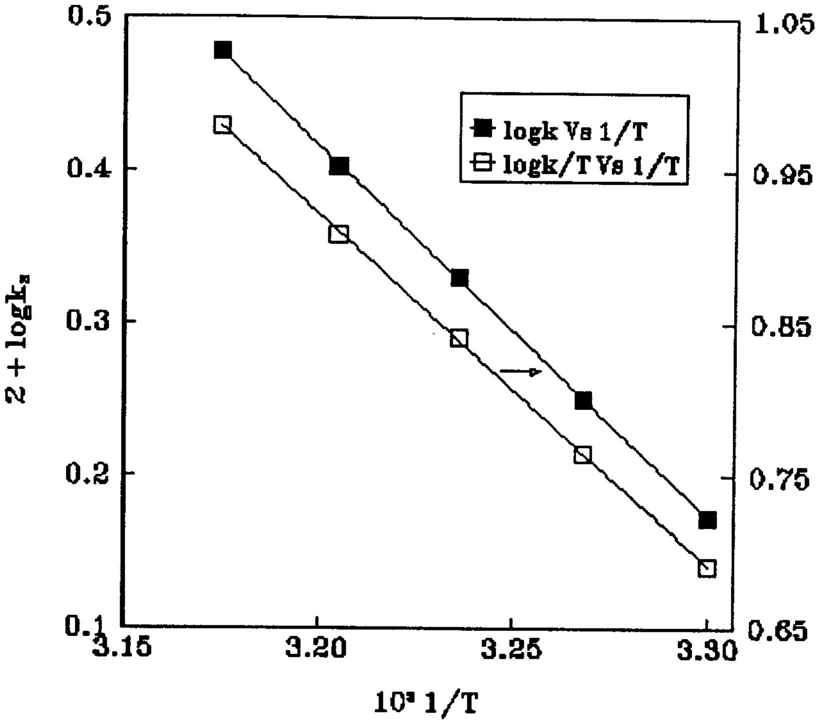


Fig 3.8.3 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PhCHO catalysed by ACD in aq. dioxane

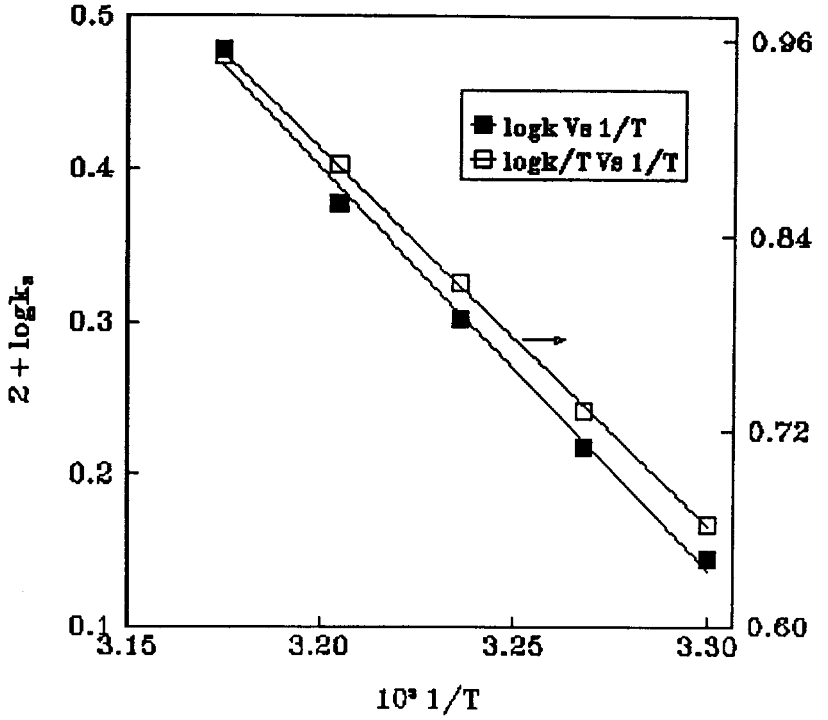


Fig 3.8.4 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PhCHO catalysed by BCD in aq. dioxane

## Table 3.8.1 (b)

**Effect of temperature on the oxidation of benzaldehyde in aq. dioxane medium in presence of BCD**

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [BCYD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$ βCD

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

Solvent: 20% aq. dioxane

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5 k_{obs}$ s$^{-1}$ | 13.95 | 16.5 | 20.02 | 23.84 | 28.05 |
| Corr. Coeft. | 0.9998 | 0.9987 | 0.9974 | 0.9959 | 0.9970 |

Activation parameters were determined from the plots of log k versus 1/T and log k/T versus 1/T (fig. 3.8.3 and fig. 3.8.4)

### 3.8.2 Effect of substituents on the rate of oxidation of benzaldehyde in aq. dioxane medium in presence of cyclodextrin

The substituent effect on the rate of oxidation of benzaldehyde in aq. dioxane medium using ACD was investigated for various para substituted derivatives, (Table 3.8.2)

### Table 3.8.2

### Effect of substituents on the hypochlorite oxidation of benzaldehyde in aq. dioxane medium catalysed by ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ [ACYD] = 2.1 x $10^{-3}$ mol $dm^{-3}$

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$

Solvent: 20% aq. dioxane

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 10.77 | 14.88 | 16.72 | 18.5 | 51.25 |
| Corr. Coeft. | 0.9974 | 0.9998 | 0.9987 | 0.9980 | 0.9940 |

### 3.8.3 Effect of temperature on the rate of oxidation of substituted benzaldehydes in aq. dioxane medium catalysed by ACD

The catalytic effect of cyclodextin at various temperatures were investigated for different substituted benzaldehydes in aq. dioxane medium the rate constants for different substituents at various temperatures are given in 3.8.3. The activation parameters were also determined and discussed (Table 4.2.9 d).

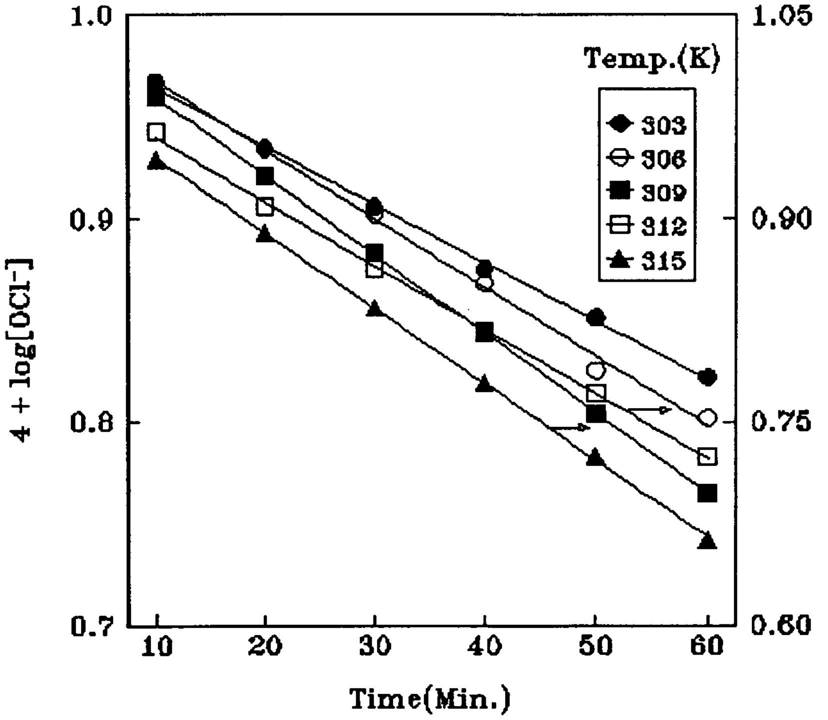


Fig 3.8.5 Effect of temperature on the oxidation of PMB catalysed by ACD in aq. dioxane

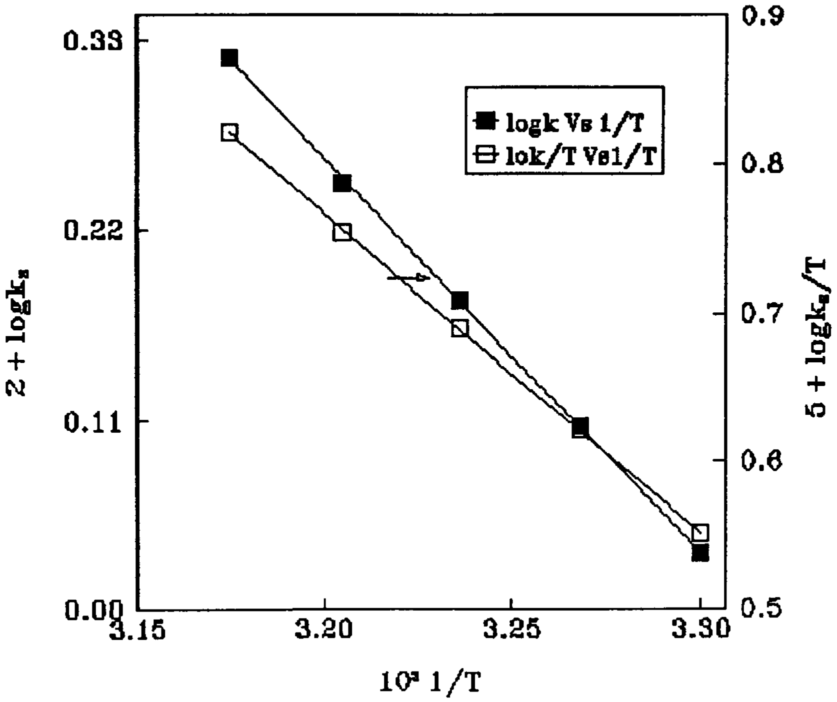


Fig 3.8.6 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PMB catalysed by ACD in aq. dioxane

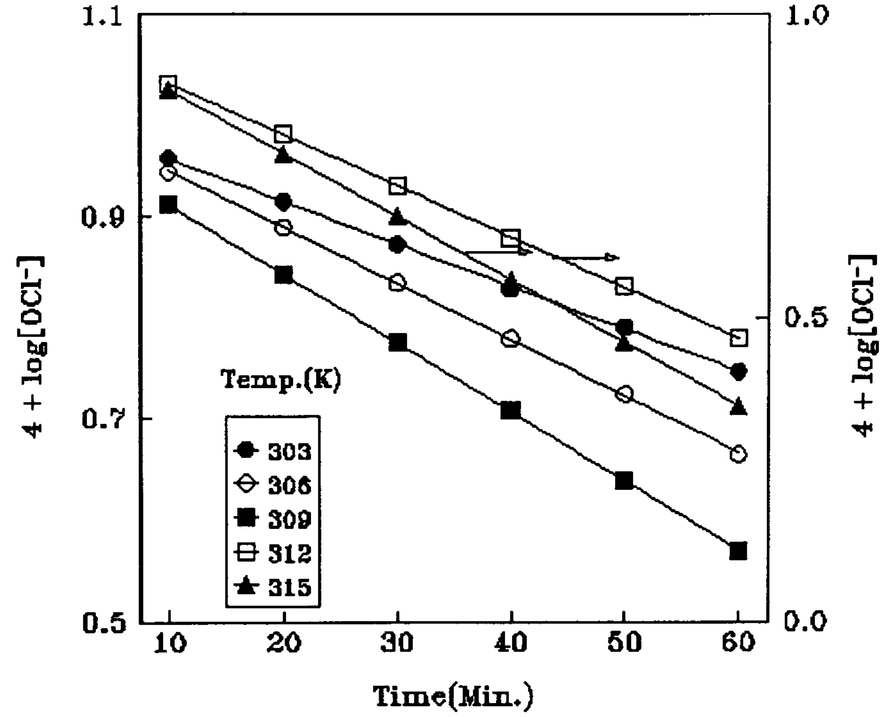


Fig 3.8.7 Effect of temperature on the oxidation of PCB catalysed by ACD in aq. dioxane

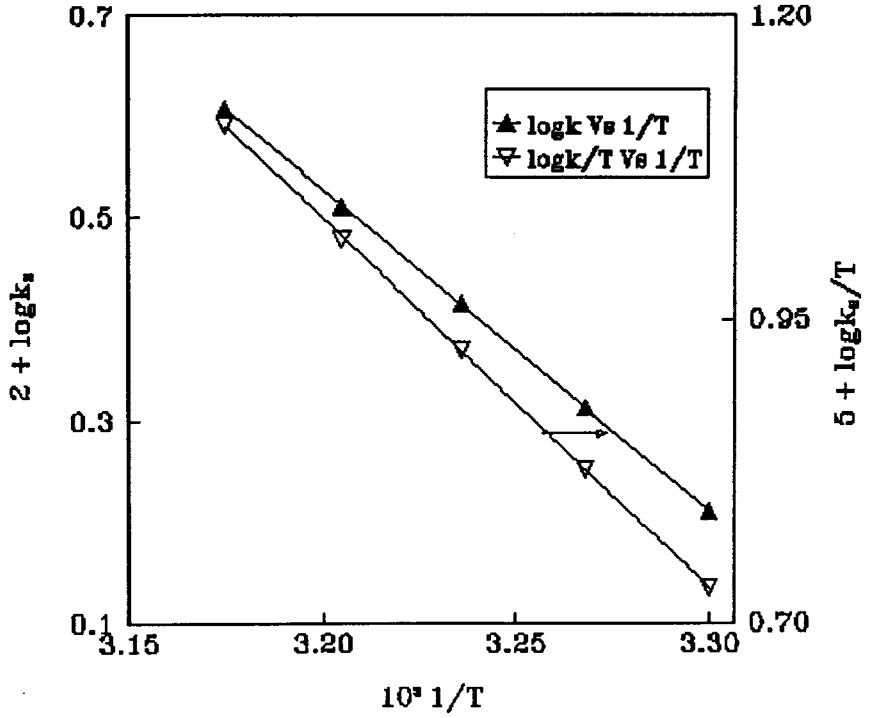


Fig 3.8.8 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PCB catalysed by ACD in aq. dioxane

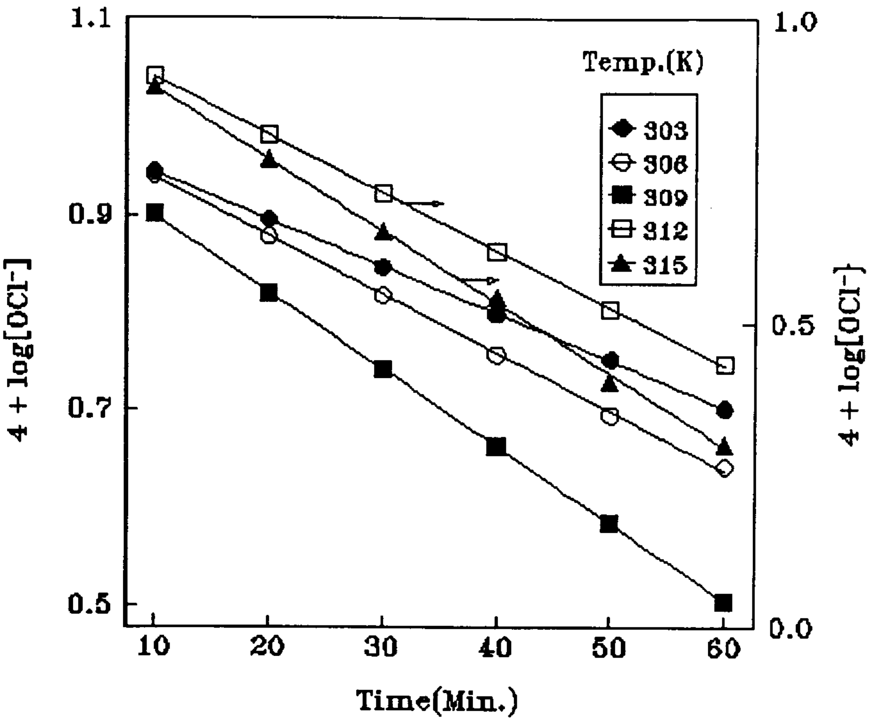


Fig 3.8.9 Effect of temperature on the oxidation of PBB catalysed by ACD in aq. dioxane

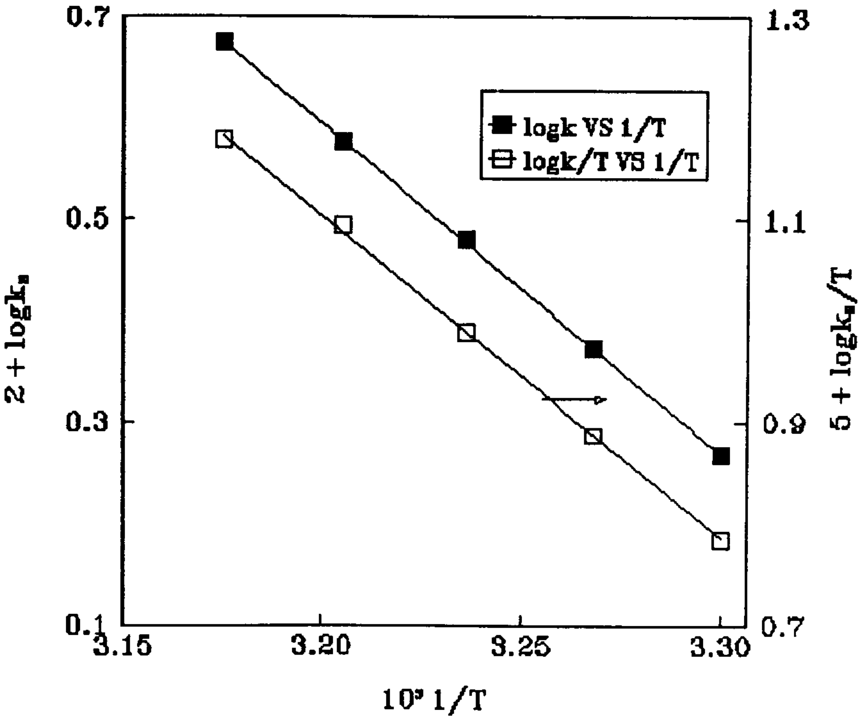


Fig 3.8.10 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PBB catalysed by ACD in aq. dioxane

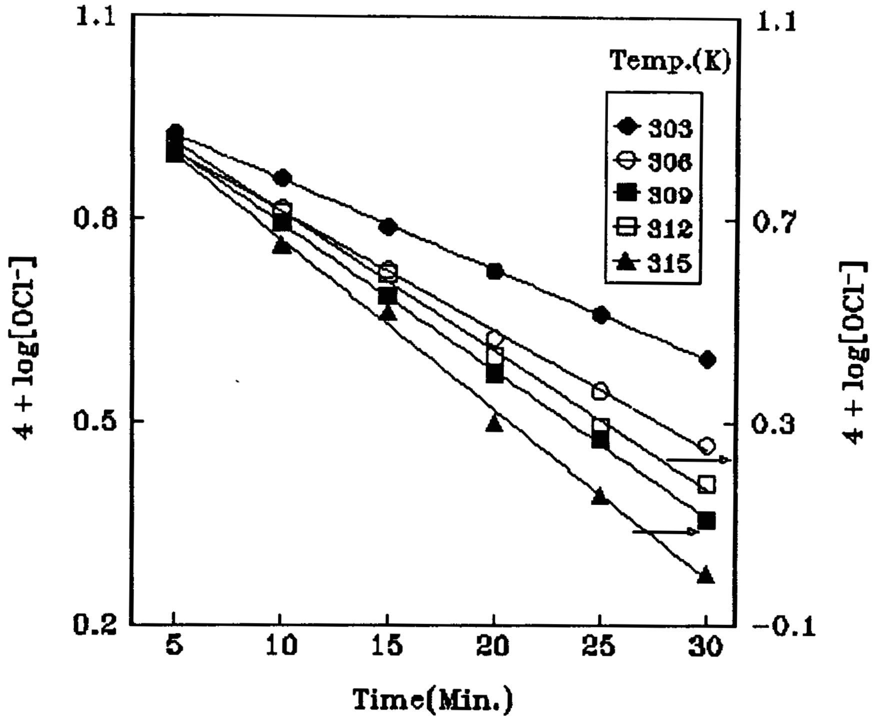


Fig 3.8.11 Effect of temperature on the oxidation of PNB catalysed by ACD in aq. dioxane

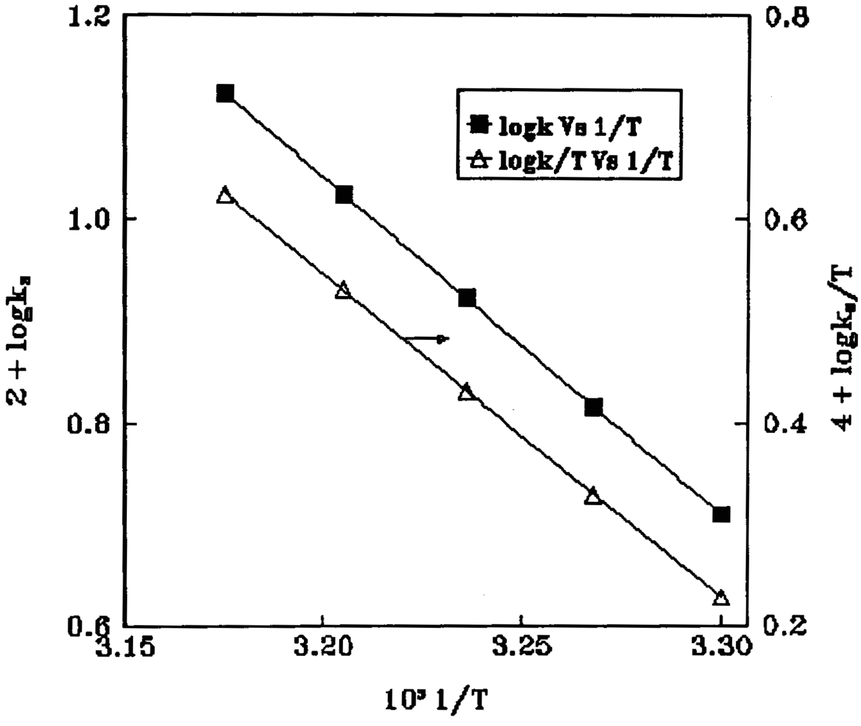


Fig 3.8.12 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PNB catalysed by ACD in aq. dioxane

### Table 3.8.3

### Effect of temperature on the rate of oxidation of susbtituted benzaldehydes in 20% aq. dioxane medium catalysed by ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Temperature (K) | $10^5$ $k_{obs}$ s $^{-1}$ | | | | |
| 303 | 10.77 | 14.88 | 16.22 | 18.5 | 51.25 |
| 306 | 12.8 | 17.79 | 20.54 | 23.58 | 65.31 |
| 309 | 15.13 | 21.38 | 26.00 | 30.19 | 83.66 |
| 312 | 17.68 | 25.26 | 32.36 | 37.58 | 105.93 |
| 315 | 20.9 | 30.05 | 40.5 | 47.32 | 132.59 |

## 3.9 KINETIC STUDIES IN ACETONITRILE MEDIUM

The kinetic measurements in respect of the oxidation of $C_6H_5CHO$ using NaOCl were also carried out in aqueous acetonitrile medium under pseudo first order condition. A linear plot of log [$OCl^-$] against time indicated the first order dependence with respect to the oxidant. Effect of varying concentration of the substrate was studied and a linear plot of log $k_{obs}$ versus log [substrate] with unit slope indicated the first order dependence on substrate concentration. The second order rate constant ($k_2$) showed constancy with varying substrate concentration the data are presented in table 3.9.1.

## Table 3.9.1

### Effect of varying substrate concentration for the oxidation of benzaldehyde in aq. acetonitrile

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ T =- 303K

$\mu$ = 0.2 mol $dm^{-3}$ Solvent: 20% aq. dioxane ?

| $10^2$[Substrate] | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 7.25 | 10.86 | 14.75 | 18.25 | 21.72 |
| $k_{obs}$ / [sub] | 7.25 | 7.18 | 7.22 | 7.30 | 7.24 |
| Corr. Coeft. | 0.9997 | 0.9920 | 0.9905 | 0.9982 | 0.9966 |

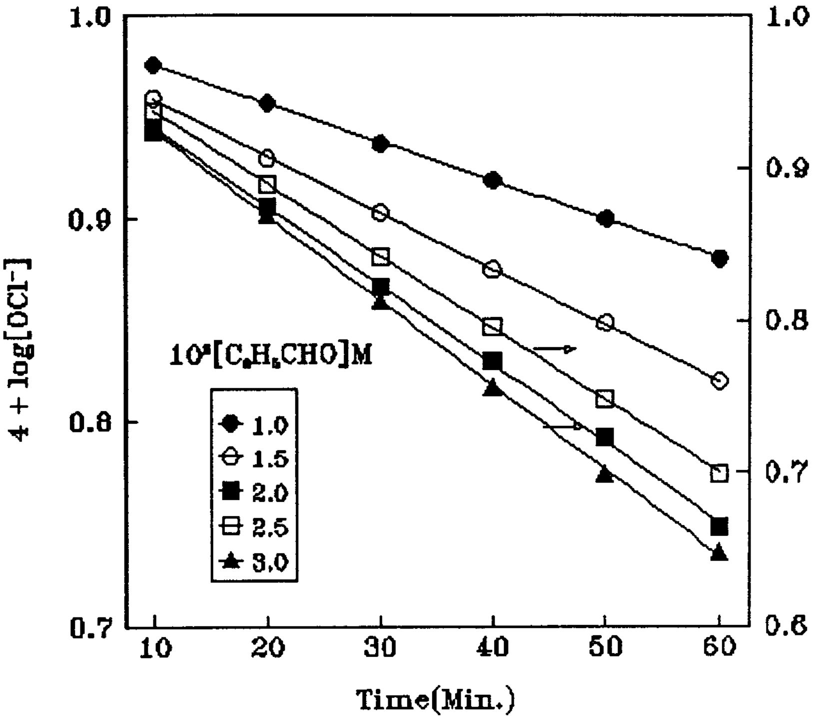


Fig 3.9.1 Effect of [substrate] on the oxidation of PhCHO in aq. acetonitrile medium

The effect of polarity of the medium on reaction rate was studied by conducting the kinetic measurements with varying percentage of acetonitrile and water keeping all other parameters identical. The data given in table 3.9.2 and fig.3.9.2 showed that rate of oxidation increases with percentage of acetonitrile in the medium.

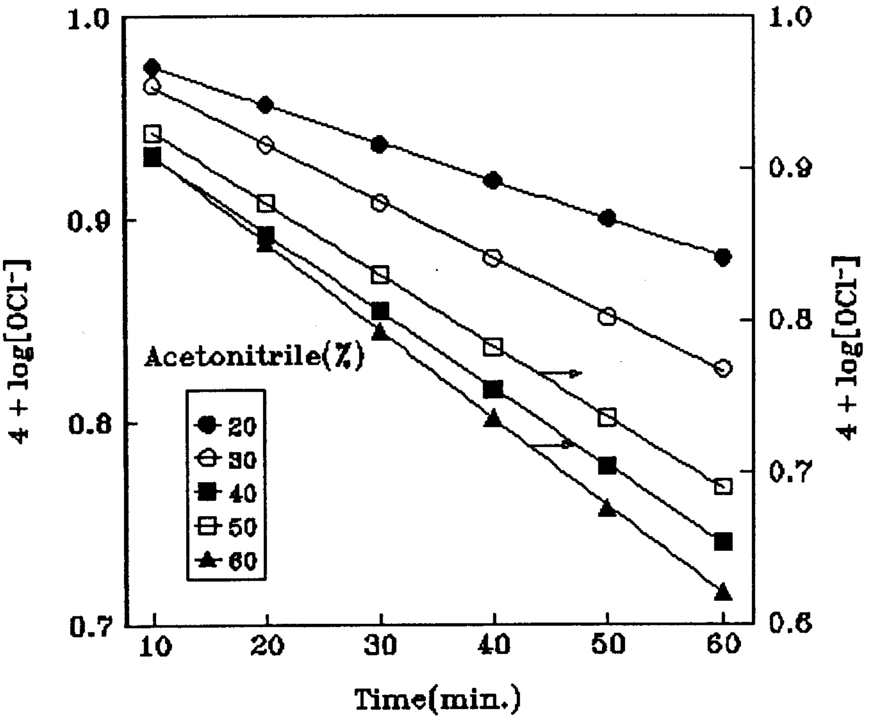


**Fig 3.9.2 Effect of varying percentage of acetonitrile on the oxidation of PhCHO**

## Table 3.9.2

## Effect of polarity of the medium on the oxidation of benzaldehyde in aq. acetonitrile

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| % of Acetonitrile | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 7.25 | 10.82 | 14.66 | 18.0 | 22.10 |
| Corr. Coeft. | 0.9997 | 0.9992 | 0.9984 | 0.9970 | 0.9988 |

The effect of temperature on oxidation of benzaldehyde in aq. acetonitrile medium was also investigated within the temperature range 303 – 315 K. The data are presented in table 3.9.3 and fig 3.9.3. The activation parameters were also determined (Fig.3.9.4).

## Table 3.9.3

## Effect of temperature on the oxidation of benzaldehyde in aq. acetonitrile medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. acetonitrile

| Temp. (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^5$ $k_{obs}$ $s^{-1}$ | 7.25 | 8.56 | 10.09 | 12.51 | 15.20 |
| Corr. Coeft. | 0.9997 | 0.9990 | 0.9988 | 0.9967 | 0.9920 |

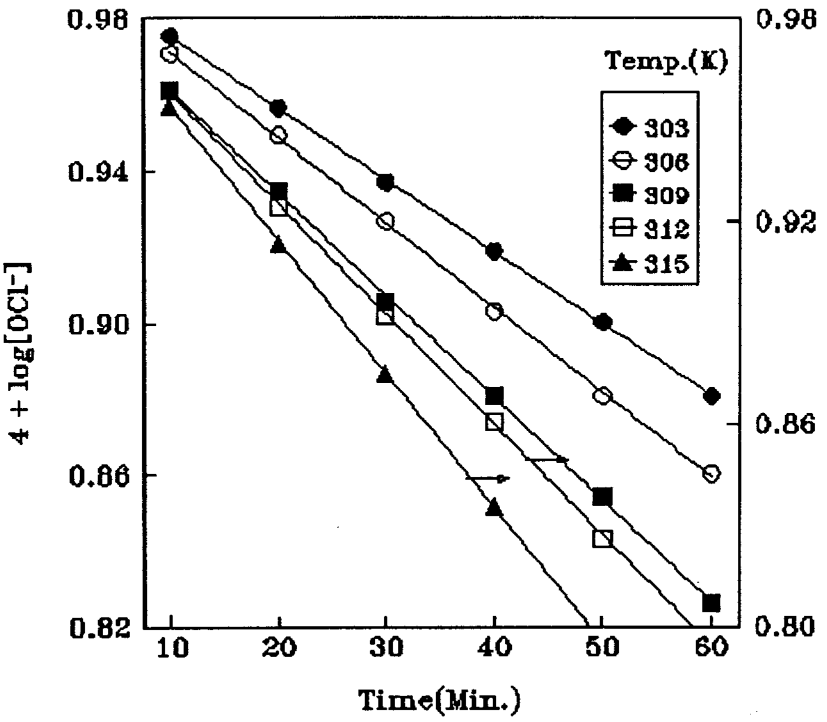


Fig 3.9.3 Effect of temperature on the oxidation of PhCHO in aq. acetonitrile medium

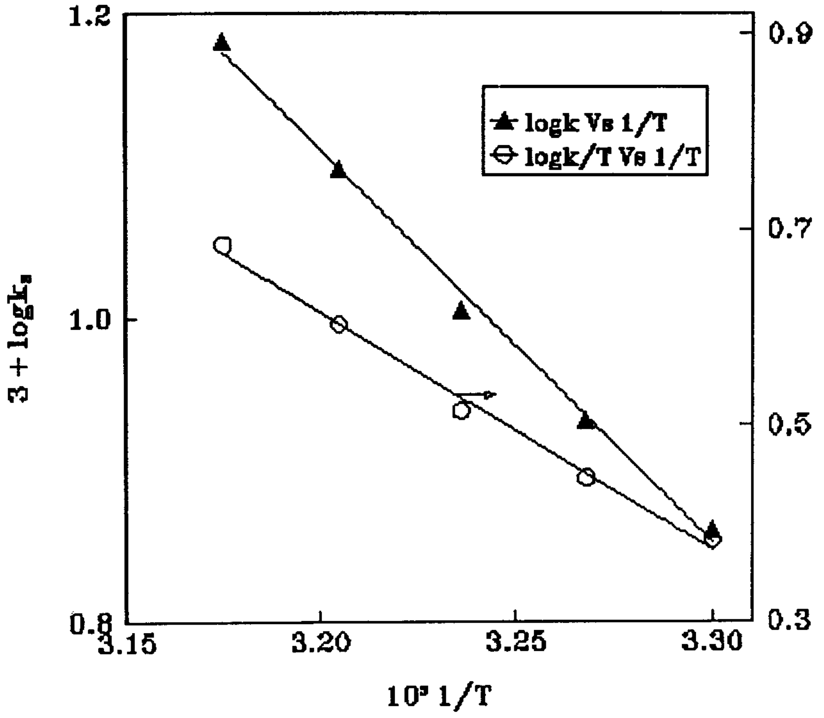


Fig 3.9.4 Plots of log k vs 1/T and log k/T vs 1/T for the oxidation of PhCHO in aq. acetonitrile

## 3.10 Oxidation of Benzaldehyde in Presence of Phase Transfer Catalysts

The oxidation of benzaldehyde was carried out in an organic solvent using phase transferred hypochlorite ion. Tetra butyl ammonium bromide (TBAB) was used as the phase transfer catalyst . The extraction of hypochlorite ion from aqueous phase into the organic phase was the first step in phase transfer technique. For this, a known concentration of aqueous solution of hypochlorite was mixed with benzene containing TBAB as PT catalyst. The mixture was stirred at room temperature for 45 minutes using a magnetic stirrer. The two layers were then seperated and the concentration of $OCl^-$ remained in the aqueous layer was determined. From this the amount of $OCl^-$ transferred into the organic phase can be calculated.

Extraction studies showed that for maximum extraction of hypochlorite into the organic phase, the amount of PT catalyst taken should be twice the amount of the oxidant. Thus when 20 ml of 0.05M aqueous $OCl^-$ solution was stirred with 0.1M TBAB in 20 ml of benzene, 95% hypochlorite was transferred into the organic phase in the form of tetrabutyl ammonium hypochlorite

### 3.10.1 Kinetic studies using phase transferred hypochlorite as oxidant

For carrying out kinetic measurements, requisite amounts of benzaldehyde in the organic solvent, benzene and the phase transferred hypochlorite ($Q^+OCl^-$) were mixed together in such a way that the pseudo- first order condition ie [substrate]>> [oxidant] was maintained. 1 ml aliquots were withdrawn at various time intervals from the reaction mixture and diluted to five times its volume with benzene. The progress of the reaction was followed by measuring the absorbance of the unreacted hypochlorite using Shimadzu double beam UV-Visible Spectrophotometer (UV-1602). $Q^+OCl^-$ absorbs with a $\lambda_{max}$ of 309 nm in benzenes.

### 3.10.2 Effect of varying [$Q^+OCl^-$] and [PhCHO] on the rate of oxidation

Under the condition of [PHCHO]>>[$Q^+OCl^-$], the plot of log (Absorbance) Vs time were linear indicating the first order dependence w.r.t. the concentration of $Q^+OCl^-$. The $k_{obs}$ values can be determined from the slope of the curve. It was shown that the first order rate constant $k_{obs}$ remained practically unchanged by varying concentration of $Q^+OCl^-$ (Table 3.10.2(a))

## Table 3.10.2(a)

### Effect of [$Q^+OCl^-$] on the oxidation of benzaldehyde

Solvent - Benzene PT Catalyst- TBAB

[PhCHO] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ Temperature 303K

| $10^3$ [$Q^+OCl^-$] mol dm$^{-3}$ | 0.5 | 0.8 | 1.0 |
|---|---|---|---|
| $10^4$ $k_{obs}$ s$^{-1}$ | 1.21 | 1.23 | 1.20 |
| Corr.coeft. | 0.9970 | 0.9985 | 0.9992 |

The effect of varying [PhCHO] was studied in the range $1.0 \times 10^{-2}$ – $2.5 \times 10^{-2}$ mol dm$^{-3}$, keeping all other kinetic conditions the same (table 3.10.2b) The $k_{obs}$ values increases with [PhCHO]. The second order rate constant $k_2$ showed a constancy indicating first order dependence on [PhCHO]. This was further confirmed from the plot of log $k_{obs}$ with log [PhCHO].

## Table. 3.10.2 (b)

## Effect of [PhCHO] on the oxidation of benzaldehyde in Benzene

$[Q^+OCl^-] = 1.0x\ 10^{-3}$ mol dm $^{-3}$ Temperature 303K

| $10^2$ [PhCHO] mol dm$^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 |
|---|---|---|---|---|
| $10^4$ $k_{obs}$ $s^{-1}$ | 1.15 | 1.81 | 2.40 | 2.97 |
| $K_{obs}$ /[PhCHO] | 1.15 | 1.20 | 1.21 | 1.18 |
| Corr.Coeft. | 0.9950 | 0.9998 | 0.9999 | 0.9999 |

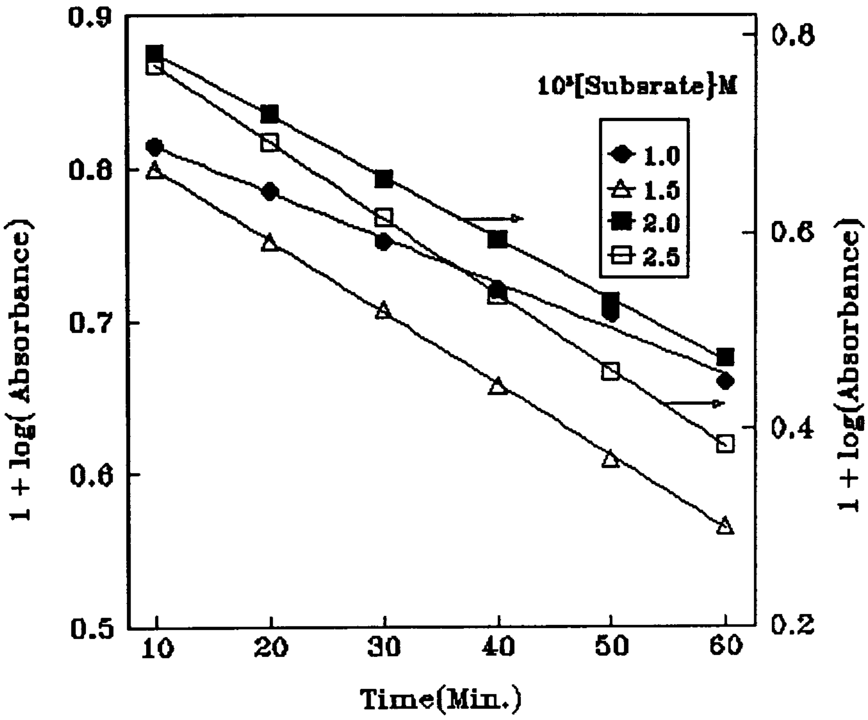


Fig. 3.10.1 Effect of [substrate] on the oxidation of PhCHO by$Q^+OCl^-$

### 3.10.3 Effect of substituents on the oxidation of benzaldehyde in benzene using phase transferred hypochlorite

The effect of substituents on the aromatic ring of benzaldehyde on the rate of oxidation was studied in organic solvent, benzene in presence of PT catalyst, TBAB. For various substituted benzaldehydes, the rate increased in the order p-methyl <H<p-chloro <p-bromo <p-nitro. The data are given in table 3.10.3 and Fig. 4.25.

**Table 3.10.3**

**Effect of substituents on the rate of oxidation of benzaldehyde in benzene**

[substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ Temperature = 303K

[$Q^+OCl^-$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| $10^2\ k_2$ dm$^3$ mol$^{-1}$s$^{-1}$ | 0.89 | 1.15 | 1.55 | 1.69 | 3.37 |
| Corr. Coeft. | 0.9978 | 0.9950 | 0.9996 | 0.9967 | 0.9999 |

### 3.10.4 Effect of temperature on the oxidation of benzaldehyde in benzene using phase transfer catalyst

The rate constant for the oxidation of PhCHO in benzene using the phase transferred hypochlorite was studied in the temperature range 303-315K in presence of TBAB. The rate constant increased from 1.15 x $10^{-4}$ $s^{-1}$ to 2 x$10^{-4}$ $s^{-1}$ (Table 3.10.4 and Fig 3.10.2).

**Table 3.10.4**

**Effect of temperature on the oxidation of benzaldehyde using hypochlorite in presence of TBAB**

[PhCHO] = 1.0 x $10^{-2}$ mol $dm^{-3}$ Solvent - benzene

[$Q^+$ $OCl^-$] = 1.0 x $10^{-3}$ mol $dm^{-3}$

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| $10^4 k_{obs} s^{-1}$ | 1.15 | 1.38 | 1.57 | 1.79 | 2.00 |
| Corr.coeft. | 0.9950 | 0.9994 | 0.9994 | 0.9998 | 0.9998 |

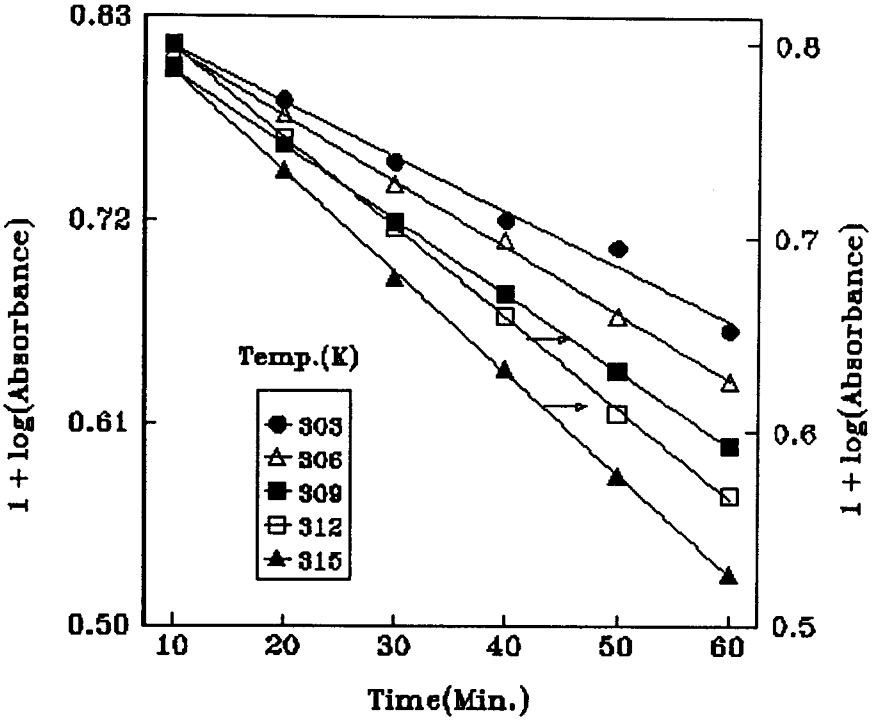


Fig. 3.10.2 Effect of temperature on the oxidation of PhCHO by$Q^+OCl^-$

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# CHAPTER IV

# RESULTS AND DISCUSSION

## General

In this chapter the results obtained on the kinetics of the oxidation of benzaldehyde and some of its p-methyl, p-chloro, o-chloro, p-bromo, and p-nitro derivatives using sodium hypochlorite in aqueous acetic acid, aqueous dioxane and aqueous acetonitrile media are discussed. Some of these typical oxidations were also carried out in non-polar organic solvents such as benzene using phase transferred hypochlorite. In addition, the catalytic effects of cyclodextrins were also investigated. The oxidation of benzaldehyde followed first order dependence with respect to the hypochlorite concentration. However variable orders with respect to the oxidant concentrations have been reported in the literature[162,165,210,211] under different experiments.

## 4.1 Stoichiometry and Product Analysis

Stoichiometry of the reaction has been investigated by equilibrating known amounts of benzaldehyde and known excess concentration of sodium hypochlorite till the completion of the reaction. By the estimation of the unreacted hypochlorite, the stoichiometry of the reaction was determined. It was found that one mole of benzaldehyde reacts with one mole of the hypochlorite as per equation,

$$C_6H_5CHO + NaOCl \rightarrow C_6H_5COOH + NaCl$$

The product of oxidation was isolated and analysed qualitatively as well as by spectral methods. It was identified to be benzoic acid from its melting point (120$^0$C) and the IR spectrum (Fig 3.4.1).

## 4.2 Kinetic Studies

The rate constants for the reaction between benzaldehyde and hypochlorite were determined under different experimental conditions of temperature, concentration, different solvent composition, ionic strength etc. The effect of inclusion catalysts, cyclodextrins were also investigated. Studies were also carried out in organic medium by phase transferred hypochlorite.

### 4.2.1 Effect of [NaOCl] on rate of oxidation

In the present study on the oxidation of benzaldehyde using NaOCl, the measurements have been carried out under pseudo first order condition by the isolation of the oxidant such that oxidant concentration is 10-25 times less than the substrate concentration. Thus the effect of varying

[NaOCl] was studied by keeping the concentration of the substrate at 1.0 x$10^{-2}$ mol $dm^{-3}$ and the concentration was of NaOCl varied from 4 x $10^{-4}$ mol $dm^{-3}$ to 10 x $10^{-4}$ mol $dm^{-3}$. Ionic strength of the medium was kept constant through out by the addition of NaCl. Linear plot of log [$OCl^-$] with time indicated first order dependence of the reaction on the oxidant concentration. The experimental data presented in table 4.2.1 shows that the rate coefficients are practically the same in spite of varying the NaOCl concentration from $0.4\times10^{-3}$ to $1.0\times10^{-3}$ in both aqueous acetic acid (20% v/v) and aq. dioxane (20% v/v).

**Table 4.2.1**

**Effect of [NaOCl] on the rate of oxidation of benzaldehyde**

| $10^3$ [NaOCl] mol $dm^{-3}$ | $10^5k_{obs}$ $s^{-1}$ | |
|---|---|---|
| | 20% aq. HOAc | 20% aq. dioxane |
| 0.4 | 4.98 | 8.94 |
| 0.6 | 5.01 | 9.24 |
| 0.8 | 5.18 | 9.25 |
| 1.0 | 5.10 | 9.14 |

### 4.2.2 Effect of the concentration of the aldehyde

The concentration of the substrate viz. the aldehyde was varied in the range 1.0 x $10^{-2}$ mol $dm^{-3}$ – 3x$10^{-2}$ mol $dm^{-3}$ by taking benzaldehyde under otherwise identical kinetic conditions. The $k_{obs}$ values showed an increase with increase of the benzaldehyde concentration (Table 4.2.2). A plot of log $k_{obs}$ with log [substrate] gave linear curve with unit slope (corr. coeft. 0.998) indicates first order dependence of the reaction with respect to the concentration of substrate (Fig 4.1 and Fig 4.2.). The ratio of $k_{obs}$ to [substrate] showed constancy confirming the operation of an overall second order reaction ; first order with respect to [hypochlorite] and first order with respect to [aldehyde].

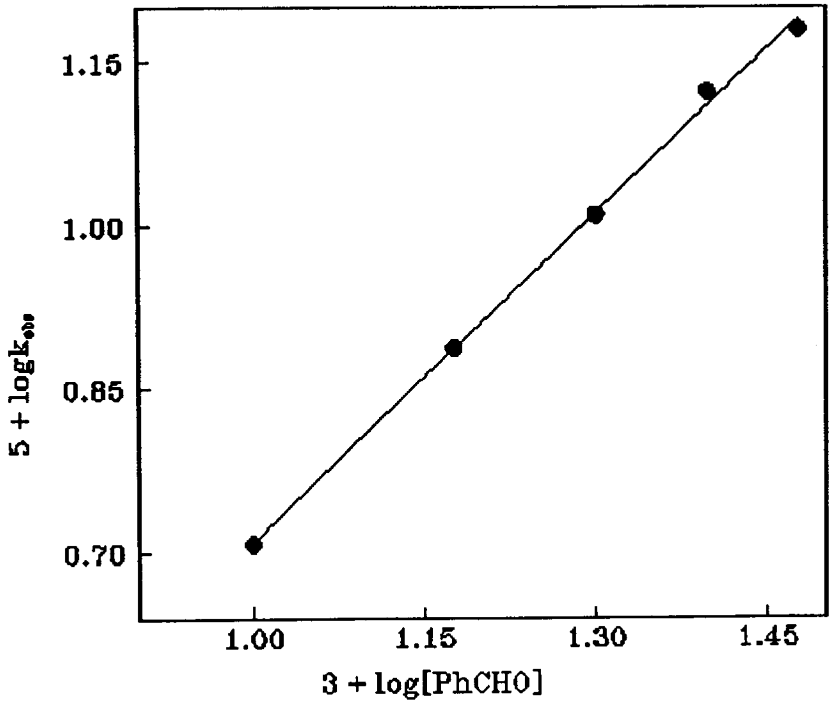


Fig 4.1 Plot of log $k_{obs}$ vs log [PhCHO] in aq. HOAc

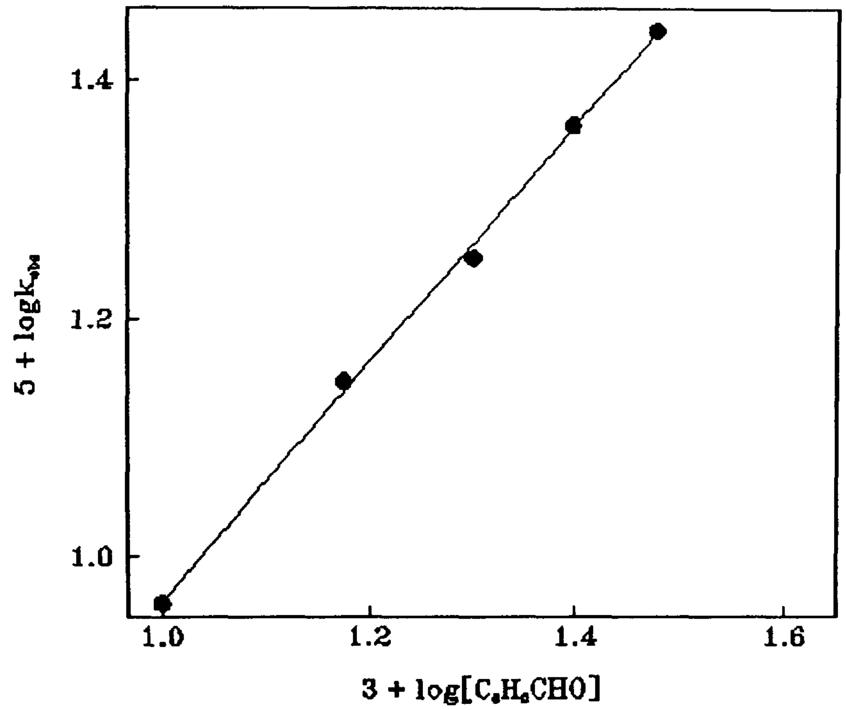


Fig 4.2 Plot of log $k_{obs}$ vs log [PhCHO] in aq. dioxane

## Table 4.2.2

## Effect of [PhCHO] on the rate of oxidation

| $10^2$ [$C_6H_5CHO$] mol $dm^{-3}$ | Aq. HOAc (20% v/v) | | Aq. dioxane (20%, v/v) | |
|---|---|---|---|---|
| | $10^5k_{obs}\,s^{-1}$ | $10^3k_{obs}$ / [PhCHO] | $10^5k_{obs}\,s^{-1}$ | $10^3k_{obs}$/ [PhCHO] |
| 1.0 | 5.10 | 5.10 | 9.14 | 9.14 |
| 1.5 | 7.72 | 5.14 | 14.0 | 9.33 |
| 2.0 | 10.25 | 5.12 | 17.85 | 8.93 |
| 2.5 | 13.25 | 5.31 | 23.03 | 9.21 |
| 3.0 | 15.16 | 5.11 | 27.69 | 9.22 |

### 4.2.3 Effect of mineral acid

The effect of mineral acid on the rate of hypochlorite oxidation of the aldehydes was studied using different concentrations of $H_2SO_4$ ($0.25 \times 10^{-2} - 5.0 \times 10^{-2}$ mol dm$^{-3}$). The results shows that under otherwise identical conditions, the rate increased with [$H^+$] with a fractional order dependence (table 4.2.3 and figure 4.3 & 4.4).

**Table 4.2.3**

**Effect [$H^+$] on the rate of oxidation of benzaldehyde using hypochlorite**

9

$10^3$

| $10^2$ [$H^+$] mol dm$^{-3}$ | $10^2 k_2$ dm$^3$ mol$^{-1}$s$^{-1}$ | |
|---|---|---|
| | 20% aq. HOAc | 20% aq. dioxane |
| 0 | 5.10 | 9.14 |
| 0.5 | 6.53 | 12.66 |
| 1.0 | 7.41 | 13.97 |
| 2.0 | 8.44 | 16.54 |
| 5.0 | 9.90 | 19.77 |
| 10.0 | 11.32 | 22.95 |

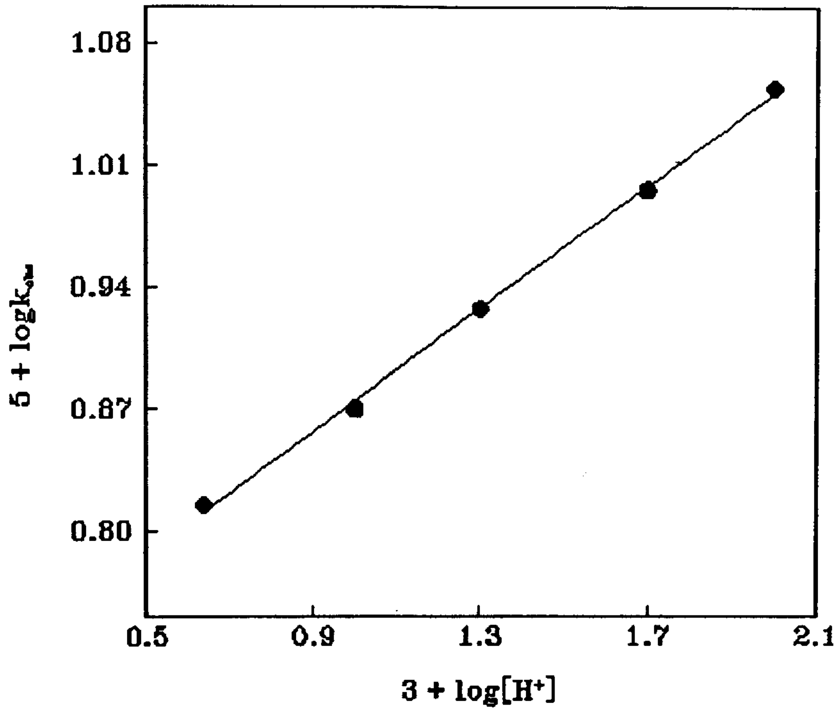


Fig 4.3 Plot of log $k_{obs}$ vs log [$H^+$] in aq. HOAc

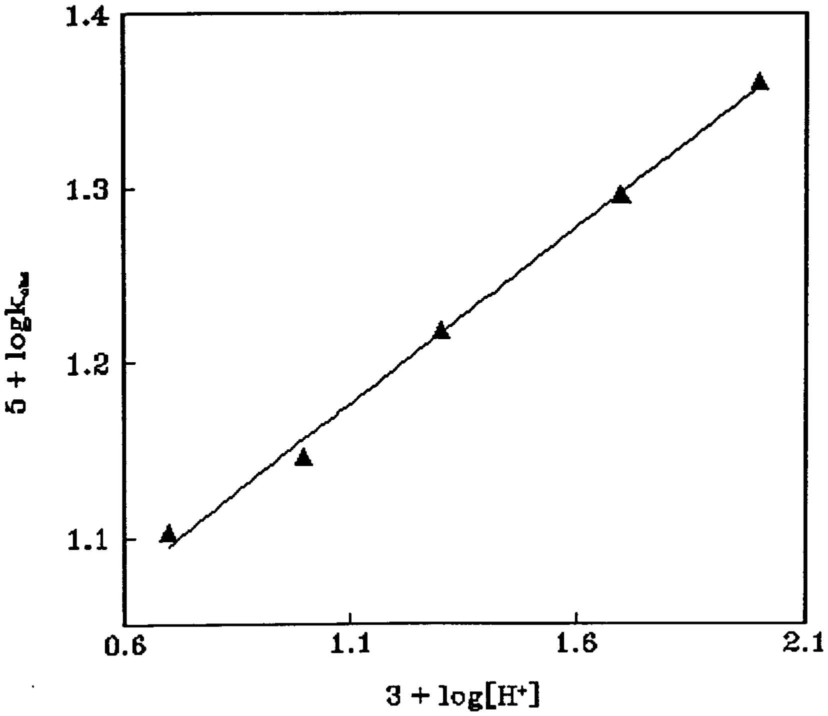


Fig 4.4 Plot of log $k_{obs}$ vs log [$H^+$] in aq. dioxane

### 4.2.4 Effect of ionic strength of the medium

The influence of ionic strength of the medium on rate was studied by using requisite amounts of NaCl ($1.0 \times 10^{-2} - 10 \times 10^{-2}$ mol dm$^{-3}$). The results shows that ionic strength has practically negligible effect on rate of oxidation both in aqueous HOAc and aq. dioxane solvents (Table 4.2.4).

**Table 4.2.4**

**Effect [H$^+$] on the rate of oxidation of benzaldehyde using hypochlorite**

| $\mu \times 10^2$ mol dm$^{-3}$ | $10^2$ $k_2$ dm$^3$ mol$^{-1}$s$^{-1}$ | |
|---|---|---|
| | 20% aq. HOAc | 20% aq. dioxane |
| 1.0 | 5.07 | 9.14 |
| 2.0 | 4.91 | 9.52 |
| 3.0 | 5.10 | 9.36 |
| 5.0 | 4.79 | 9.12 |
| 10.0 | 5.03 | 9.28 |

The negligible effect of ionic strength of the medium on rate showed that the reaction is either between two neutral dipolar molecules or between a dipolar molecule and an ion[11,12]. The possibility of an ion-ion type interaction is thus ruled out.

### 4.2.5 Effect of addition of benzoic acid and acrylonitile to the reaction mixture

Effect of addition of product of reaction was studied by adding calculated amounts of benzoic acid to the reaction mixture. The negligible effect on rate (Table.3.5.6) indicate that it is not involved in the pre-equilibrium to the rate limiting step.

Effect of addition of radical trapper was also investigated by adding acrylonitrile to the reaction mixture. No polymerisation was observed indicating the absence of any radical formation during the course of reaction.

### 4.2.6 Effect of dielectric constant of the medium on the rate of oxidation of benzaldehyde

Effect of polarity of the medium on the rate of oxidation was studied by using aqueous solutions of different protic and aprotic solvents viz. dioxane,acetonitrile, DMSO and DMF. The kinetic data revealed that for a particular solvent, the rate of oxidation increased with the percentage of the solvent in the aqueous mixture. This would indicate that the rate of oxidation is increased with decrease of dielectric constant of the medium. The results were given in table 4.2.6(a) for the oxidation of benzaldehyde with varying percentage of acetic acid (20%-60%) The data showed that the specific rate increased with decrease of dielectric constant of the medium.

### Table 4.2.6(a)

### Effect of polarity of the medium on the rate of oxidation of benzaldehyde

| **Percentage of HOAc** | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| **Dielectric constant (D)** | 61 | 54 | 47 | 39.8 | 32 |
| **$10^3$ $k_2$ $dm^3$ $mol^{-1}$ $s^{-1}$** | 5.18 | 5.49 | 5.86 | 6.65 | 7.6 |

A plot of log $k_{obs}$ vs (D-1)/ (2D+1) gave a linear curve with negative slope (corr.coeff. 0.994) indicating a dipole-dipole interaction between the substrate and the oxidant (Fig. 4.5).

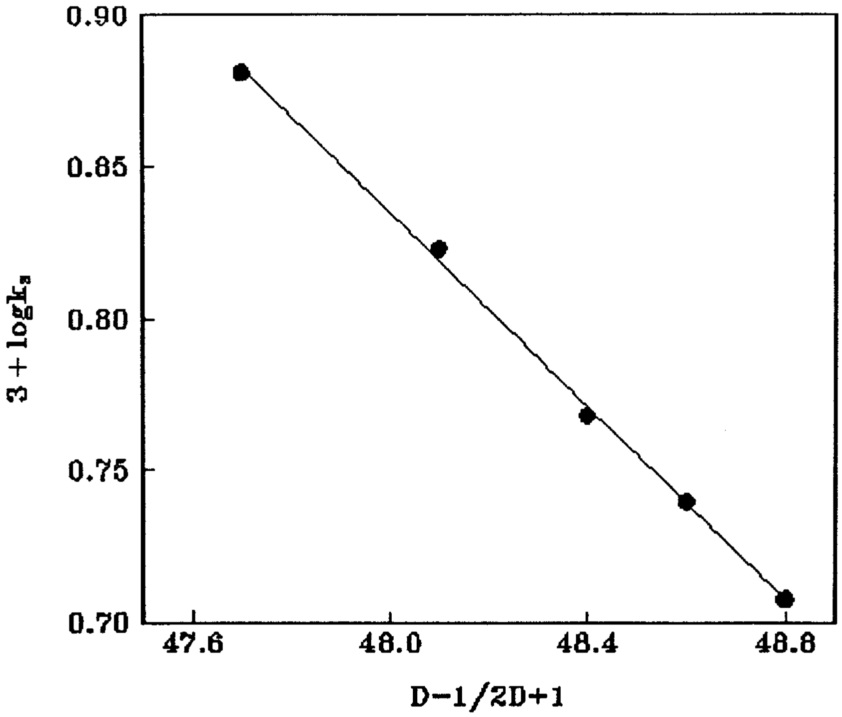


**Fig 4.5 Plot of log k vs (D-1)/(2D+1) for the oxidation of PhCHO in aq. HOAc**

Banerji *et al*[144], in their studies on the oxidation of substituted benzaldehydes by a permanganate complex, suggested that with increase of percentage of acetic acid, the reaction becomes acid catalysed. This amounts to protonation of the oxidant leading to enhanced rate of oxidation.

The rate of increase of rate coefficient with percentage of acetic acid has been quite low. This can be attributed to the larger solvation extended to the reactants in acetic acid medium so that the decrease in the energy barrier is not adequate. This goes hand in hand with the solvent effects predicted by Hughes, Ingold and Laidler[213,214].

Effect of polarity of the medium on the rate of oxidation was also studied in aqueous dioxane and aqueous acetonitrile solvents (Table 4.2.6 b). The specific rate increased with percentage of the organic solvent in all situations. These effects are in keeping with the influences of dipolar aprotic solvents in their ability to associate with water molecules, there by effecting a decrease in the solvation extended.

**Table 4.2.6(b)**

**Effect of varying percentage of solvent on the rate of oxidation**

| Percentage of solvent | $10^3$ $k_2$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | | |
|---|---|---|---|
| | HOAc | Dioxane | Acetonitrile |
| 20 | 5.18 | 9.09 | 7.25 |
| 30 | 5.49 | 33.12 | 10.82 |
| 40 | 5.87 | 56.57 | 14.66 |
| 50 | 6.64 | 82.29 | 18.0 |
| 60 | 7.6 | 103.32 | 22.10 |

Kinetic investigations were also carried out in aqueous DMSO and aqueous DMF media with different composition of solvent and water. Here the rates of oxidation were too fast to be measured satisfactorily under the normal experimental conditions.

Thus kinetic measurements using different aqueous solvents revealed that the rates of hypochlorite oxidation of benzaldehyde varied in the order DMF>DMSO>Dioxane>Acetonitrile>Acetic acid.

### 4.2.7 Effect of substituents on the rate of oxidation of benzaldehyde

The effect of substituents on the benzene ring of benzaldehyde was investigated using p-methyl, o-chloro, p-chloro, p-bromo and p-nitrobenzaldehyde. The results presented in the table 4.2.7 shows that the rate of oxidation are in the order p-nitro> p-bromo> p-chloro > o-chloro>H>p-methyl. The same trend was observed both in aqueous HOAc and aqueous dioxane solvents.

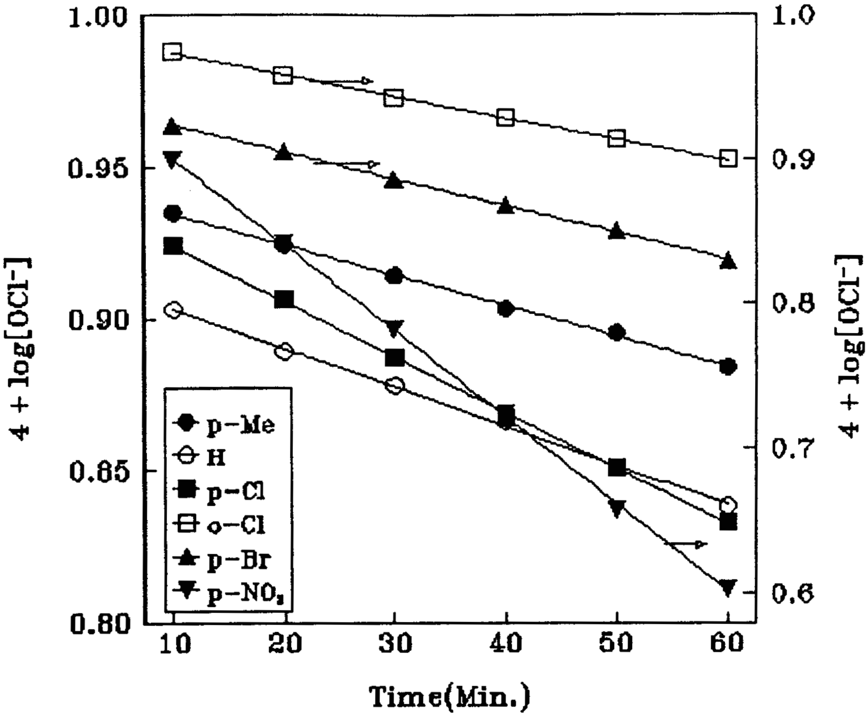


Fig 4.6 Effect of substituents on the rate of oxidation of PhCHO in aq. HOAc

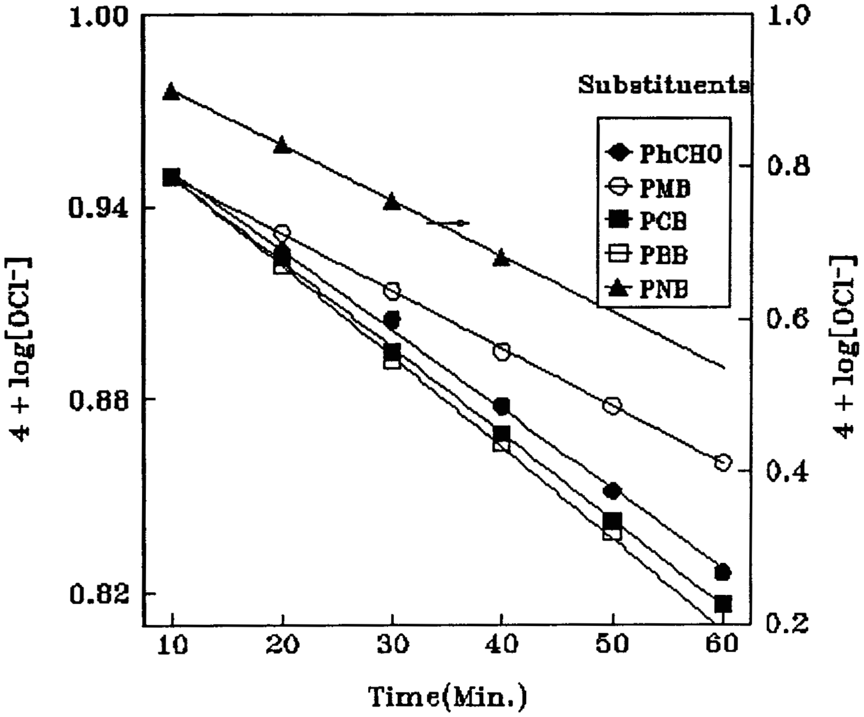


Fig 4.7 Effect of substituents on the rate of oxidation of PhCHO in aq. dioxane

## Table 4.2.7

## Effect of substituents on the rate of oxidation of benzaldehyde

| Substrate | $10^3$ $k_2$ $dm^3$ $mol^{-1}$ $s^{-1}$ | |
|---|---|---|
| | 20% Aq.HOAc | 20% Aq.Dioxane |
| PMB | 3.88 | 6.87 |
| PhCHO | 5.10 | 9.14 |
| OCB | 5.76 | - |
| PCB | 7.02 | 10.28 |
| PBB | 7.18 | 10.86 |
| PNB | 22.42 | 28.47 |

The results in table 4.2.7 showed that electron-withdrawing groups facilitate the oxidation of benzaldehyde whereas electron-donating groups retard the oxidation. The Hammett plot of log $k_2$ vs substituent constant ($\sigma$) gave a linear fits with a reaction constant ($\rho$) of 0.81 (Corr. Coeff. 0.9949) in aq. acetic acid medium and a value of 0.70 (corr. Coeff. 0.990) in aq. dioxane medium. The linear free energy relation according to Hammett relationship (Fig. 4.8 & 4.9) also indicate that same mechanism is operative among all substituted benzaldehydes during the oxidation. The positive value of reaction constant shows that the reaction is facilitated by electron withdrawing groups.

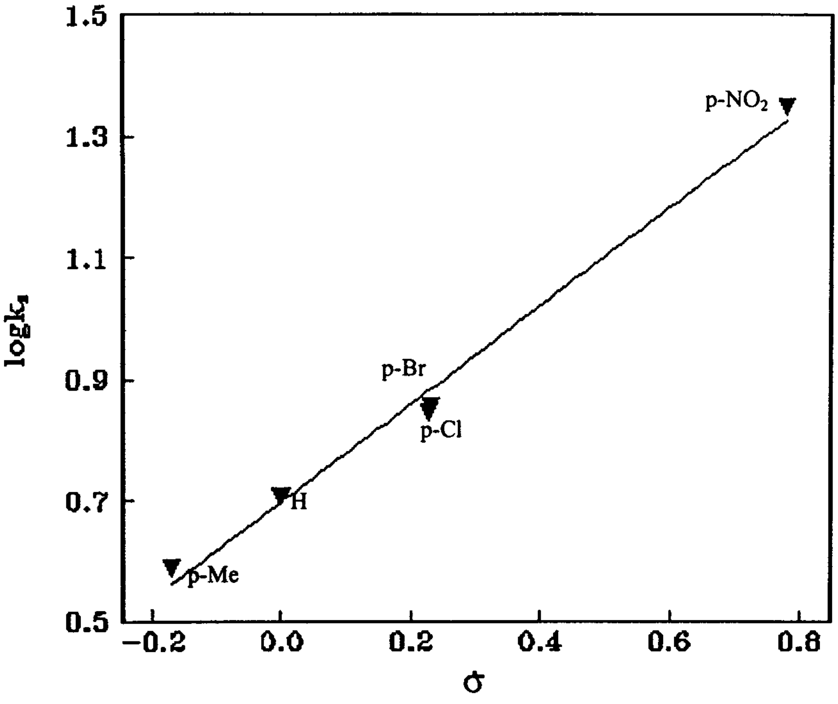


Fig 4.8 Hammett plot for the oxidation of PhCHO in aq. HOAc

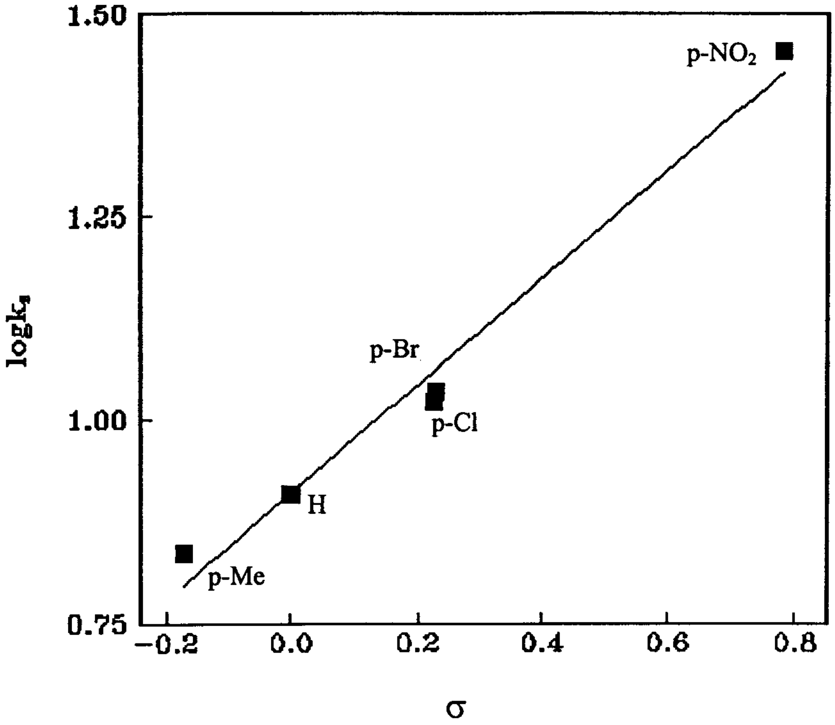


Fig 4.9 Hammett plot for the oxidation of PhCHO in aq. dioxane

### 4.2.8 Effect of temperature on the rate of oxidation

The temperature coefficient of the reaction was studied in the range of 303K to 315K (table 4.2 8a).

**Table 4.2.8(a).**

**Effect of temperature on the rate of oxidation of benzaldehyde**

| Temperature | $10^3$ $k_2$ $dm^3$ $mol^{-1}$ $s^{-1}$ | |
|---|---|---|
| | 20% Aq.HOAc | 20% Aq.Dioxane |
| 303 | 5.10 | 9.14 |
| 306 | 6.14 | 10.94 |
| 309 | 7.33 | 13.43 |
| 312 | 8.18 | 16.27 |
| 315 | 10.29 | 19.15 |

Linear plots of log k vs 1/T and log k/T vs 1/T were plotted (Fig 4.12 to 4.15) and the various thermodynamic parameters Ea, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were calculated. The results are given in table 4.2.8 (b & c).

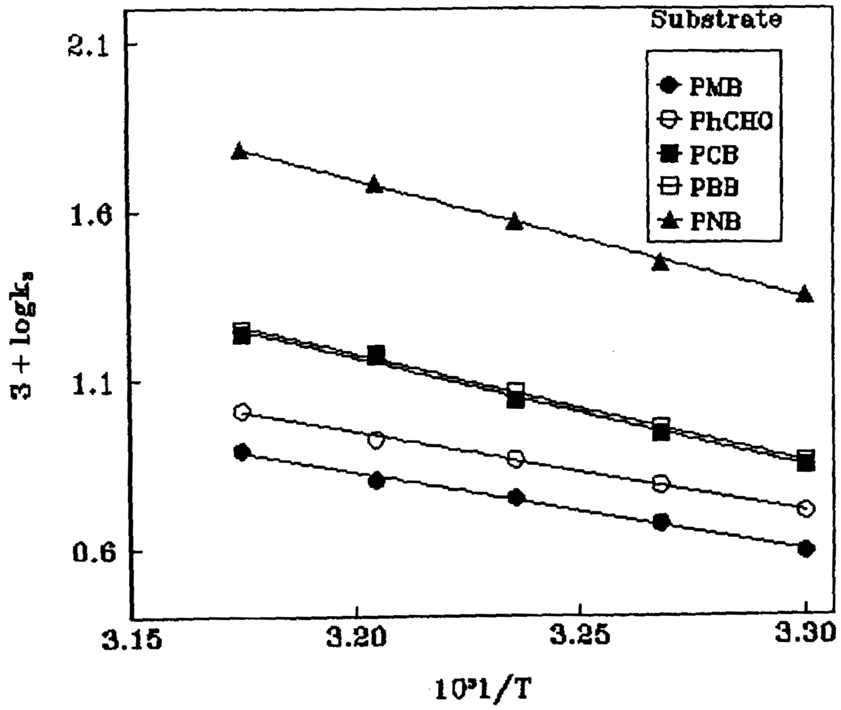


Fig 4.10 Plot of log k vs 1/T for the oxidation of substituted benzaldehydes in aq. HOAc

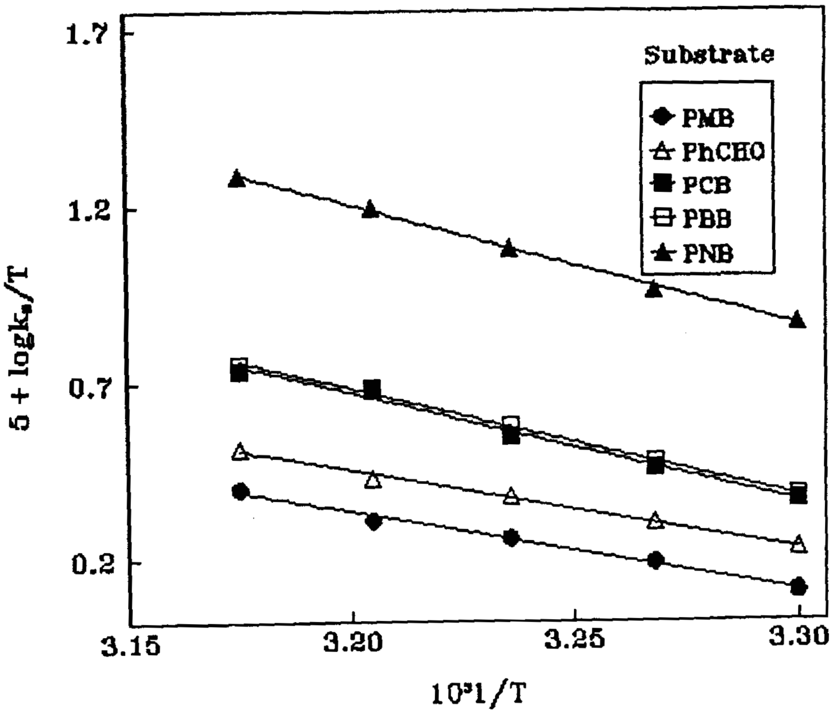


Fig 4.11 Plot of log k/T vs 1/T for the oxidation of substituted benzaldehydes in aq. HOAc

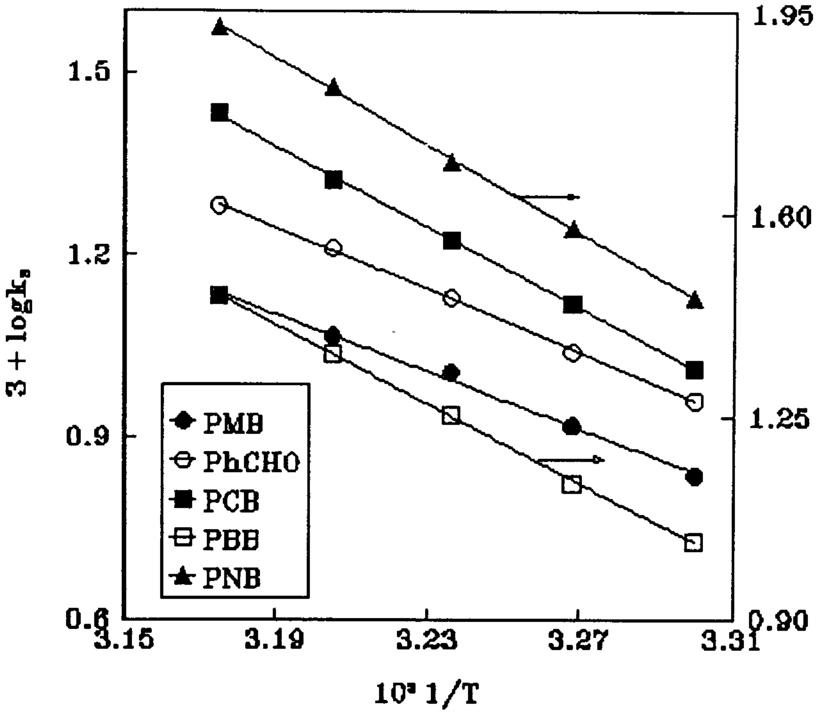


Fig 4.12 Plot of log k vs 1/T for the oxidation of substituted benzaldehydes in aq. dioxane

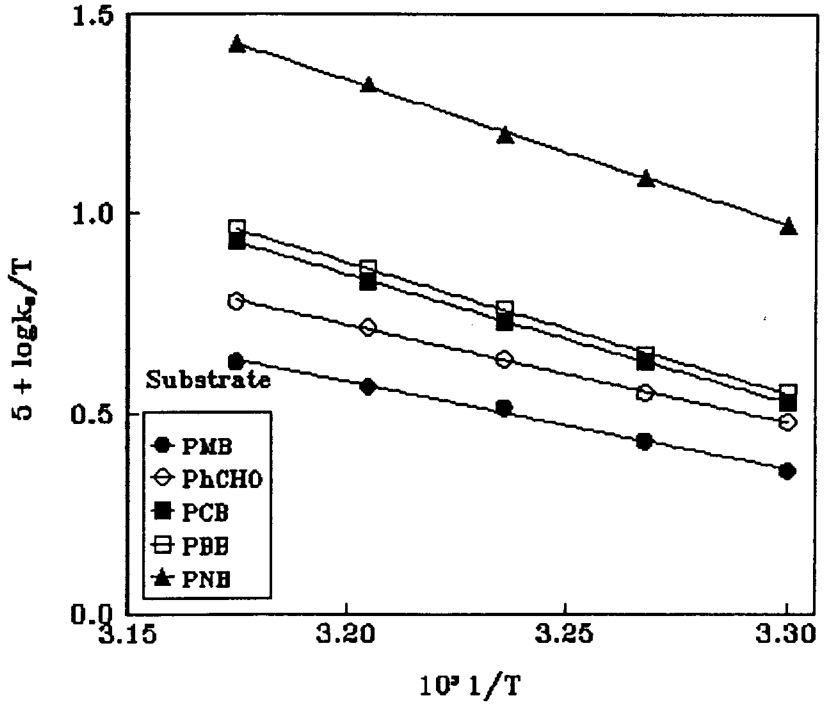


Fig 4.13 Plot of log k/T vs 1/T for the oxidation of substitued benzaldehydes in aq. dioxane

## Table 4.2.8(b)

## Activation parameters for the oxidation of benzaldehyde using hypochlorite in Aq. HOAc (20%)

| Substrate | $E_a$ kJ mol$^{-1}$ | $\Delta H^\#$ kJ mol$^{-1}$ | $-\Delta S^\#$ JK$^{-1}$ mol$^{-1}$ | $\Delta G^\#$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| PMB | 44.88 | 42.36 | 151.3 | 89.05 |
| PhCHO | 47.05 | 44.45 | 142.28 | 87.5 |
| OCB | 64.89 | 62.3 | 82.45 | 87.25 |
| PCB | 62.12 | 59.56 | 90.5 | 87.3 |
| PBB | 61.79 | 59.22 | 90.70 | 87.2 |
| PNB | 67.45 | 64.87 | 62.90 | 84.1 |

## Table 4.2.8(c)

## Activation parameters for the oxidation of benzaldehyde using hypochlorite in Aq. dioxane(20%)

| Substrate | $E_a$ kJ mol$^{-1}$ | $\Delta H^\#$ kJ mol$^{-1}$ | $-\Delta S^\#$ JK$^{-1}$ mol$^{-1}$ | $\Delta G^\#$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| PMB | 44.87 | 42.28 | 146.7 | 86.7 |
| PhCHO | 49.75 | 47.28 | 128 | 86.9 |
| OCB | - | - | - | - |
| PCB | 63.85 | 61.26 | 81.4 | 86.3 |
| PBB | 65.29 | 62.71 | 75.75 | 85.7 |
| PNB | 72.4 | 69.78 | 44.4 | 83.5 |

Comparison of various thermodynamic parameters showed that the reaction is entropy controlled, in both HOAc and Aq.dioxane medium Similar behaviour has been observed by Sheeba P.S.[212] in the permanganate oxidation of acetophenones and by Revathi *et al*[143] in the chloramine-B oxidation of substituted benzaldehydes. A negative value of $\Delta S^{\#}$ suggested that the transition state is more ordered than the reactants. This would mean that the reactants have to surrender some of their degrees of freedom during the formation of the transition state. The values of the free energy of activation, $\Delta G^{\#}$ are almost the same for various substituents. This would indicate that a similar mechanism is operating among all substituents studied. This was further confirmed by the linear isokinetic plot of $\Delta H^{\#}$ Vs $\Delta S^{\#}$ (Leffller-Grundwald isokinetic plot[15]). The isokinetic temperature (β) obtained from the plot was 269 (Fig. 4.14).

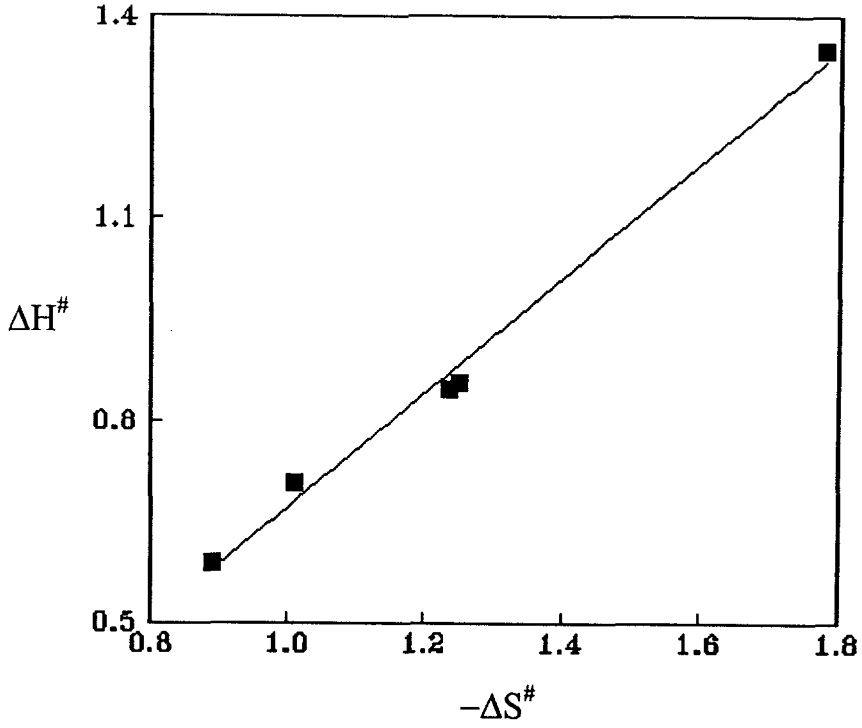


**Fig 4.14 Leffler-Grundwald isokinetic plot in aq. HOAc**

The isokinetic temperature was also calculated from the Exner's plot (4.15 & 4.16) which was found to be 262. A lower isokinetic temperature than the experimental temperature suggested the reaction to be entropy controlled[25].

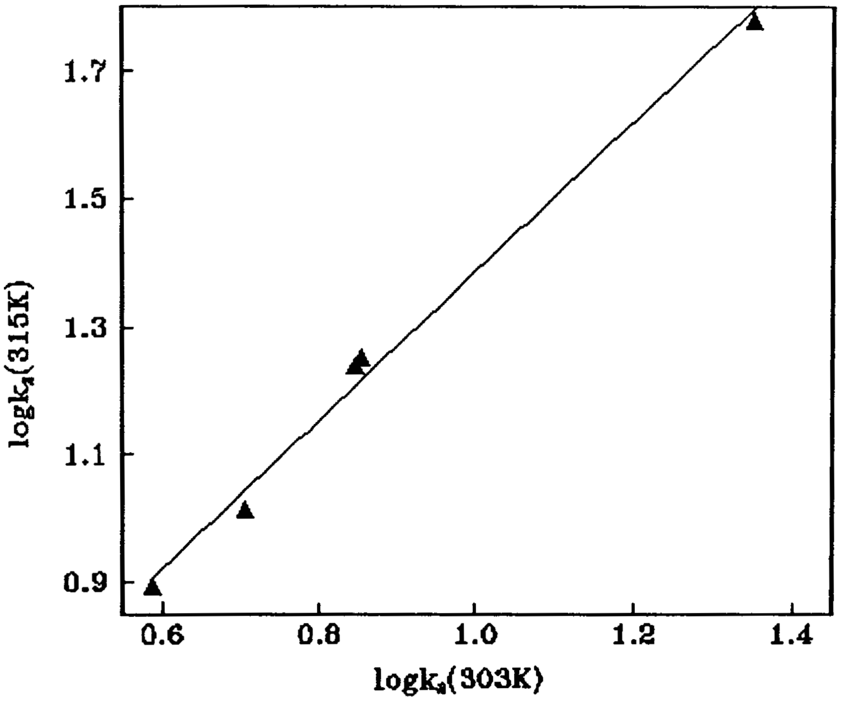


Fig 4.15 Exner's plot for the oxidation of PhCHO in aq. HOAc

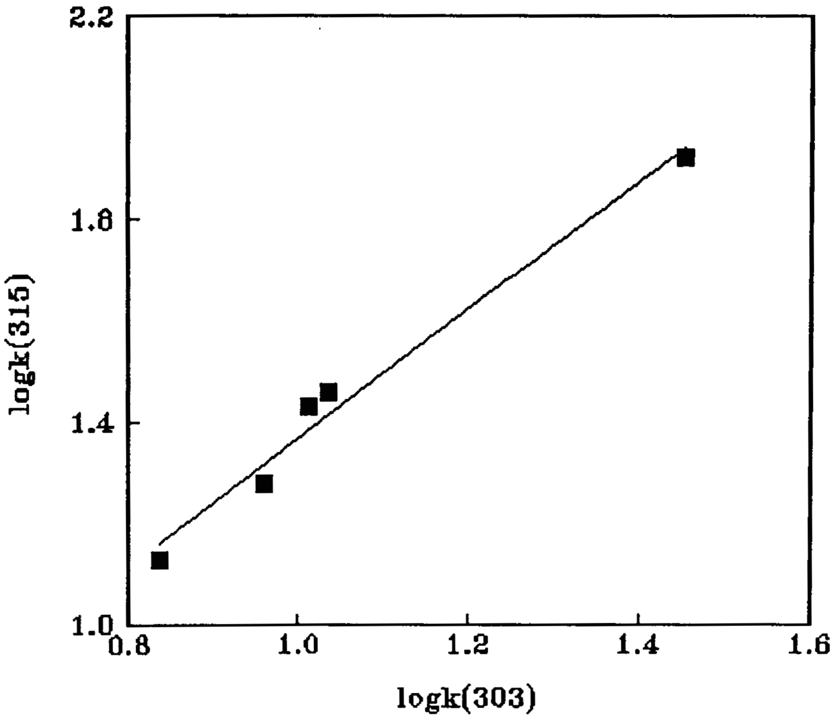


Fig 4.16 Exner's plot for the oxidation of PhCHO in aq. dioxane

### 4.2.9 Effect of cyclodextrins on the rate of oxidation

Cyclodextrins are known to provide an apolar and sterically restricted cavity for the inclusion of the substrate molecules of appropriate size. These inclusion complexes can catalyse reactions resulting in the acceleration of reaction rate. When used in catalytic amounts, cyclodextrins were found to catalyse the hypochlorite oxidation of benzaldehyde significantly. The catalytic activity of CD's varied with concentration of catalyst. The maximum rate was observed at a concentration of $2\text{x}10^{-3}$M. ACD exhibited comparatively higher catalytic effect compared to BCD (table 4.2.9a). Among substituted benzaldehydes, the catalytic effect is more pronounced with the para nitro derivative.

**Table 4.2.9(a)**

**Effect of ACD and BCD on the rate of oxidation of Benzaldehyde using $OCl^-$**

| Solvent | $10^3$ $k_2$ $dm^3$ $mol^{-1}$ $s^{-1}$ | | |
|---|---|---|---|
| | Without CD | With ACD | With BCD |
| Aq. HOAc (20%) | 5.10 | 6.12 | 6.02 |
| Aq. Dioxane (20%) | 9.14 | 14.88 | 13.95 |

The effect of addition of catalytic amounts of cyclodextrins on the oxidation of various substituted benzaldehydes were investigated (table 4.2.9 b). The kinetic results showed that the specific rate increased in the cases of all benzaldehydes, and the para nitro derivative showed a marked increase in rate. The ratio ($k_{cat}/k_{un}$) for catalysed and uncatalysed reaction was higher in aq. dioxane medium than in aq. acetic acid medium.

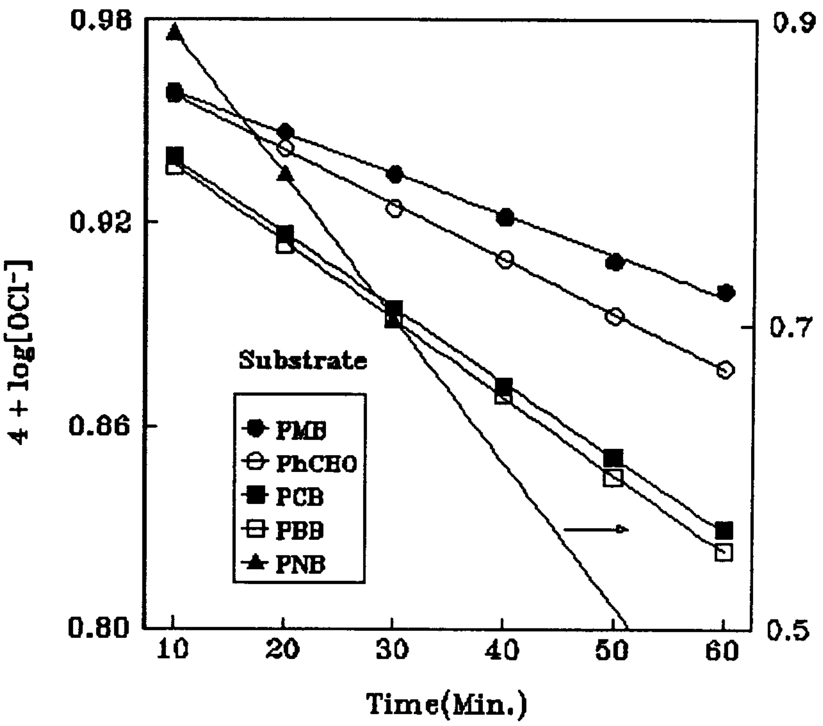


**Fig 4.17 Effect of ACD on the rate of oxidation of substituted bezaldehydes in aq. HOAc**

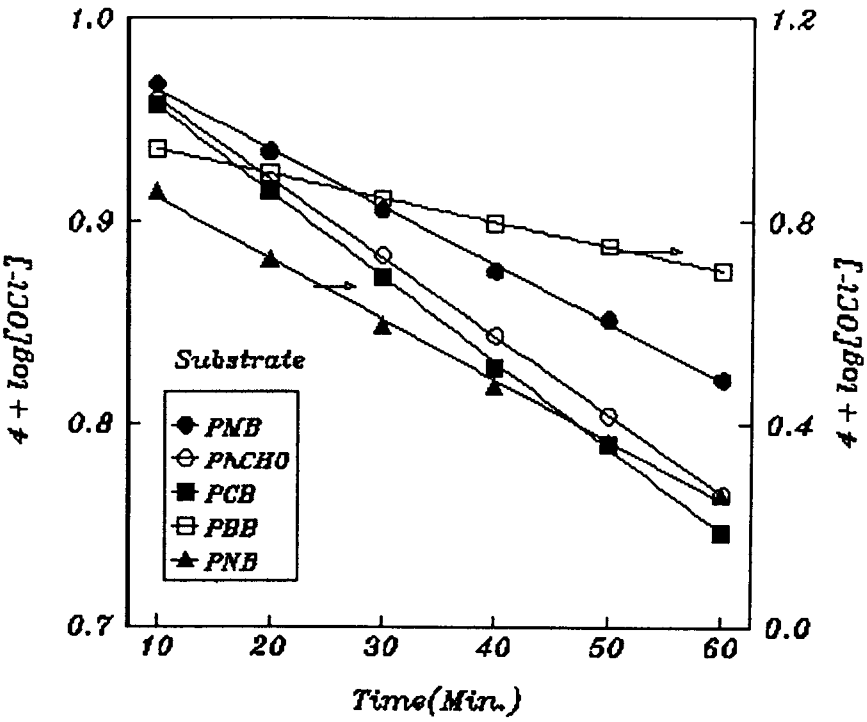


**Fig 4.18 Effect of ACD on the rate of oxidation of substituted bezaldehydes in aq. dioxane**

**Table 4.2.9(b).**

**Catalytic effect of ACD on the rate of oxidation of substituted benzaldehyde**

| substrate | | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|---|
| 20%HOAc | $10^3$ $k_{un}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | 3.88 | 510 | 7.2 | 718 | 22.42 |
| | $10^3$ $k_{cat}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | 4.65 | 6.12 | 8.56 | 8.90 | 35.87 |
| 20% Dioxane | $10^3$ $k_{un}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | 6.87 | 9.14 | 10.28 | 10.86 | 28.47 |
| | $10^3$ $k_{cat}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | 10.77 | 14.88 | 16.72 | 18.50 | 51.25 |

The kinetic data for the oxidation of substituted benzaldehydes at different temperatures in presence of cyclodextrins were also determined and activation parameters calculated. (table 4.2.9(c) & 4.2.9(d) and Fig 4.19 to 4.22). It can be seen that the energy of activation values were decreased in presence of CD as expected for typical catalysed reaction. The energy profile and mechanistic pathway are similar for both uncatalysed and catalysed reaction except that there is a decrease in energy of activation in the later.

**Table 4.2.9 (c)**

**Activation parameters for the hypochlorite oxidation of substituted benzaldehydes in the presence of ACD in aq. acetic acid medium**

| Substrate | $E_a$ kJ mol$^{-1}$ | $\Delta H^{\#}$ kJ mol$^{-1}$ | $-\Delta S^{\#}$ JK$^{-1}$ mol$^{-1}$ | $\Delta G^{\#}$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| PMB | 40.20 | 37.55 | 165.8 | 88.70 |
| PhCHO | 42.50 | 39.98 | 155.5 | 80.02 |
| PCB | 56.05 | 53.70 | 107.5 | 86.80 |
| PBB | 54.50 | 51.90 | 112.5 | 86.60 |
| PNB | 56.50 | 54.10 | 94.2 | 83 |

## Table 4.2.9 (d)

## Activation parameters for the hypochlorite oxidation of substituted benzaldehydes in presence of ACD in aq. Dioxane medium

| Substrate | $E_a$ kJ $mol^{-1}$ | $\Delta H^\#$ kJ $mol^{-1}$ | $-\Delta S^\#$ $JK^{-1}$ $mol^{-1}$ | $\Delta G^\#$ kJ $mol^{-1}$ |
|---|---|---|---|---|
| PMB | 43.3 | 40.8 | 148 | 86.5 |
| PhCHO | 45.9 | 43.4 | 136.8 | 85.7 |
| PCB | 60 | 57.6 | 89.2 | 85.1 |
| PBB | 61.2 | 58.8 | 84.1 | 84.6 |
| PNB | 62.2 | 59.7 | 72.7 | 82.1 |

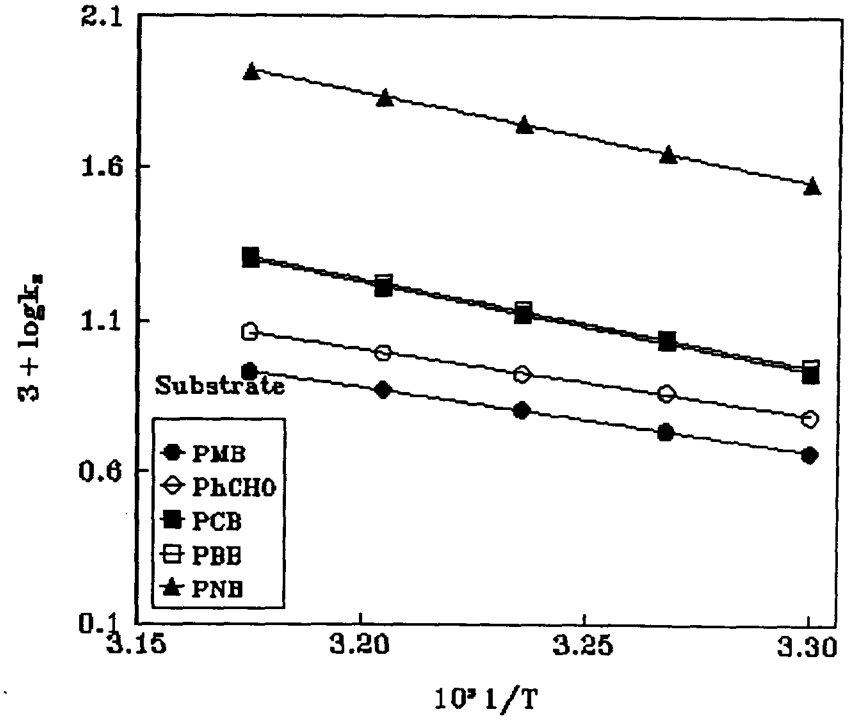


Fig 4.19 Plot of log k vs 1/T for the oxidation of substituted bezaldehydes in presence of ACD in aq. HOAc

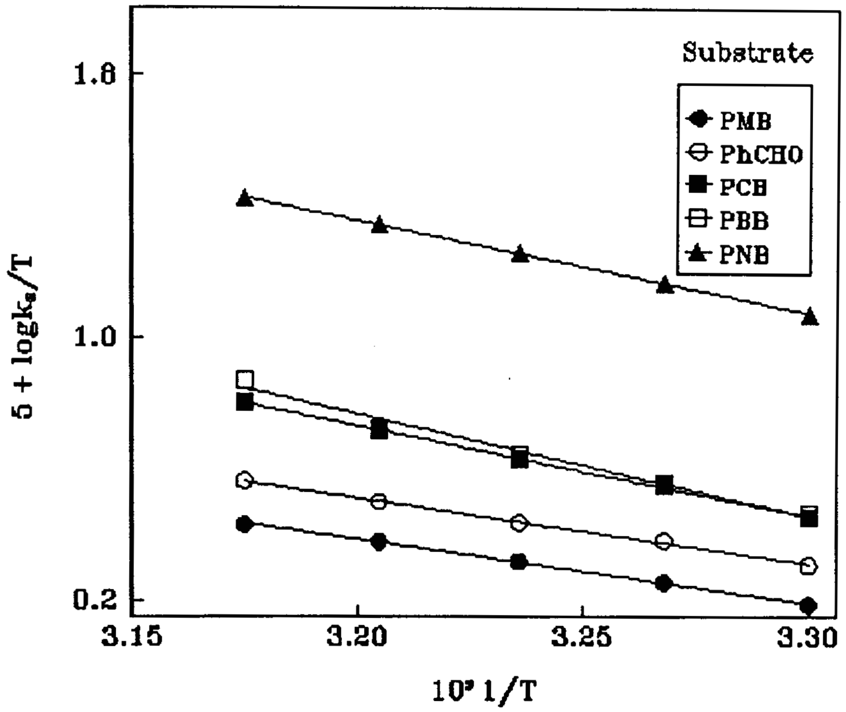


Fig 4.20 Plot of log k/T vs 1/T for the oxidation of substituted bezaldehydes in presence of ACD in aq. HOAc

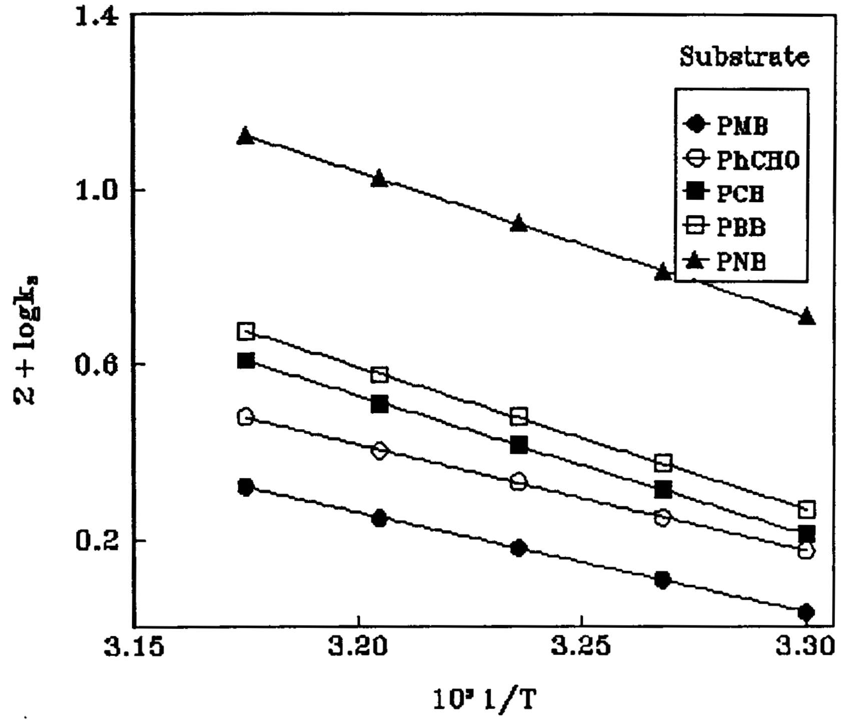


Fig 4.21 Plot of log k vs 1/T for the oxidation of substituted bezaldehydes in presence of ACD in aq. dioxane

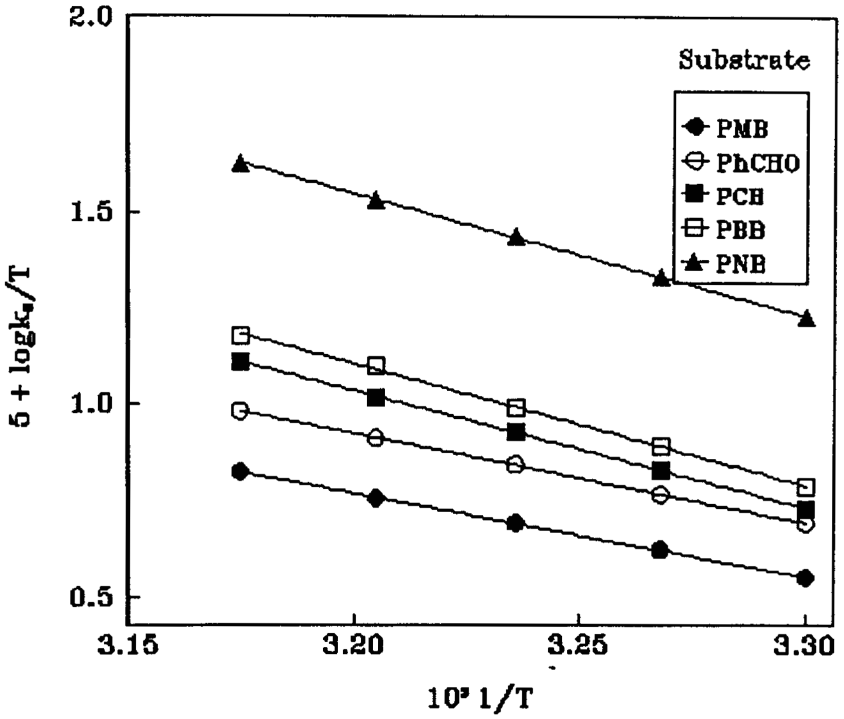


Fig 4.22 Plot of log k/T vs 1/T for the oxidation of substituted bezaldehydes in presence of ACD in aq. dioxane

### 4.2.10 Oxidation of benzaldehyde using phase transferred hypochlorite ($Q^+OCl^-$)

Kinetic measurements were being carried out in organic medium using using phase transferred hypochlorite ($Q^+OCl^-$). The phase transfer catalyst used was tetrabutylammonium bromide (TBAB). The rate of oxidation was much higher under PT condition than in the aqueous medium. The order with respect to oxidant was unity and the $k_{obs}$ varied negligibly with varying concentration $Q^+OCl^-$ (Table 3.10.2a). However, the $k_{obs}$ values increased with the concentration of the substrate (Table 3.10.2b). The plot of $k_{obs}$ with log [substrate] was linear with slope of unity indcating first order dependence with respect to the substrate concentration (Fig 4.23).

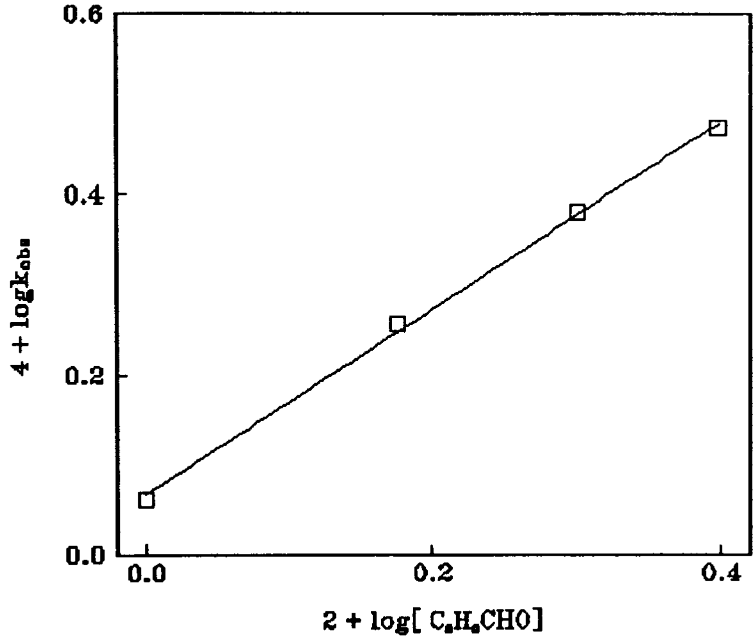


**Fig 4.23 Plot of log k $_{obs}$ vs log [substrate] for the oxidation of PhCHO in presence of TBAB**

The effect of substituents on the benzene ring of benzaldehyde on the rate of oxidation was also investigated. The rate of oxidation for various substituents are in the order p-nitro >p-bromo >p-chloro > H > p-methyl (Table 3.10.3 & Fig 4.24). This showed that the substituent effects are similar for the oxidation in aq. medium and that in organic medium by PTC.

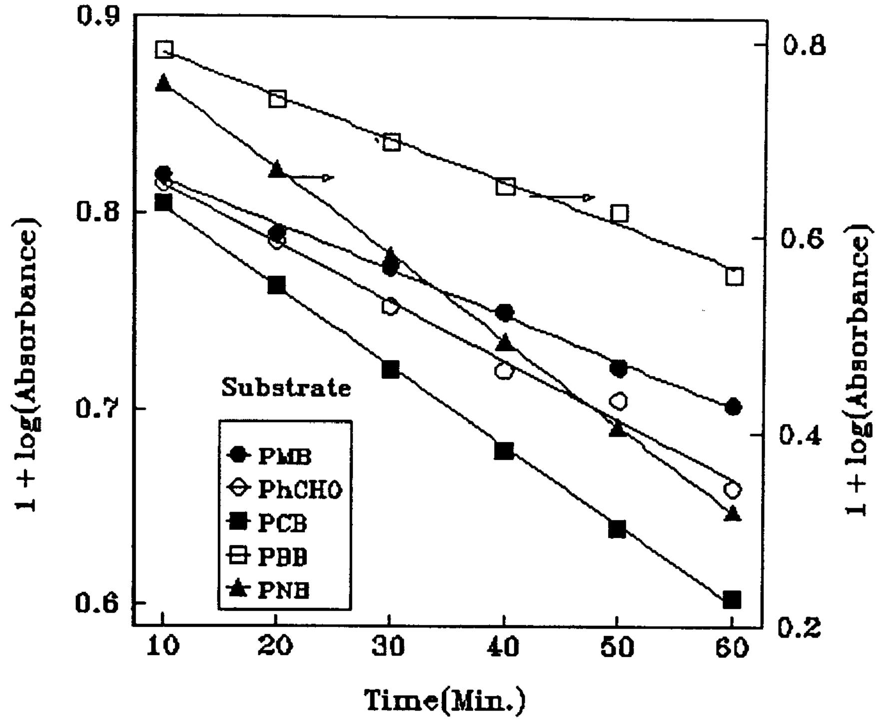


**Fig 4.24 Effect of substituents for the oxidation of PhCHO in presence of TBAB**

The temperature coefficient of the rate of oxidation of benzaldehyde under PTC condition was determined (Table.3.10.4). The activation parameters were calculated from the linear plots of log k versus 1/T (corr. 0.9967) and log k/T versus 1/T (Corr. 0.9962) (Fig 4.25). The values of the various thermodynamic parameters $E_a$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are 36.3 kJ $mol^{-1}$, 33.8 kJ $mol^{-1}$, -170.5 $JK^{-1}$ $mol^{-1}$ and 86.5 kJ $mol^{-1}$ respectively.

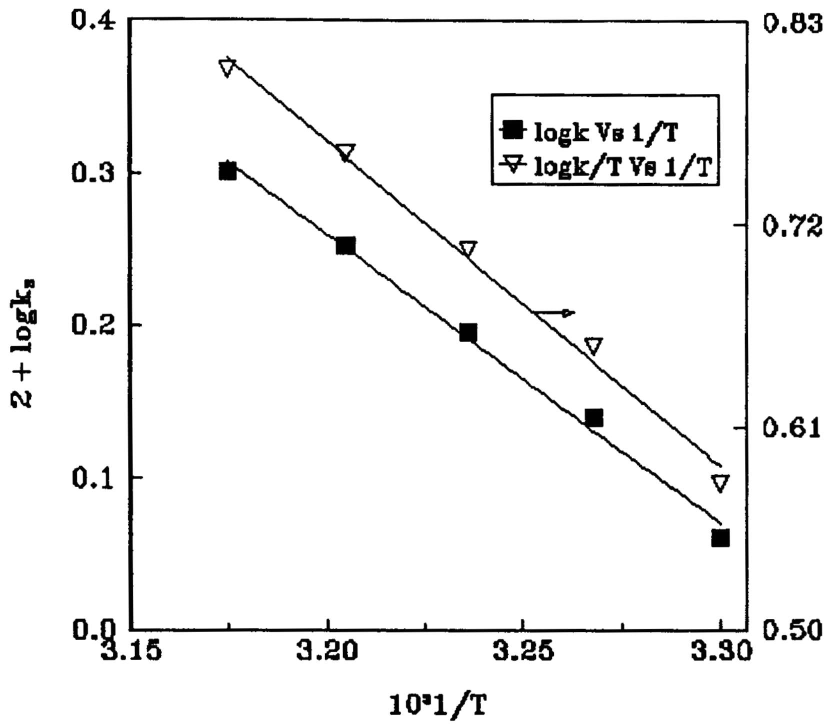


**Fig 4.25 Plot of log k vs 1/T and log k/T vs 1/T for the oxidation of PhCHO using $Q^+OCl^-$**

## 4.3 Mechanism and rate law

The elucidation of mechanism of reaction requires determination of certain essential kinetic parameters. These include the determination of order of the reaction with respect to different reactants, viz. the substrate and oxidant, the study of the effect of ionic strength, effect of additives including catalysts, effect of polarity of the medium and effect of temperature on the reaction rate. Determination of stoichiometry of the reaction, isolation and identification of the products of reaction are also important in the context for determining the probable mechanism under operation.

The stoichiometric analysis revealed that one mole of the aldehyde reacts with one mole the hypochlorite to form benzoic acid as the major product. This was isolated and identified by spectral studies (fig.3.4.1) and by usual qualitative analysis. The reaction was found to be first order each with respect to the oxidant and first order with respect to the substrate concentrations so that the overall order is two. Similar results were also reported in literature[162].

Kinetic studies showed that variation of ionic strength had only negligible effect on the rate of oxidation of benzaldehyde. This suggested that the reaction would be either between neutral dipolar molecule and an ion or between two dipolar molecules.

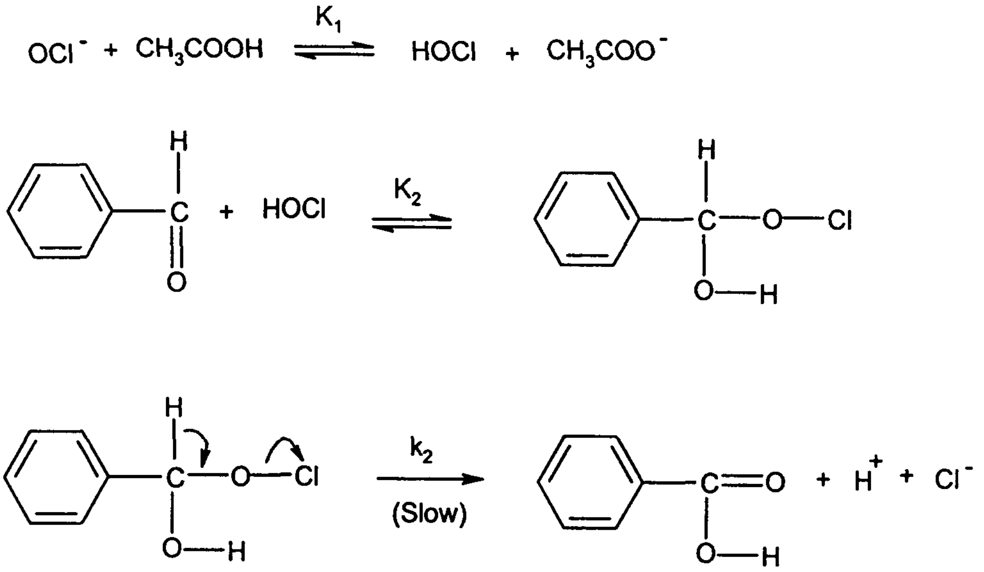
Kinetic investigation to study the effect of polarity of the medium showed that the rate of oxidation increased with increase of percentage of acetic acid i.e. decrease of dielectric constant of the medium. This observation is in conformity with equations of Kirkwood[10] and Laidler[214] for reactions involving two dipolar molecules in which the activated complex is less polar compared to the reactants. The above results would prove that the protonated form of the hypochlorite interacts with benzaldehyde during the reaction.

Kinetic measurements carried out by introducing various substituents on the benzene ring of benzaldehyde showed that the electron withdrawing groups facilitate and electron- releasing groups retard the oxidation. A plot of log k vs substituent constant according to the Hammett equation resulted in a linear fit (fig. 4.8) with positive value of $\rho$ supports the above observations. This in turn is an indicative of the enhancement of reaction rate with electron withdrawing substituents. A linear Hammett plot is also an indication of the operation of the same mechanism among all substituted benzaldehydes.

The isokinetic plot (fig.4.14) and Exner's plot (fig.4.15) are linear with correlation coefficients 0.998 and 0.996 respectively, supporting the operation of similar mechanism for all the aldehydes studied. The isokinetic temperature (β) from the isokinetic and Exner's plots are 269 and 262 respectively. Since $\beta < T$, which suggested that the reaction was entropy controlled. A large negative value of $\Delta S^{\#}$ indicated the formation of a more ordered transition state. Identical values of $\Delta G^{\#}$ for all substituents ($\Delta G^{\#} = 86 \pm 3$ kJ mol $^{-1}$) further supported the operation of similar mechanism for all substituted benzaldehydes.

The oxidation of benzaldehyde through a free radical pathway can be ruled out since no polymerisation reaction was observed in presence of acrylonitrile

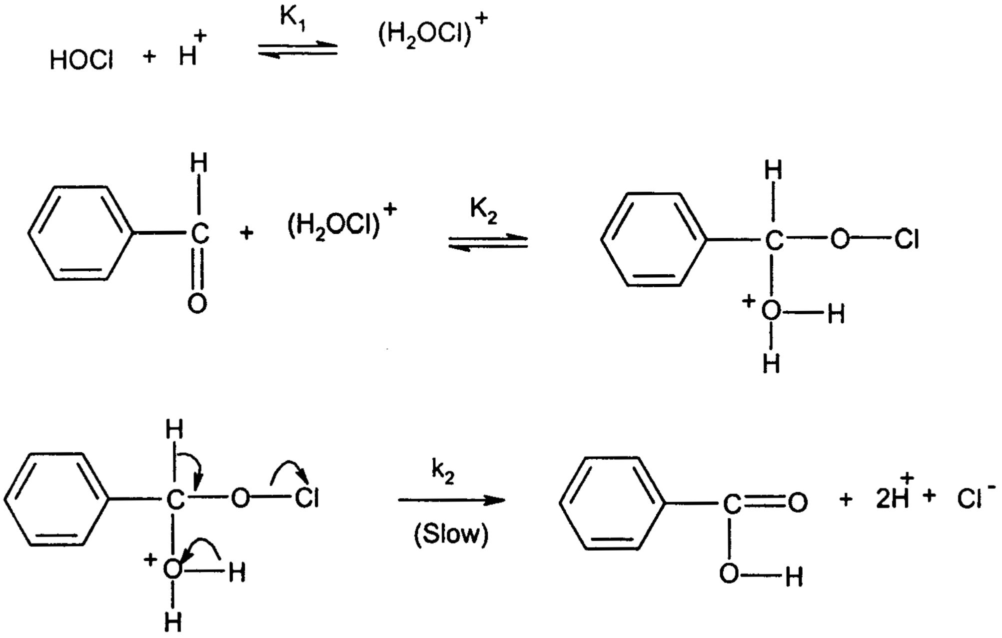
Based on the evidence from kinetic studies undertaken and from similar observations in literature, the following plausible mechanism is proposed for the oxidation of benzaldehyde using hypochlorite in aqueous acetic acid medium.



**Scheme I**

The reaction proceeds through the formation of a hypochlorite ester and its subsequent decomposition. This ester is in rapid equilibrium with the aldehyde and hypochlorite. The hypochlorite ester complex then undergo C-H bond cleavage in the rate determining step by the abstraction of the proton of the aldehyde by a weak base and the removal of a $Cl^-$ ion.

In presence of mineral acid, the rate of oxidation increases due to the formation of a stronger oxidising species viz., $(H_2OCl)^+$



As per scheme I the rate of oxidation of benzaldehyde is given by

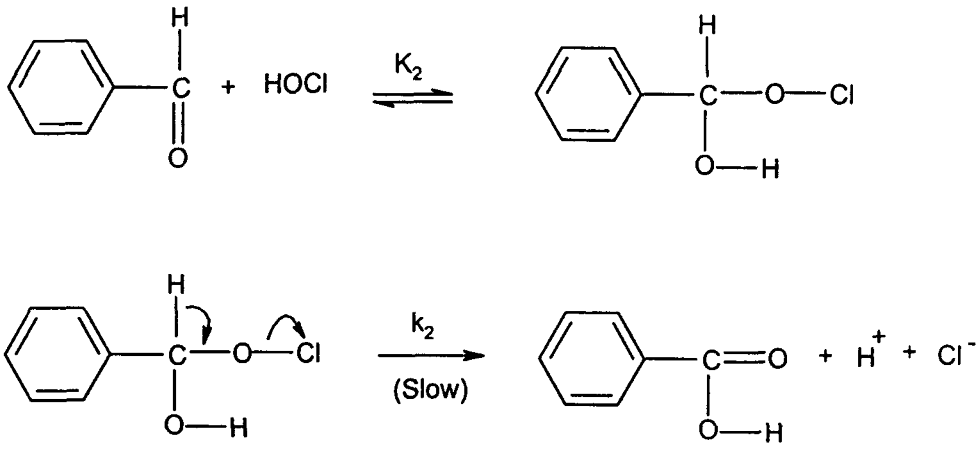
$dx/dt = k_2$ [complex]

but [complex] = $K_2[C_6H_5CHO][HOCl]$

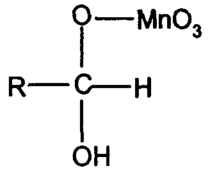
Therefore $dx/dt = K_2 k_2 [C_6H_5CHO][HOCl]$

In dioxane medium the mechanism may be depicted as

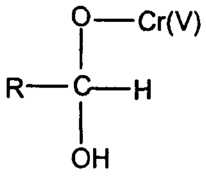
$$OCl^- + OH_2 \overset{K_1}{\rightleftharpoons} HOCl + OH^-$$



Mechanism similar to scheme I have been proposed in literature by Freeman[215] in the oxidation of aromatic aldehydes in neutral and acid medium where the formation of a permanganate ester (I) was predicted. Wiberg and Richardson [216] also reported a similar chromate ester complex (II) in the dichromate oxidation of aldehydes.



**I**



**II**

The mechanism (scheme I) and the rate law given above is in agreement with the experimental observations such as stoichiometry, ionic strength, effect of dielectric constant of the medium, effect of mineral acid and effect of substitutents on the benzene ring of the aldehyde. The mechanism proposed does not involve in any free radical as observed by the non polymerisation of added acrylonitrile.

## 4. 4 Conclusion

Studies on the oxidation of aromatic aldehydes using hypohalites are of great significance both theoretically and practically. The present project has been undertaken with the objective to determine the kinetic results of the oxidation of benzaldehyde and some of its ortho and para substituted derivatives using NaOCl in aqueous medium with the use of co-solvents acetic acid, dioxane, acetonitrile, DMSO and DMF.

Kinetic analysis showed that NaOCl could be used as a mild reagent which oxidises most of the aldehydes smoothly to the corresponding carboxylic acids. The reagent is inexpensive, easily available, non-toxic and causes no environmental problems. The oxidant is fairly stable for sufficient time when kept in air tight bottles away from heat and light. The concentration of the hypochlorite should be checked at regular intervals.

Kinetic experiments revealed that the rates of oxidation of are faster in aqueous media containing aprotic solvents compared with that of protic solvents. Studies also showed that the hypochlorite oxidation of benzaldehyde can be made effective even in organic media if carried out in presence of phase transfer catalysts such as tetrabutyl ammonium bromide (TBAB).

Effect of inclusion catalysts viz. cyclodextrins were also investigated. Cyclodextrins catalysed the oxidation of benzaldehyde through the formation of inclusion complexes. Due to their hydrophilic nature, non-toxicity and selectivity, catalytic studies using cyclodextrins are significant.

## 4.5 Summary

Kinetic studies on the oxidation of benzaldehydes viz. PMB. OCB, PCB, PBB and PNB have been carried out using NaOCl in aqueous acetic medium. Similar studies using the same substrates and oxidants were also carried out in aqueous media containing other co-solvents dioxane, acetonitrile, DMSO and DMF. Besides these the effect of inclusion catalysts viz. cyclodextrins and phase transfer catalysts viz. TBAB were also investigated.

The stoichiometry of the reaction is found to be 1:1 for the stubstrate and oxidant. The main product of the oxidation was found to be benzoic acid. The effects of varying [substrate], [oxidant], ionic strength, solvent polarity and added acid were studied. The reaction was first order each with respect to the substrate and oxidant concentrations and fractional order dependence with respect to acid concentration. Effect added salt on rate was negligible. The rate increased with decrease in dielectric constant of the medium. Effect of temperature was studied and activation parameters were determined. The effects of various substituents were investigated using different substituted benzaldehydes. The rate increased in the order PMB < PhCHO< OCB< PCB< PBB< PNB. The electron withdrawing groups were found to increase the rate while electron releasing groups decreased the rate. The rate of oxidation in various co-solvents are in the order DMF > DMSO>Dioxane>acetonitrile > acetic acid. The rate of oxidation was faster when carried out the organic medium containing phase transferred hypochlorite. Both α and β cyclodextrins accelerated the rate of oxidation; the alpha form is found to exert a more catalytic effect.

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# REFERENCES

1. Gardiner,W.C. *Rates and mechanism of chemical reactions,* Benjamin-Cummings,USA,**1969**
2. Glasstone,S.; Laidler,K.J.; Eyring,H. *The theory of rate processes,* McGraw Hill: New York,**1941**
3. Eyring,H. *J.Chem. Phys.***1935**,3,107
4. Evans,M..G.; Polanyi,M. *Trans. Faraday Soc.* **1935**,31,875
5. Wyne-Jones, W.F.K.; Eyring, H. *J. Chem. Phys.***1935**,3, 493
6. Issac, N.S *Physical Organic Chemistry,* Longman Scientific Technical: London, **1987**
7. Scatchard, G. *Chem. Rev.* **1932,** 10, 221.
8. Laidler, K.J.; Eyring, H. *Ann. N.Y. Acad. Sci.* **1940,** 39, 303.
9. Amis, E.S. *solvent effect on Reaction rate mechanism,* Academic press: New York, **1966.**
10. Kirkwood, J.G. *J.Chem. Phys.* **1934**,2,351
11. Bronsted, J.N. *Z. Phy. Chem.* **1922**, 102, 169; **1925**, 115, 337.
12. Bjerrum, B. *Z. Phy. Chem.* **1924**, 108, 182; **1925**, 118, 251.
13. Lei Liu; Qing Xiang Guo, *Chem. Rev.* **2001**, 101, 673-695.
14. Exner, O. *Collec. Chem. Czech. Commun.* **1973**, 38, 411.
15. Leffler, J.E. *J. Org. Chem.* **1955**, 20, 1202.

16. Leffler,J.E.; Gurundwald, E. *Rates Equilibria of Org. Reactions*, John Wiley Inc: NewYork, **1963**,325

17. Zuman, P.; Patel, R.C. *Techniques of Org. Reactions Kinetics,* Wiley: New York, **1996**.

18. Davies, C.W. *Progress in Reaction Kinetics,* G. Porter Ed. Vol. I: Oxford, **1961**.

19. Wiberg, K.B. *Physical Organic Chemistry*, Wiley:New York, **1964**.

20. Hammett, L.P. *Phy. Org. Chemistry*, McGraw-Hill, 2ndEdn.: Tokyo, **1970.**

21. Taft, R.W. *Steric effectis in Organic Chemistry* M. Newman, Ed. Wiley: New York, **1956**.

22. Chapman, N.B.; Shorter, J. *Correlation Analysis in Chemistry;* Plemum: New York, **1978**.

23. Klein, F.S. *Isotope Effect in Chemical Kinetics: Ann. Rev. Phys. Chem.* **1975**, 26, 191.

24. Klumpp, *Reactivity in Org. Chemistry*, Wiley: New York, **1982,** 167.

25. Falnberg, A.H.; Winstein, S.J. *Am. Chem. Soc.* **1956**, 78, 2770, 417.

26. Sconce, J.S. *Chlorine, Its manufacture, Props and uses*; Hoolker Chemical Corporation: Niagra Falls, New York, **1962**.

27. Long, W.S. *Trans., Kanas. Acad. Sc.* **1931**, 34, 164.

28. Cady, C.H. *Inorg. Synthesis*, **1957**, 5, 156.

29. Mellor, J.W. *A Comprehensive Treatise in Inorganic a theoretical chemistry,* **1929**, 2.

30. Soper; F.G. *J. Chem. Soc.* **1924**, 125, 1899.

31. Davis, H. *Quart. J. Pharm. Pharmacol.* **1931**, 4, 560.

32. Griffin, M.C.; Hedallen. *J. Soc.Chem. Ind.*, **1915**, 34, 530.

33. Yumoto, Y.; Hashizuma, R. *Chemical abstr.* **1970**, 62, 1354.

34. Rita, S.L. Q.S. *Chem. Abstr.* **1967**, 67, 1186966.

35. Patel, M.C.; Mankad, B.N. *J. Ind. Chem. Soc.* **1954**, 17, 236.

36. Rusin, B.A; Roshchin, A.L.; Leksin, *A.N. Chem. Abstr.* **1978**, 89, 128832.

37. Churganova, S.S.; Tumanova, T.A.*Chem. Abstr.* **1972**, 77, 74578.

38. Churganova, S.S.; Tumanova, T.A. *Zh. Khim.* **1971**, 27, 242.

39. Avasthi, V.; Chatterjee, A.C. *Z. Phy. Chem.* **1972**, 249.

40. Feher, F.; Linka, K.H. *J. Prakt Chem.* **1966**, 32, 190.

41. Woodruff, W.H.; Margerum, D.V. *Inorg. Chem.* **1973**, 12, 1490.

42. Vasilev, K. *Chem. Abstr.* **1965**, 62, 7163.

43. Freund, H.E.; Hans, *J. Chem. Abstr.* **1959**, 53, 14788.

44. Wedekind, B. *Metall.* **1958**, 12, 515.

45. Maria, A.; et al. *Chem. Abstr.* **1977**, 86, 160718.

46. Kantouch, A.; Abdel Fattah, S.H. *Chem. Zvesti.* **1971**, 25, 222.

47. Stankovic, I..L.; Vasatko, *J. Chem. Zvesti.* **1961**, 14, 434.

48. Grigor, T.T.; Tumanova, T.A. *Chem. Abstr.* **1966**, 73, 103557.

49. Patel, K.P.; Mehta, H.V.; Srivastava, K.K. *Staerke*, **1973**, 25, 266.

50. Cuo, J.L.; Aymard, C.; Besancon, P.; Cheffal, C. *Ann. Nutr. Ailment,* **1978**, 32, 307.

51. Masamitsu. N.; Keiji, O. *Chem. Abstr.* **1973**, 79, 43559.

52. Golumbioschi.; Facsco, G. *Chem. Abstr.* **1980**, 92, 114109.

53. Tarugi, N.; Lenci. F. *J. Chem. Soc.* **1911**, 102, 397.

54. Bazin, *Compt. Rend. Soc. Biol.* **1918**, 81, 122.

55. Austin, J.; Taylor, H.D. *J. Exp. Med.* **1918**, 27, 627.

56. Adams, A. *Tubercle.* **1938**, 19, 208.

57. Cunningham, H.M. *Am. J. Vet. Res.* **1980**, 41, 295.

58. Finley, J.W. *J. Food Sc.* **1976**, 41, 822. *Chem. Abstr.* **1976**, 85, 61615.

59. National Patent Development Corporation, U.S.; *Chem. Abstr.* **1974**, 86, 111193.

60. D' Souza, V.T.; Lipkowitz, K.B. *Chem. Rev.* **1998**, 98, 1743.

61. Ramamurthy, V. *Ed. Photochemistry in Organised and Contrained media*, VCH: New York, **1991**.

62. Saenger, W. *Ang. Chem.* Int.Ed.:Eng., **1980**, 19, 344.

63. Jeffrey, G.A.; Saenger, W. *Hydrogen bonding in biological systems,* Springer-Verly: Berlin, **1991**, chapter 18.

64. Bender, M.L.; Komiyama, M. *Cyclodextrin chemistry*, Springer: New York, **1978**.

65. Ramamurthy, V.; Eaton. D.F. *Acc. Chem. Res.* **1988**, 21, 300.

66. Wojoik, J.F.; Rohrbach, R.P. *J. Phy. Chem.* **1975**, 79, 2251.

67. Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, 97, 6869.

68. Va Etten, R.L.; Sebastian, J.F.; Clowes, G.A.; Bender, M.L. *J.Am. Chem. Soc.* **1967**, 89, 3242.

69. Hennrich, N.; Cramer, F. *J. Am. Soc.* **1965**, 87, 1121.

70. Van Etten, R.L.; Clowes, G.A., *J. Am. Chem. Soc.* **1967**, 89, 3253.

71. Bender, M.L. *Trans. N.Y. Acad. Sci.* **1967**, 29, 301.

72. Tutt, D.E.; Schwatz, M.A. *J. Am. Chem.Commun.* **1970**, 113

73. Tutt, D.E.; Schwatz, M.A. *J. Am. Chem. Soc.* **1971**, 6, 323.

74. Komiyama, M.; Bender, M.L. *Bio. Org. Chem.* **1977**, 6, 323.

75. Komiyama, M.; Bender, M.L. *J. Am. Chem. Soc.* **1977**, 99, 8021.

76. Cramer, F. *Angen. Chem.* **1961,** 73, 49.

77. Heunirich, N.; Cramer, F. *Chem and Ind. (Lonond)* **1961**, 1224.

78. Mochida, K.; Matsu, Y.; Ota, Y. *Bull. Chem. Soc. Tapan,* **1976**, 49, 3119.

79. Pagington, *Chem. Br.* **1987**, 23, 455.

80. Cramer, F.; Dietsche, W. *Chem. And Ind. (London)* **1958**, 892.

81. Breslow, R..; Kohn, H.; Siegel, B. *Tetrahedron Lett.* **1976**, 20, 1645.

82. Tabushi, I.; Fujita, K.; Kanakubo, H. J. *Am. Chem. Soc.* **1977**, 99, 6456.

83. Hamada, Y.; Nambu. N.; Nagai, T. *Chem. Pharm. Bull.* **1975**, 23, 1205.

84. Kurozumi. M.; Nambu, N.; Nagai, I. *Chem. Pharm. Bull.* **1975**, 23, 3062.

85. Koizumi, K..; Fujimura, K.. *Yakugaku Zasshi* **1972**, 92, 32.

86. Shibusawa, T.; Hamayosu, T.; Sasaki, M. *Nippon Kagaku kaishi* **1975**, 12, 2171.

87. Trommsdorff, H. *Chem. Abstr.* **1975**, 82, 1449574.

88. Kawamura, S.; Murakami, M. *Chem. Abstr*, **1975**, 83, 197823p.

89. Mifune, A.; Katsuda, Y.; Yoneda, T. *Chem. Abstr.* **1975**, 82, 39586p.

90. Kinoshita, T.; Linuma, F. *Anal. Biochem.* **1974**, 61, 632.

91. Kinoshita, T.; Linuma F.; *Chem. Pharm. Bull.* **1974**, 22, 2421.

92. Dehmlow,E.V.; Dehmlow,S.S. *Phase Transfer Catalysis,* VCH edition: New York,**1993**

93. Starks,C.M.; Liotta,C. Phase Transfer Catalysis, Academic Press: New York,**1978**

94. Weber, W. P; Gokel, G.W. *Phase transer catalysis in The organic Synthesis,* Spirnger –Verlag: New York, **1977**

95. Menger, F.M. *Chem. Soc. Rev.* **1972,** 1, 229

96. Verughese, P. *J.Chem. Edu.* **1977**, 54, 666

97. Knipe, A.C. *J. Chem. Edu.* **1976**, 53, 618

98. Lehn, J.M. *Structure and bonding*. **1973**, 16

99. Yanagida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jap.* **1977**, 50, 1386.

100. Yanagida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jap.* **1978**, 51, 3111.

101. Brandstrom, A.; Gustavii, K. *Acta. Chem.Scand.* **1969**, 23, 1215

102. Jarrouse, J. *Acad.Sci.Ser.* ***1951*,**232, 1424

103. Maercker, G.; Carmichael, J.F.; Port, W. S. *J. Org. Chem.* **1961,** 26, 2681

104. Menger, F. M. *Chem. Soc. Rev.* **1972,** 1, 229

105. Ladini, D.; Quici, S.; Rolla, F. *Synthesis.* **1975,** 430

106. Reeves, W. P.; White, M.R. *Synthesis*. **1976,** 193

107. Newman, M.S.; Chung, H. M. *J. Org. Chem.* **1974,** 39, 1036

108. Landini, O.; Montanori, F.; Prisi, F. M. *Chem. Commun.* **1974**, 879

109. Herriott, A.W.; Picker, D. *Tetrahedron Lett.* **1976**, 4521

110. Campbell, J. B., U.S. Patent III. **1975,** 876, 716

111. Gani, V.A.; Lapinte, C.; Viout, P. *Tetrahedron Lett.* **1973,** 4435

112. Mikulajezk, M.; Grzejszezak, S.; Zatorski, A. *Tetrahedron Lett.* **1975,** 3557

113. Makosza, M. *Pure Appl. Chem.* **1975**, 43, 439

114. Cinquini, M.; Montanori, F.; Tundo, P. *Chem. Commu.* **1974,** 878

115. Dietl, H.; Brannock, K.C. *Tetrahedron Lett* **1973**, 1273

116. Babicheva, A. F.; Vovk, A.I.; Yasnikov, A. *Ukr. Khim. Zh.* **1976,** 42, 259.

117. Solodor,J. *Tetrahedron Lett.* **1971**,287

118. Tagaki,W.;Hara,H.J.*Chem.Soc.Chem.Commun.***1973**,891

119. Gokel,G.W.;Gerdes,H.M.;Rebert,N.W. *Tetrahedron Lett.* **1976**,653

120. Demlov,E.V. *Tetrahedron Lett.***1976**,91

121. Dehmlow,E.V. *Justus Liebigs Ann. Chem.* **1972**,758,142

122. Dehmlow,E.V. *Tetrahedron* **1972**,28,175

123. Boswell,R; Bass,R.G. *J.Org.Chem.***1975**,40,2419

124. Chau,L.V;Schlosser,M. *Synthesis* **1973**,112

125. Starks, C. M. *J. Am. Chem. Soc..* **1971**, 93, 195

126. Arcus. C. L.; Gonzalez. C. G.; Linnecar, D. F. C. *J. Chem. Soc.* **1969**, 1377.

127. Pedersen, C. *J. Am. Che. Soc.* **1967**, 89, 2485

128. Alneri, E.; Bottaccio, G.; Carletti, V. *Tetrahedron Lett.* **1977**, 2117

129. Yange, K; Reedi, J. D; Continental Oil Company, U.S. Patent, No., III, **1972**, 649, 482

130. Dietrich, B.; Lehn, J. M. *Tetrahedron Lett* **1973**, 1225

131. Colonna, S.; Fornasier, R. *Synthesis*, **1975**, 531

132. Masse, J.P.; Parayre, E. R. *J. Chem. Soc.* **1976,** 438

133. Hutchins, R. O.; Candasamy, D. *J. Am. Chem. Soci.* **1973,** 95, 6131

134. Pierre, J. L.; Handel, H. *Tetrahedron Lett,* **1974**, 2317

135. Burst, H.D. *Tetrahedron Lett* **1974**, 2421

136. Akabori, A.; Ohtomi, M. *Bull. Chme. Soc.* **1975,** 48, 2921

137. Knipe, A. C.; Sridhar, N.; Loughran, A. *J. Chem. Soc. Che. Commu.* **1976**, 630

138. Yamoto, Y.; Oda, J.; Inouye, Y. *Tetrahedron Lett* **1979**, 2411

139. Wiberg, K.B.; Ford, P.C. *J. Am. Chem. Soc.* **1969**, 91, 124.

140. Krishna Pillai, M.; Abdul Jamed, A.; Ind. J. Chem. **1992**, 31A, 46.

141. Elango, K.P.; Karunakaran, K.. *Asian J. Chem.* **1995**, 7, 798.

142. Balasubramanian, K.; Lashmanan, K.; Sekar, K.G. *Asian. J. Chem.* **1999**, 11, 1451.

143. Revathi, S.K.; Ranga Swami; Anands, S. *Asian J. Chem.* **1999**, 11, 1271.

144. Kavitha Mohnot; Pradeep K.Sharma; Kalyan K. Banerji, *J. Org. Chem.* **1996**, 61, 1310.

145. Mythily, C.K.; Rangappa, K.S.; Mahadevappa D.S. *Ind. J. Chem.* **1990**, 29A, 676.

146. Panigrahi, G.P.; Misra, *Ind. J. Chem.* **1977**, 15A, 1066.

147. Manikyamba, P.; Raghunatha Rao, P.; Sundaram, E.V. *Ind.J. Chem.* **1981**, 20A, 1217.

148. Radhakrishna Murthy, P.S.; Sarangi, L.D. *Ind.J. Chem.* **1981**, 19A, 1124.

149. Ali, V.; Upadhyaya, S.K. *Z. Phy. Chem. (Leipzig)*, **1990**, 271, 1191.

150. Radhakrishanamurthy, P.S.; Sahu, B. *Ind. J. Chem.* **1977**, 15A, 700.

151. Lucchi, E.; *Gazz. Chim. Ital*, **1941**, 71, 729.

152. Wiberg, K.B.; Mill, T. J. *Am. Chem. Soc.* **1958**, 80, 3022.

153. Graham, G.T.E.; Westheimer, F.H. *J. Am. Chem. Soc.* **1958**, 80, 3030.

154. Tompkins, F.C. *Trans, Faraday Soc.*, **1943**, 29, 280.

155. Wiberg, K.B.; Free man; Fillmore, *J. Org. Chem.* **2000**, 65, 573.

156. Mahanti; Mahendra, K. *Oxid. Commun.*, **1999**, 22, 142.

157. Galstyan, G.A.; Plyzhik, I..M.; Galstyan, A.G.; Potapenku. E.V. *Kinetic Catal.* **1998**, 39, 682.

158. Banzal Varsha; Sharma Pradeep, K.; Banerji, K.K.. *J. Chem. Res. Synop.* **1999**, 8, 480.

159. Sen Gupta, K.K.; Sen Pratik Kumar; Mukhopadhyay, G. *Transition met. Chem. (London)*, **1993**, 18, 369.

160. Keith Bowden; Radhakrishnan Nair,T.D. *J.Chem.Res.(S),* **1993**,33

161. Nwaukwa, S.O.; Keehn, P.A. *Tetra hedron lett.* **1982**, 23, 35.

162. Kudesia, V.P.; Sharma, B.K. *Ind. J. Chem.* **1978**, 1619, 327.

163. Cal Y. Meyers, *J. Org. Chem.* **1961**, 26, 1046.

164. Guthrie, T.P.;Cossar, *J. Can. J. Chem.* **1986**,64,1250

165. Jain, D.K.; Singh, S.V.; Gupta, S.P.P. *Cellul. Chem. Technol.* **1976**, 10, 703.

166. Vladimir, R; Vode-hospod, *Vz duchotech. Ak triel*, **1979**, 13, 5.

167. Vasilev; Godishnik, *Khim Technol. Inst.* **1962**, 9, 67.

168. Vasilev; Godishnik. *Khim Technol. Inst.* **1962**, 12, 5.

169. Iordanoc; Zeilkman, A.N. *Khim. Ind.* **1961**, 33, 171.

170. Kalinina, V.E.; Shredova, L.V.; Yatsimrishi, K.B. Kinetic Katd. 1973, 14, 558.

171. Zakaror, A.N.; Lofa B.Z.; Nermeyanor, A.N. *Dohl. Akad. Nauk*, **1977**, 233, 119.

172. Antelo, T.M.; Area, R.; Barbadillio, F; Cassado, J.; *Sc. Techol.* **1981**, 15, 912.

173. Stasiak, M., *Prazemys. Chem.* **1966**, 45, 395

174. Karayannis, M.I., *Chem. Chronicle*, **1975**, 4., 15

175. Rashkovan, B.A.; Sementovskoya, G.P. *KhimZh.* **1978**, 44, 1310.

176. Vorobeva, T.P.; Yu. N.Kozlov, *Ser. Khim.* **1976**, 10, 2187.

177. Isacson, U.J.; Kowaleskur; Wettermark. *J. Inorg. Nucl. Chem.,* **1978**, 40, 1653.

178. Churganova, S.S.; Tumanova, T.A. *Tr. Lemingrad. Technol. Inst. Tsellyl. Bum. Prom.* **1969**, 24, 25.

179. Churganova, S.S.; Tumanova, T.A. *Tr. Lemingrad. Technol. Inst. Tsellyl. Bum. Prom.* **1970**, 27, 242.

180. Lok, H.T.; Hall. T.W. *Syn. Commun.* **1975**, 5, 309.

181. Amin, G.C.; Wadekkar, S.D.; Mehta, H.V. *Indian. J. Text. Res.* **1977**, 2, 20.

182. Crossley, W. *Pharm. J.* **1925**, 115, 693.

183. Grigor, T.T.; tumanova, T.A., *Zh. Prikl. Khim.* **1972**, 45, 4999, *Chem. Abstr.* (**1970**), 73, 103557.

184. Patel, K.P.; Mehta, H.V.; Srivastava, H.K. *Staerke.* **1973**, 25, 266.

185. Lawless, J.J.; Searle, H.T. *J. Chem. Soc.* **1962**, 4200.

186. Srivastava, R.D.; Nigam, P.C.; Goyal, S.K. *Ind. Eng. Chem. Fundam.* **1980**, 19, 207.

187. Vickerey, B.; Kaderia, F. *Experientia,* **1979**, 35, 299.

188. Rusin, B.A.; Roschin, A.L.; Moisseev, G.P. *Chem. Abstr.* **1980**, 92, 5866.

189. Wright, N.C. *Biochem. J.* **1926**, 20, 524.

190. Kantouch, A.; Abdel Fattah, S.H. *Chem. Zvesti.* **1971**, 25, 222.

191. Stankovic, I.L; Vasatko, *J. Chem. Zvesti.* **1961**, 14, 434.

192. Rausch, Thomas; Hofman; Friedev; Hilgenberg; Wily. Z. Naturforsch. B. *Anorg. Chem. Org. Chem.* **1981**, 36B, 359.

193. Asai, S.; Nakamura, H.; Sumita, T., *Alche Journal*, **1994**, 40, 2028.

194. Abramovici, S.; Neumann, R.; Sasson, Y. *J. Mol. Catal.* **1985**, 29, 299.

195. Do, J.S.; Cochou, T. *J. App. Electrochem.* **1990**, 20, 978.

196. Tabushi, I.; Koga, N. *Tetrahedron Lett.* **1979**, 38, 3681.

197. Do, J.S.; Do, Y.L. **Electrochimica Acta, 1994**, 39, 2037.

198. Do, J.S.; Do, Y.L. *Electrochimica Acta,* **1994**, 39, 2311.

199. Trifonov, A.Z.; Kuzmanova, R.B. *Chem. Eng. Commun.* **1983**, 21, 273.

200. Amsterdamsky, C. *J. Chem. Educ.* **1996**, 73, 92.

201. Ishii, F.; Kishi, K.I. *Synthesis,* **1980**, 706.

202. Lee, G.A.; Freedman, H.H. *Israel Journal of chem.* **1985**, 26, 229.

203. Sasson, Y.; Zappi, G.D.; Neumann, R. *J. Org. Chem.* **1986**, 51, 2880.

204. Trotta, F.; Moraglio,G.; Rappasell, A. *J. Inclusion Phenon. Mol. Recognit. Chem.* **1995**, 20, 353.

205. Trotta, F.; Francesco. *J. mol. Catal.* **1993**, 85, 265.

206. Maheswaran, M.M.; Divaker. *Ind. J. Chem.*, **1991**, 30A, 181

207. Banerji, K. K *J. Org. Chem.* **1988**, 53, 2154

208. Weissberger, A.; Prabankar, E.S *Organic solvents: Physical Properties and Method of Purification*, Interscience, 390, 170.

209. Perrin, D.D; Armarego, W.C; Perrin, D.R *Purification of Organic Compounds*, Pergamon: Oxford, **1966.**

210. Thimma Gowda, B; Moodithaya, B.S *J. Ind. Chem. Soc.* **2000**, 77, 194.

211. Perlmutter, B.; Hayman; Weissmann, Y. *J. Am. Che. Soc.* **1969**, 3, 91.

212. Sheeba, P.S. *Ph.D. Thesis, Calicut University,* **2000**, 79.

213. Hughes, E. D.; Ingold, C.K *J.Chem. Soc.* **1935**, 244

214. Laidler, K.J *Chemical Kinetics*, Harper & Row: New York, **1987**, 190-204

215. Freeman; Lin; Moore *J. Org.Chem.* **1982,** 47, 56

216. Wieberg; Richardson *J.Ame. Chem. Soc.* **1962**, 84, 2800

# KINETIC STUDIES ON THE OXIDATION AND CATALYSIS OF AROMATIC ALDEHYDES USING SODIUM HYPOCHLORITE

*Thesis submitted to the Faculty of Science,*
*University of Calicut in partial fulfilment of the*
*requirements for the Degree of* ***Doctor of Philosophy*** *in Chemistry*

By

**ABDURAHIMAN, K.K**

**2002**
**DEPARTMENT OF CHEMISTRY**
**UNIVERSITY OF CALICUT**
**KERALA – 673 635**
**INDIA**

# APPENDIX: KINETIC DATA

## Table 3.5.1

## Effect of varying [NaOCl] on the rate of oxidation of benzaldehyde in aq. Acetic acid

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K

$\mu = 0.2$ mol dm$^{-3}$ Solvent = 20% aq.HOAc (v/v)

| $10^3$[NaOCl] mol dm$^{-3}$ | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|
| Time | $\log [OCl^-] + 4$ | | | |
| 10 | 0.4983 | 0.7314 | 0.8293 | 0.9030 |
| 20 | 0.4842 | 0.7201 | 0.8162 | 0.8860 |
| 30 | 0.4698 | 0.7032 | 0.8027 | 0.8750 |
| 40 | 0.4548 | 0.6902 | 0.7924 | 0.8630 |
| 50 | 0.4470 | 0.6766 | 0.7781 | 0.8480 |
| 60 | 0.4313 | 0.6623 | 0.7634 | 0.8320 |
| 70 | 0. 4230 | 0.6532 | 0.7520 | 0.8200 |
| Slope by reg. analysis | -0.00131 | -0.00129 | -0.00135 | -0.00130 |
| $10^5 k_{obs}$ s$^{-1}$ | 5.03 | 4.95 | 5.18 | 4.98 |
| Corr. Coeft. | 0.9988 | 0.9987 | 0.9967 | 0.9907 |

## Table 3.5.2

## Effect of varying the concentration of substrate on the rate of oxidation is 20% aq. HOAc (v/v)

[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ T = 303K

$\mu = 0.2$ mol dm$^{-3}$ Solvent = 20% HOAc (v/v)

| $10^2[C_6H_5CHO]$ mol dm$^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.900 | 0.903 | 0.900 | 0.898 | 0.901 |
| 20 | 0.886 | 0.881 | 0.875 | 0.863 | 0.860 |
| 30 | 0.875 | 0.860 | 0.848 | 0.829 | 0.819 |
| 40 | 0.863 | 0.839 | 0.823 | 0.796 | 0.778 |
| 50 | 0.843 | 0.820 | 0.796 | 0.767 | 0.740 |
| 60 | 0.832 | 0.803 | 0.767 | 0.728 | 0.703 |
| 70 | 0.820 | 0.781 | 0.740 | 0.686 | 0.663 |
| Slope by reg. Analysis | -0.00133 | -0.00201 | -0.00267 | -0.00346 | -0.00395 |
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 7.72 | 10.25 | 13.28 | 15.16 |
| Corr. Coeft. | 0.9975 | 0.9987 | 0.9996 | 0.9974 | 0.9997 |

### Table 3.5.3

### Effect of added acid on the rate of oxidation of benzaldehyde using NaOCl in aq. HOAc

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ T = 303K
$\mu = 0.2$ mol dm$^{-3}$ Solvent = 20% HOAc (v/v)

| $10^2[H^+]$ mol dm$^{-3}$ | 0 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | | |
| 10 | 0.9031 | 0.914 | 0.908 | 0.911 | 0.914 | 0.914 |
| 20 | 0.8893 | 0.897 | 0.889 | 0.886 | 0.889 | 0.981 |
| 30 | 0.8779 | 0.881 | 0.869 | 0.866 | 0.863 | 0.851 |
| 40 | 0.8663 | 0.863 | 0.851 | 0.842 | 0.836 | 0.813 |
| 50 | 0.8513 | 0.845 | 0.829 | 0.820 | 0.813 | 0.792 |
| 60 | 0.8380 | 0.829 | 0.813 | 0.799 | 0.785 | 0.763 |
| 70 | 0.8195 | 0.813 | 0.792 | 0.779 | 0.760 | 0.736 |
| Slope by reg. Analysis | -.00133 | -0.0017 | -.00193 | -.00220 | -.00258 | -.00295 |
| Corr. Coeft. | 0.9976 | 0.9998 | 0.9994 | 0.9988 | 0.9997 | 0.9958 |
| 105 $k_{obs}$ $s^{-1}$ | 5.10 | 6.53 | 7.41 | 8.44 | 9.90 | 11.32 |

### Table 3.5.4

### Effect of ionic strength on the rate of oxidation of Benzaldehyde using NaOCl in 20% aq. HOAc

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20%aqHOAc

| $10^2$[NaCl] mol dm$^{-3}$ | 1.0 | 2.0 | 3.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.924 | 0.929 | 0.914 | 0.908 | 0.924 |
| 20 | 0.909 | 0.916 | 0.900 | 0.895 | 0.914 |
| 30 | 0.898 | 0.903 | 0.886 | 0.884 | 0.898 |
| 40 | 0.880 | 0.893 | 0.872 | 0.869 | 0.880 |
| 50 | 0.869 | 0.875 | 0.860 | 0.854 | 0.866 |
| 60 | 0.857 | 0.863 | 0.848 | 0.842 | 0.857 |
| 70 | 0.845 | 0.854 | 0.839 | 0.833 | 0.848 |
| Slope by reg. Analysis | -0.00132 | -0.00128 | -0.00127 | -0.00130 | -0.00133 |
| Corr. Coeft. | 0.9972 | 0.9967 | 0.9963 | 0.9976 | .9986 |
| $10^5$ $k_{obs}$ $s^{-1}$ | 5.07 | 4.91 | 4.93 | 4.98 | 5.10 |

### Table 3.5.5
### Effect of polarity of the medium on the rate of oxidation of benzaldehyde using NaOCl

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$

| Acetic acid (%) | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.929 | 0.898 | 0.887 | 0.881 | 0.878 |
| 20 | 0.919 | 0.884 | 0.872 | 0.863 | 0.857 |
| 30 | 0.904 | 0.869 | 0.851 | 0.845 | 0.839 |
| 40 | 0.895 | 0.854 | 0.839 | .830 | 0.820 |
| 50 | 0.878 | 0.839 | 0.826 | .813 | 0.799 |
| 60 | 0.863 | 0.826 | 0.813 | 0.796 | 0.778 |
| Slope by reg. Analysis | -.00132 | -.00141 | -.00153 | -0.00173 | -.00198 |
| Corr. Coeft. | 0.9936 | 0.9975 | 0.9986 | 0.9996 | 0.9960 |
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 5.49 | 5.87 | 6.64 | 7.60 |

### Table 3.5.6
### Effect of addition of benzoic acid on the rate of oxidation

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. HOAc
$\mu = 0.2$ mol dm$^{-3}$

| $10^2[C_6H_5COOH]$ mol dm$^{-3}$ | 0 | 1.0 | 1.5 | 2.0 |
|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | |
| 10 | 0.903 | 0.924 | 0.929 | 0.895 |
| 20 | 0.886 | 0.907 | 0.903 | 0.884 |
| 30 | 0.875 | 0.898 | 0.893 | 0.868 |
| 40 | 0.863 | 0.880 | 0.875 | 0.854 |
| 50 | 0.848 | 0.869 | 0.863 | 0.842 |
| 60 | 0.832 | 0.857 | 0.854 | 0.833 |
| Slope by reg. analysis | -.00133 | -.00132 | -.00128 | -.00130 |
| Corr. Coeft. | 0.9976 | 0.9972 | 0.9968 | 0.9970 |
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 5.07 | 4.91 | 5.03 |

### Table 3.5.8

### Effect of temperature on the rate of oxidation of benzaldehyde using NaOCl

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.903 | 0.908 | 0.906 | 0.866 | 0.851 |
| 20 | 0.889 | 0.892 | 0.881 | 0.845 | 0.823 |
| 30 | 0.878 | 0.884 | 0.863 | 0.826 | 0.799 |
| 40 | 0.866 | 0.860 | 0.842 | 0.803 | 0.775 |
| 50 | 0.851 | 0.845 | 0.826 | 0.782 | 0.744 |
| 60 | 0.838 | 0.829 | 0.806 | 0.760 | 0.716 |
| Slope by reg. Analysis | -.00133 | -.00160 | -0.00196 | -.00213 | -.00268 |
| Corr. Coeft. | 0.9976 | 0.9953 | 0.9981 | 0.9997 | 0.9992 |
| $10^5 k_{obs}$ s$^{-1}$ | 5.10 | 6.14 | 7.33 | 8.18 | 10.29 |

### Table 3.5.9

### Effect of substituents on the rate of oxidation of benzaldehyde using NaOCl

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K
$[NaOCl] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc

| Substituents | PMB | PhCHO | PCB | OCB | PBB | PNB |
|---|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | | |
| 10 | 0.935 | 0.903 | 0.924 | 0.975 | 0.924 | 0.900 |
| 20 | 0.924 | 0.889 | 0.906 | 0.959 | 0.906 | 0.842 |
| 30 | 0.914 | 0.878 | 0.887 | 0.944 | 0.887 | 0.782 |
| 40 | 0.903 | 0.866 | 0.869 | 0.929 | 0.869 | .724 |
| 50 | 0.895 | 0.851 | 0.851 | 0.914 | 0.851 | 0.658 |
| 60 | 0.884 | 0.838 | 0.833 | 0.900 | 0.829 | 0.604 |
| Slope by reg. Analysis | -.00101 | -.00133 | -.00183 | -.00150 | -.00187 | -.00584 |
| Corr. Coeft. | 0.9984 | 0.9976 | 0.9992 | 0.9996 | 0.9990 | 0.9995 |
| $10^5 k_{obs}$ s$^{-1}$ | 3.88 | 5.10 | 7.02 | 5.76 | 7.18 | 22.42 |

### Table 3.5.10(a)
### Effect of temperature on the rate of oxidation of p- methyl benzaldehyde using NaOCl

[PMB] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 10 | 0.935 | 0.932 | 0.932 | 0.927 | 0.924 |
| 20 | 0.924 | 0.919 | 0.916 | 0.911 | 0.903 |
| 30 | 0.914 | 0.908 | 0.903 | 0.892 | 0.884 |
| 40 | 0.903 | 0.898 | 0.889 | 0.875 | 0.863 |
| 50 | 0.895 | 0.884 | 0.875 | 0.860 | 0.845 |
| 60 | 0.884 | 0.869 | 0.857 | 0.845 | 0.826 |
| Slope by reg. Analysis | -.00101 | -.00123 | -.00146 | -.00165 | -.00203 |
| Corr. Coeft. | 0.9988 | 0.9965 | 0.9981 | 0.9982 | 0.9998 |
| $10^5$ $k_{obs}$ s$^{-1}$ | 3.88 | 4.72 | 5.60 | 6.33 | 7.79 |

### Table 3.5.10(b)
### Effect of temperature on the rate of oxidation of p-chloro benzaldehyde using NaOCl

[PCB] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 10 | 0.924 | 0.919 | 0.914 | 0.911 | 0.892 |
| 20 | 0.906 | 0.897 | 0.884 | 0.872 | 0.848 |
| 30 | 0.887 | 0.875 | 0.857 | 0.833 | 0.803 |
| 40 | 0.869 | 0.851 | 0.826 | 0.796 | 0.756 |
| 50 | 0.851 | 0.829 | 0.799 | 0.756 | 0.712 |
| 60 | 0.833 | 0.806 | 0.771 | 0.716 | 0.667 |
| Slope by reg. Analysis | -.00183 | -.00227 | -.00286 | -.00389 | -.00450 |
| Corr. Coeft. | 0.9998 | 0.9998 | 0.9996 | 0.9998 | 0.9998 |
| $10^5$ $k_{obs}$ s$^{-1}$ | 7.02 | 8.71 | 10.98 | 14.93 | 17.27 |

## Table 3.5.10(c)

## Effect of temperature on the rate of oxidation of o-chloro benzaldehyde using NaOCl

[OCB] = 1.0 x $10^{-2}$ mol $dm^{-3}$ μ = 0.2 mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [$OCl^-$] | | | | |
| 10 | 0.975 | 0.971 | 0.968 | 0.959 | 0.949 |
| 20 | 0.959 | 0.952 | 0.944 | 0.927 | 0.911 |
| 30 | 0.944 | 0.932 | 0.919 | 0.895 | 0.869 |
| 40 | 0.929 | 0.914 | 0.895 | 0.863 | 0.829 |
| 50 | 0.914 | 0.895 | 0.872 | 0.833 | 0.792 |
| 60 | 0.900 | 0.878 | 0.848 | 0.806 | 0.756 |
| Slope by reg. Analysis | -.00150 | -.00187 | -.00242 | -.00308 | -.00396 |
| Corr. Coeft. | 0.9996 | 0.9997 | 0.9998 | 0.9997 | 0.9995 |
| $10^5$ $k_{obs}$ $s^{-1}$ | 5.76 | 7.18 | 9.28 | 11.82 | 15.22 |

## Table 3.5.10(d)

## Effect of temperature on the rate of oxidation of p-bromo benzaldehyde using NaOCl

[PBB] = 1.0 x $10^{-2}$ mol $dm^{-3}$ μ = 0.2 mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [$OCl^-$] | | | | |
| 10 | 0.924 | 0.922 | 0.9138 | 0.908 | 0.903 |
| 20 | 0.906 | 0.897 | 0.884 | 0.869 | 0.857 |
| 30 | 0.887 | 0.875 | 0.854 | 0.829 | 0.809 |
| 40 | 0.869 | 0.851 | 0.823 | 0.792 | 0.763 |
| 50 | 0.851 | 0.827 | 0.793 | 0.752 | 0.716 |
| 60 | 0.829 | 0.804 | 0.763 | 0.712 | 0.672 |
| Slope by reg. Analysis | -.00187 | -.00236 | -.00302 | -.00392 | -.00464 |
| Corr. Coeft. | 0.9992 | 0.9999 | 0.9993 | 0.9998 | 0.9998 |
| $10^5$ $k_{obs}$ $s^{-1}$ | 7.18 | 9.06 | 11.59 | 15.05 | 17.81 |

### Table 3.5.10(e)
### Effect of temperature on the rate of oxidation of p-nitro benzaldehyde using NaOCl

[PNB] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 5 | 0.929 | 0.911 | 0.903 | 0.900 | 0.854 |
| 10 | 0.900 | 0.872 | 0.854 | 0.836 | 0.771 |
| 15 | 0.872 | 0.836 | 0.806 | 0.775 | 0.690 |
| 20 | 0.842 | 0.799 | 0.756 | 0.708 | 0.613 |
| 25 | 0.813 | 0.960 | 0.708 | 0.648 | 0.531 |
| 30 | 0.782 | 0.724 | 0.658 | 0.580 | 0.455 |
| 35 | 0.756 | 0.695 | 0.613 | 0.525 | 0.380 |
| Slope by reg. analysis | -.0058 | -.00729 | -.00973 | -.0126 | -.0158 |
| Corr. Coeft. | 0.9978 | 0.9994 | 0.9998 | 0.9997 | 0.9998 |
| $10^5$ $k_{obs}$ $s^{-1}$ | 22.42 | 27.99 | 37.35 | 48.36 | 60.68 |

### Table 3.6.2(a)
### Effect of temperature on the oxidation of benzaldehyde using NaOCl in presence of α-Cyclodextrin

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.9580 | 0.9498 | 0.9498 | 0.9427 | 0.9423 |
| 20 | 0.9420 | 0.9345 | 0.9395 | 0.9216 | 0.9111 |
| 30 | 0.9243 | 0.9165 | 0.9070 | 0.8951 | 0.8808 |
| 40 | 0.9094 | 0.8976 | 0.8864 | 0.8894 | 0.8510 |
| 50 | 0.8928 | 0.8779 | 0.8633 | 0.8419 | 0.8228 |
| 60 | 0.8772 | 0.8388 | 0.8419 | 0.7993 | 0.7923 |
| Slope | -0.00159 | -0.00191 | -0.0022 | -0.00257 | -0.003 |
| Corr. coeft. | 0.9975 | 0.9982 | 0.9996 | 0.9972 | 0.9952 |

## Table 3.6.2(b)

## Effect of temperature on the oxidation of Benzaldehyde using NaOCl in aq. acetic acid in presence of β-Cyclodextrin

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [BCD] = $2.1 \times 10^{-3}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9708 | 0.9685 | 0.9661 | 0.9651 | 0.9665 |
| 20 | 0.9566 | 0.9494 | 0.9444 | 0.9389 | 0.9395 |
| 30 | 0.9395 | 0.8320 | 0.9217 | 0.9131 | 0.9031 |
| 40 | 0.9243 | 0.9138 | 0.9004 | 0.8865 | 0.8722 |
| 50 | 0.9085 | 0.8948 | 0.8808 | 0.8603 | 0.8420 |
| 60 | 0.8921 | 0.875 | 0.8573 | 0.8350 | 0.8124 |
| Slope | -0.00157 | -0.00186 | -0.00204 | -0.00260 | -0.00305 |
| Corr. coeft. | 0.9982 | 0.9973 | 0.9968 | 0.9996 | 0.9970 |

## Table 3.6.3

## Effect of substituents on the oxidation of benzaldehyde using NaOCl in aq. acetic acid in presence of ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc T = 303K

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9590 | 0.9580 | 0.9395 | 0.9370 | 0.8920 |
| 20 | 0.9469 | 0.9420 | 0.9165 | 0.9138 | 0.7993 |
| 30 | 0.9444 | 0.9243 | 0.8948 | 0.8920 | 0.7032 |
| 40 | 0.9216 | 0.9094 | 0.8721 | 0.8692 | 0.6156 |
| 50 | 0.9084 | 0.8928 | 0.8512 | 0.8450 | 0.5317 |
| 60 | 0.9000 | 0.8772 | 0.8293 | 0.8228 | 0.4519 |
| Slope | -0.00121 | -0.00159 | -0.00223 | -0.00238 | -0.00935 |
| Corr. coeft. | 0.9998 | 0.9975 | 0.9977 | 0.9984 | 0.9980 |

### Table 3.6.4(a)

### Effect of temperature on the oxidation of p-methyl benzaldehyde in presence of ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ [ACD] = 2.05 x $10^{-3}$ mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ $moldm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$
Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9590 | 0.9542 | 0.9518 | 0.9449 | 0.9420 |
| 20 | 0.9469 | 0.9420 | 0.9344 | 0.9268 | 0.9191 |
| 30 | 0.9344 | 0.9268 | 0.919 | 0.9058 | 0.8976 |
| 40 | 0.9216 | 0.9138 | 0.903 | 0.8865 | 0.8750 |
| 50 | 0.9084 | 0.8976 | 0.8836 | 0.8663 | 0.8543 |
| 60 | 0.900 | 0.8864 | 0.8692 | 0.8492 | 0.8325 |
| Slope | -0.0021 | -.00142 | -0.00167 | -0.00194 | -0.00222 |
| Corr. coeft. | 0.9998 | 0.9987 | 0.9994 | 0.9974 | 0.9950 |

### Table 3.6.4(b)

### Effect of temperature on the oxidation of p-chloro benzaldehyde in acetic acid medium using ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ [ACD] = 2.05 x $10^{-3}$ mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$
Solvent = 20% aq. HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9395 | 0.9345 | 0.9268 | 0.9217 | 0.9190 |
| 20 | 0.9165 | 0.9058 | 0.8920 | 0.8779 | 0.8692 |
| 30 | 0.8948 | 0.8751 | 0.8573 | 0.8357 | 0.8162 |
| 40 | 0.8721 | 0.8512 | 0.8228 | 0.7924 | 0.7634 |
| 50 | 0.8512 | 0.8228 | 0.7888 | 0.7520 | 0.7160 |
| 60 | 0.8293 | 0.8129 | 0.7558 | 0.7075 | 0.6674 |
| Slope | -0.00223 | -0.00284 | -0.00345 | -0.00422 | -0.00520 |
| Corr. coeft. | 0.9977 | 0.9970 | 0.9945 | 0.9979 | 0.9988 |

### Table 3.6.4(c)

### Effect of temperature on the oxidation of p-bromo benzaldehyde in aq. acetic acid medium in presence of ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.937 | 0.9294 | 0.9242 | 0.9190 | 0.911 |
| 20 | 0.9138 | 0.903 | 0.8893 | 0.875 | 0.8573 |
| 30 | 0.8920 | 0.8721 | 0.8512 | 0.8325 | 0.8028 |
| 40 | 0.8692 | 0.845 | 0.8195 | 0.7889 | 0.7520 |
| 50 | 0.845 | 0.8129 | 0.7817 | 0.7481 | 0.6900 |
| 60 | 0.8228 | 0.7853 | 0.7442 | 0.7032 | 0.6483 |
| Slope | -0.00232 | -0.00287 | -0.00356 | -0.00433 | -0.00530 |
| Corr. coeft. | 0.9984 | 0.9980 | 0.9991 | 0.9990 | 0.9955 |

### Table 3.6.4(d)

### Effect of temperature on the oxidation of p-nitro benzaldehyde using ACD in aq. HOAc medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ [ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 5 | 0.9394 | 0.9268 | 0.9111 | 0.8921 | 0.8779 |
| 10 | 0.8920 | 0.8692 | 0.8388 | 0.8061 | 0.7708 |
| 15 | 0.8450 | 0.8129 | 0.7671 | 0.7160 | 0.6627 |
| 20 | 0.7993 | 0.7559 | 0.6946 | 0.6283 | 0.5563 |
| 25 | 0.7520 | 0.6989 | 0.6232 | 0.5440 | 0.4548 |
| 30 | 0.7032 | 0.6384 | 0.5563 | 0.4548 | 0.3429 |
| Slope | -0.00935 | -0.01163 | -0.01448 | -0.01716 | -0.02167 |
| Corr. coeft. | 0.9980 | 0.9910 | 0.9990 | 0.9982 | 0.9898 |

### Table 3.7.1

### Effect of varying [NaOCl] on the rate of oxidation $C_6H_5CHO$ in aqueous dioxane

[$C_6H_5CHO$] = 1.0 x $10^{-2}$ mol dm$^{-3}$ T = 303K
μ = 0.2 mol dm$^{-3}$ Solvent: 20% aq. HOAc(v/v)

| $10^3$[NaOCl] mol dm$^{-3}$ | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|
| Time (min) | 4 + log [OCl$^-$] | | | |
| 10 | 0.5250 | 0.6989 | 0.8261 | 0.9493 |
| 20 | 0.4983 | 0.6766 | 0.8027 | 0.9260 |
| 30 | 0.4771 | 0.6532 | 0.7817 | 0.905 |
| 40 | 0.4548 | 0.6283 | 0.75558 | 0.8779 |
| 50 | 0.4313 | 0.6020 | 0.7284 | 0.8512 |
| 60 | 0.4065 | 0.5797 | 0.7070 | 0.8260 |
| Slope by reg. Analysis | -0.00233 | -0.00241 | -0.00242 | -0.00238 |
| Corr. Coeft. | 0.9941 | 0.9992 | 0.9987 | 0.9982 |

### Table 3.7.2

### Effect of varying substrate concentration on the rate of oxidation of $C_6H_5CHO$ in aqueous dioxane medium

[NaOCl] = 1.0 x $10^{-2}$ mol dm$^{-3}$ T = 303K
μ = 0.2 mol dm$^{-3}$ Solvent: 20% aq. dioxane

| $10^2$[$C_6H_5CHO$] mol dm$^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [OCl$^-$] | | | | |
| 10 | 0.9493 | 0.942 | 0.9294 | 0.9190 | 0.9111 |
| 20 | 0.9260 | 0.9058 | 0.8836 | 0.8603 | 0.8388 |
| 30 | 0.905 | 0.8692 | 0.8356 | 0.7993 | 0.7671 |
| 40 | 0.8779 | 0.8325 | 0.7888 | 0.7403 | 0.6946 |
| 50 | 0.8512 | 0.7958 | 0.7403 | 0.6812 | 0.6232 |
| 60 | 0.826 | 0.7596 | 0.6989 | 0.618 | 0.5502 |
| Slope by reg. analysis | -0.00238 | -0.00365 | -0.00465 | -0.006 | -0.00721 |
| Corr. Coeft. | 0.9998 | 0.9999 | 0.9998 | 0.9999 | 0.9998 |
| $k_{obs}$/[$C_6H_5CHO$] | 9.14 | 9.33 | 8.93 | 9.21 | 9.22 |

### Table 3.7.3
### Effect of added mineral acid on the oxidation of benzaldehyde in dioxane medium

[$C_6H_5CHO$] = 1.0 x $10^{-2}$ mol dm$^{-3}$ T = 303K
[NaOCl] = 1.0 x $10^{-3}$ mol dm$^{-3}$ $\mu$ = 0.2 mol dm$^{-3}$
Solvent: 20% aq. dioxane

| $10^2$[H$^+$] mol dm$^{-3}$ | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [OCl$^-$] | | | | |
| 10 | 0.9242 | 0.9058 | 0.8949 | 0.8751 | 0.8603 |
| 20 | 0.8921 | 0.8692 | 0.8513 | 0.8226 | 0.7993 |
| 30 | 0.8603 | 0.8325 | 0.8095 | 0.7708 | 0.7403 |
| 40 | 0.8260 | 0.7958 | 0.7634 | 0.7201 | 0.6812 |
| 50 | 0.7924 | 0.7596 | 0.7202 | 0.6675 | 0.6180 |
| 60 | 0.7597 | 0.7242 | 0.6812 | 0.6180 | 0.5623 |
| Slope by reg. analysis | -0.00330 | -0.00364 | -0.00431 | -0.00515 | -0.00598 |
| Corr. Coeft. | 0.9998 | 0.9999 | 0.9995 | 0.9990 | 0.9992 |

### Table 3.7.4
### Influence of ionic strength on the rate of oxidation of $C_6H_5CHO$ in aq. dioxane medium

[$C_6H_5CHO$] = 1.0 x $10^{-2}$ mol dm$^{-3}$ T = 303K
[NaOCl] = 1.0 x $10^{-3}$ mol dm$^{-3}$ Solvent: 20% aq. dioxane

| $10^2$[NaCl] mol dm$^{-3}$ | 1.0 | 2.0 | 3.0 | 5.0 | 10.0 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [OCl$^-$] | | | | |
| 10 | 0.9396 | 0.9395 | 0.9243 | 0.9111 | 0.9190 |
| 20 | 0.9138 | 0.9138 | 0.900 | 0.8836 | 0.8837 |
| 30 | 0.8893 | 0.8893 | 0.8751 | 0.8692 | 0.8603 |
| 40 | 0.8660 | 0.8662 | 0.8512 | 0.8450 | 0.8388 |
| 50 | 0.8388 | 0.8419 | 0.8261 | 0.8195 | 0.8129 |
| 60 | 0.8020 | 0.8162 | 0.8061 | 0.7959 | 0.7888 |
| Slope by reg. analysis | -0.00238 | -0.00244 | -0.00239 | -0.00242 | -0.00238 |
| Corr. Coeft. | 0.9998 | 0.9997 | 0.9990 | 0.9991 | 0.9920 |

### Table 3.7.5
### Effect of polarity of the medium on the rate of oxidation of benzaldehyde in aq. Dioxane medium

[$C_6H_5CHO$] = 1.0 x $10^{-2}$ mol $dm^{-3}$ T = 303K
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$

| % of dioxane | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [$OCl^-$] | | | | |
| 5 | 0.9614 | 0.9493 | 0.9243 | 0.8808 | 0.8512 |
| 10 | 0.9493 | 0.9056 | 0.8512 | 0.7708 | 0.7118 |
| 15 | 0.9396 | 0.8633 | 0.7745 | 0.6675 | 0.574 |
| 20 | 0.926 | 0.8195 | 0.7032 | 0.5563 | 0.4393 |
| 25 | 0.9138 | 0.7781 | 0.6284 | 0.4548 | 0.3117 |
| 30 | 0.905 | 0.7324 | 0.5563 | 0.3424 | 0.1761 |
| Slope by reg. analysis | -0.00237 | -0.00863 | -0.0147 | -0.0214 | -0.0269 |
| Corr. Coeft. | 0.9972 | 0.9998 | 0.9999 | 0.9998 | 0.9998 |

### Table 3.7.6
### Effect of temperature on the hypochlorite oxidation of $C_6H_5CHO$ in aq. dioxane medium

[$C_6H_5CHO$] = 1.0 x $10^{-2}$ mol $dm^{-3}$ T = 303K
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$
Solvent: 20% aq. dioxane

| Temp (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [$OCl^-$] | | | | |
| 10 | 0.9493 | 0.9243 | 0.9190 | 0.9003 | 0.9115 |
| 20 | 0.926 | 0.8948 | 0.8836 | 0.8481 | 0.8663 |
| 30 | 0.905 | 0.8663 | 0.8482 | 0.7993 | 0.826 |
| 40 | 0.8779 | 0.8388 | 0.8129 | 0.7481 | 0.7818 |
| 50 | 0.8512 | 0.8095 | 0.7782 | 0.6946 | 0.7403 |
| 60 | 0.8260 | 0.7817 | 0.7442 | 0.6532 | 0.6989 |
| Slope by reg. analysis | -0.00238 | -0.00285 | -0.00350 | -0.00424 | -0.00494 |
| Corr. Coeft. | 0.9998 | 0.9999 | 0.9999 | 0.9995 | 0.9990 |

## Table 3.7.7
## Effect of substituents on the rate of oxidation of benzaldehyde in aq. dioxane medium

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm$^{-3}$ T = 303K
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
Solvent: 20% aq. dioxane

| Substituent | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9494 | 0.9485 | 0.9494 | 0.9472 | 0.9003 |
| 20 | 0.932 | 0.9260 | 0.9242 | 0.9216 | 0.8293 |
| 30 | 0.9138 | 0.9050 | 0.8948 | 0.892 | 0.7558 |
| 40 | 0.8949 | 0.8779 | 0.8692 | 0.8662 | 0.6812 |
| 50 | 0.8779 | 0.8512 | 0.8420 | 0.8383 | 0.5885 |
| 60 | 0.8603 | 0.8260 | 0.8162 | 0.8061 | 0.5004 |
| Slope by reg. analysis | -0.00179 | -0.00238 | -0.00268 | -0.00283 | -0.00741 |
| Corr. Coeft. | 0.9998 | 0.9998 | 0.9996 | 0.9990 | 0.9998 |

## Table 3.7.8(a)
## Effect of temperature on the oxidation of p- methyl benzaldehyde in aq. dioxane medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
$[NaOCl] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9494 | 0.9469 | 0.9420 | 0.9370 | 0.9243 |
| 20 | 0.9320 | 0.9243 | 0.9138 | 0.9057 | 0.9003 |
| 30 | 0.9138 | 0.9031 | 0.8893 | 0.8751 | 0.8633 |
| 40 | 0.8949 | 0.8808 | 0.8633 | 0.8450 | 0.8261 |
| 50 | 0.8779 | 0.8603 | 0.8356 | 0.8162 | 0.7888 |
| 60 | 0.8603 | 0.8388 | 0.8095 | 0.7853 | 0.7520 |
| Slope by regr. analysis | -0.00179 | -0.00216 | -0.00264 | -0.00302 | -0.00352 |
| Corr. coeft. | 0.9998 | 0.9972 | 0.9960 | 0.9937 | 0.9960 |
| $10^5$ $k_{obs}$ s$^{-1}$ | 6.87 | 8.29 | 10.13 | 11.59 | 13.51 |

### Table 3.7.8(b)

### Effect of temperature on the oxidation of p- chloro benzaldehyde in aq. dioxane medium.

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% HOAc

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.9494 | 0.942 | 0.9344 | 0.9294 | 0.9190 |
| 20 | 0.9242 | 0.9057 | 0.8893 | 0.8750 | 0.8512 |
| 30 | 0.8948 | 0.875 | 0.8451 | 0.8195 | 0.7781 |
| 40 | 0.8692 | 0.8388 | 0.8027 | 0.7634 | 0.7075 |
| 50 | 0.8420 | 0.8027 | 0.7596 | 0.7118 | 0.6384 |
| 60 | 0.8162 | 0.7708 | 0.7160 | 0.6532 | 0.5682 |
| Slope by regr. analysis | -0.00268 | -0.0343 | -0.0435 | -0.00550 | -0.00704 |
| Corr. coeft. | 0.9996 | 0.9990 | 0.9928 | 0.9965 | 0.9990 |
| $10^5 k_{obs}$ s$^{-1}$ | 10.29 | 13.17 | 16.70 | 21.11 | 27.02 |

### Table 3.7.8(c)

### Effect of temperature on the oxidation of p-bromo benzaldehyde in dioxane medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. dioxane

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.9493 | 0.9420 | 0.9045 | 0.9190 | 0.9057 |
| 20 | 0.9216 | 0.9058 | 0.8865 | 0.8603 | 0.8325 |
| 30 | 0.8920 | 0.8692 | 0.8388 | 0.7993 | 0.7559 |
| 40 | 0.8662 | 0.8356 | 0.7924 | 0.7403 | 0.6812 |
| 50 | 0.8388 | 0.7993 | 0.7481 | 0.6812 | 0.6074 |
| 60 | 0.8061 | 0.7634 | 0.6989 | 0.6232 | 0.5315 |
| Slope by regr. analysis | -0.00283 | -.00356 | -0.00468 | -0.00593 | -0.0079 |
| Corr. coeft. | 0.9990 | 0.9976 | 0.9968 | 0.9980 | 0.9945 |
| $10^5 k_{obs}$ s$^{-1}$ | 10.86 | 13.66 | 17.96 | 22.76 | 28.75 |

## Table 3.7.8(d)

## Effect of temperature on the oxidation of p- nitro benzaldehyde in dioxane medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ μ = 0.2 mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. dioxane

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 5 | 0.9344 | 0.9469 | 0.9319 | 0.8779 | 0.9084 |
| 10 | 0.9003 | 0.9003 | 0.8692 | 0.7888 | 0.7993 |
| 15 | 0.8129 | 0.8512 | 0.8061 | 0.7033 | 0.6812 |
| 20 | 0.8293 | 0.7993 | 0.7403 | 0.6180 | 0.5798 |
| 25 | 0.7853 | 0.7520 | 0.6766 | 0.5314 | 0.4698 |
| 30 | 0.7558 | 0.7032 | 0.6128 | 0.447 | 0.3617 |
| Slope by regr. analysis | -0.00741 | -0.00980 | -0.01279 | -.01721 | -0.02185 |
| Corr. coeft. | .9998 | 0.9984 | 0.9899 | 0.9920 | 0.9960 |
| $10^5$ $k_{obs}$ s$^{-1}$ | 28.47 | 37.62 | 44.09 | 66.05 | 83.87 |

## Table 3.8.1(a)

## Effect of temperature on the oxidation of Benzaldehyde in aq. dioxane catalysed by ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ μ = 0.2 mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. dioxane
[ACD] = $2.5 \times 10^{-3}$ mol dm$^{-3}$

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log [OCl^-]$ | | | | |
| 10 | 0.96054 | 0.9644 | 0.944 | 0.938 | 0.990 |
| 20 | 0.9200 | 0.9084 | 0.8895 | 0.8742 | 0.8195 |
| 30 | 0.8831 | 0.8625 | 0.8634 | 0.8102 | 0.7404 |
| 40 | 0.8435 | 0.8168 | 0.7786 | 0.7468 | 0.6627 |
| 50 | 0.8042 | 0.7708 | 0.724 | 0.683 | 0.5855 |
| 60 | 0.765 | 0.7250 | 0.6636 | 0.618 | 0.5051 |
| Slope | -.00388 | -.00464 | -0.00557 | -0.00658 | -0.00783 |
| Corr. coeft. | 0.9998 | 0.9988 | 0.9987 | 0.9989 | 0.9998 |

### Table 3.8.1(b)
### Effect of temperature on the oxidation of benzaldehyde in aq. dioxane catalysed by BCD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$
[BCD] = $2.5 \times 10^{-3}$ mol dm$^{-3}$
$\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% aq. dioxane

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 10 | 0.962 | 0.9576 | 0.950 | 0.940 | 0.9398 |
| 20 | 0.9272 | 0.9150 | 0.8994 | 0.878 | 0.875 |
| 30 | 0.8912 | 0.8726 | 0.8488 | 0.8172 | 0.8028 |
| 40 | 0.846 | 0.8280 | 0.7985 | 0.756 | 0.7323 |
| 50 | 0.816 | 0.7902 | 0.7440 | 0.694 | 0.6625 |
| 60 | 0.786 | 0.7460 | 0.7015 | 0.640 | 0.6008 |
| Slope | -.00363 | -0.00430 | -.00522 | -0.00621 | -0.00731 |
| Corr. coeft. | 0.9998 | 0.9987 | 0.9974 | 0.9959 | 0.9970 |

### Table 3.8.2
### Effect of substituents on the rate of oxidation of benzaldehyde in aq. dioxane in presence of ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$
[ACD] = $2.5 \times 10^{-3}$ mol dm$^{-3}$
$\mu = 0.2$ mol dm$^{-3}$
Solvent = 20% aq. dioxane
T = 303K

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 10 | 0.9677 | 0.9605 | 0.9576 | 0.9444 | 0.8603 |
| 20 | 0.9345 | 0.9200 | 0.9150 | 0.8949 | 0.7245 |
| 30 | 0.9058 | 0.8831 | 0.8726 | 0.8460 | 0.5952 |
| 40 | 0.8751 | 0.8435 | 0.828 | 0.7975 | 0.4742 |
| 50 | 0.8512 | 0.8042 | 0.7902 | 0.7508 | 0.3642 |
| 60 | 0.8220 | 0.765 | 0.746 | 0.7006 | 0.2602 |
| Slope | -.00281 | -.00388 | -.00423 | -0.00482 | -0.01335 |
| Corr. coeft. | 0.9974 | 0.9998 | 0.9987 | 0.9980 | 0.9940 |

## Table 3.8.3(a)

### Effect of temperature on the rate of oxidation of p-methyl benzaldehyde in aq. dioxane catalysed by ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ Solvent = 20% aq. dioxane
[ACD] = 2.05 x $10^{-3}$ mol $dm^{-3}$

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9677 | 0.967 | 0.960 | 0.9644 | 0.9440 |
| 20 | 0.9345 | 0.934 | 0.9206 | 0.9084 | 0.8895 |
| 30 | 0.9058 | 0.902 | 0.8831 | 0.8625 | 0.834 |
| 40 | 0.8751 | 0.8682 | 0.8435 | 0.8168 | 0.7786 |
| 50 | 0.8512 | 0.8250 | 0.8042 | 0.7708 | 0.724 |
| 60 | 0.8220 | 0.8020 | 0.7655 | 0.7250 | 0.6636 |
| Slope | -.00281 | -.00334 | -.00394 | -0.00461 | -0.00545 |
| Corr. coeft. | 0.9974 | 0.9970 | 0.9992 | 0.9987 | 0.9987 |

## Table 3.8.3(b)

### Effect of temperature on the rate of oxidation of p-chloro benzaldehyde in aq. dioxane in presence of ACD

[Substrate] = 1.0 x $10^{-2}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$
[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ Solvent = 20% aq. dioxane
[ACD] = 2.05 x $10^{-3}$ mol $dm^{-3}$

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9576 | 0.944 | 0.9111 | 0.8865 | 0.8750 |
| 20 | 0.9150 | 0.8895 | 0.8420 | 0.8027 | 0.7708 |
| 30 | 0.8726 | 0.834 | 0.7745 | 0.7170 | 0.6656 |
| 40 | 0.8280 | 0.7786 | 0.7075 | 0.6305 | 0.5625 |
| 50 | 0.7902 | 0.724 | 0.6384 | 0.5498 | 0.4600 |
| 60 | 0.746 | 0.6636 | 0.5682 | 0.4650 | 0.3520 |
| Slope | -.00423 | -0.00535 | -.00677 | -0.00843 | -0.001065 |
| Corr. coeft. | 0.9987 | 0.9996 | 0.9987 | 0.9994 | 0.9990 |

## Table 3.8.3(c)

## Effect of temperature on the rate of oxidation of p-bromo benzaldehyde in aq. dioxane in presence of ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. dioxane
[ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 10 | 0.9444 | 0.9412 | 0.9003 | 0.9052 | 0.8875 |
| 20 | 0.8949 | 0.8778 | 0.8195 | 0.8094 | 0.769 |
| 30 | 0.8460 | 0.8172 | 0.7404 | 0.740 | 0.6500 |
| 40 | 0.7975 | 0.7558 | 0.6627 | 0.6175 | 0.542 |
| 50 | 0.7508 | 0.6942 | 0.5840 | 0.5207 | 0.4010 |
| 60 | 0.7006 | 0.6415 | 0.5042 | 0.4308 | 0.3016 |
| Slope | -0.00482 | -.00614 | -.00787 | -0.00979 | -0.01233 |
| Corr. coeft. | 0.9980 | 0.9996 | 0.9992 | 0.9988 | 0.9964 |

## Table 3.8.3(d)

## Effect of temperature on the rate of oxidation of p-nitro benzaldehyde in aq. dioxane catalysed by ACD

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. dioxane
[ACD] = $2.05 \times 10^{-3}$ mol dm$^{-3}$

| Temperature | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | $4 + \log[OCl^-]$ | | | | |
| 5 | 0.9242 | 0.900 | 0.8990 | 0.8512 | 0.8260 |
| 10 | 0.8603 | 0.814 | 0.794 | 0.7118 | 0.6495 |
| 15 | 0.7888 | 0.725 | 0.688 | 0.5692 | 0.5198 |
| 20 | 0.7245 | 0.625 | 0.570 | 0.4310 | 0.3006 |
| 25 | 0.6605 | 0.546 | 0.475 | 0.2902 | 0.1560 |
| 30 | 0.5952 | 0.4675 | 0.3575 | 0.1828 | - |
| Slope | -0.01335 | -0.01703 | -0.02196 | -0.0276 | -0.03454 |
| Corr. coeft. | 0.9940 | 0.9992 | 0.9982 | 0.9995 | 0.9990 |

### Table 3.9.1

### Effect of [substrate] on the rate of oxidation of benzaldehyde in aq. acetonitrile medium

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ T = 303K

$\mu$ = 0.2 mol $dm^{-3}$ Solvent = 20% aq. dioxane

| $10^2$[substrate] mol $dm^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9754 | 0.959 | 0.9444 | 0.937 | 0.9243 |
| 20 | 0.9566 | 0.9294 | 0.9057 | 0.8893 | 0.8692 |
| 30 | 0.937 | 0.903 | 0.8663 | 0.842 | 0.8129 |
| 40 | 0.919 | 0.875 | 0.8293 | 0.7958 | 0.7558 |
| 50 | 0.9003 | 0.8482 | 0.7923 | 0.7481 | 0.6989 |
| 60 | 0.8803 | 0.8095 | 0.7481 | 0.6989 | 0.6483 |
| Slope | -.00189 | -0.00277 | -0.00388 | -0.00479 | -0.00557 |
| Corr. coeft. | 0.9997 | 0.9920 | 0.9905 | 0.9982 | 0.9966 |

### Table 3.9.2

### Effect of polarity of the medium on the rate of oxidation of benzaldehyde in aq. acetonitrile medium

[Substrate] = 1.0 x $10^{-3}$ mol $dm^{-3}$ T = 303K

[NaOCl] = 1.0 x $10^{-3}$ mol $dm^{-3}$ $\mu$ = 0.2 mol $dm^{-3}$

| % of Acetonitrile | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| Time (min) | 4 + log $[OCl^-]$ | | | | |
| 10 | 0.9754 | 0.9661 | 0.9319 | 0.9242 | 0.9084 |
| 20 | 0.9566 | 0.937 | 0.8920 | 0.8779 | 0.8512 |
| 30 | 0.937 | 0.9084 | 0.8543 | 0.8293 | 0.7923 |
| 40 | 0.919 | 0.8803 | 0.8162 | 0.7817 | 0.7363 |
| 50 | 0.9003 | 0.8512 | 0.7781 | 0.7363 | 0.6767 |
| 60 | 0.8808 | 0.8260 | 0.7403 | 0.6902 | 0.6211 |
| Slope | -.00189 | -0.00282 | -0.00382 | -0.00469 | -0.00576 |
| Corr. coeft. | 0.9997 | 0.9992 | 0.9984 | 0.9970 | 0.9988 |

## Table 3.9.3

## Effect of temperature on the oxidation of benzaldehyde in aq. acetonitrile medium

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ $\mu = 0.2$ mol dm$^{-3}$
[NaOCl] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Solvent = 20% aq. acetonitrile

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 4 + log [OCl$^-$] | | | | |
| 10 | 0.9754 | 0.9708 | 0.9614 | 0.959 | 0.9542 |
| 20 | 0.9566 | 0.9493 | 0.9345 | 0.9242 | 0.9138 |
| 30 | 0.937 | 0.9268 | 0.9058 | 0.892 | 0.8750 |
| 40 | 0.919 | 0.9031 | 0.8808 | 0.8603 | 0.8356 |
| 50 | 0.9003 | 0.8808 | 0.8543 | 0.826 | 0.7958 |
| 60 | 0.8808 | 0.826 | 0.826 | 0.7958 | 0.7555 |
| Slope | -.00189 | -0.00223 | -0.00263 | -0.00326 | -0.00396 |
| Corr. coeft. | 0.9997 | 0.9990 | 0.9988 | 0.9960 | 0.9920 |

## Table 3.10.2

## Effect of [PhCHO] on the rate of oxidation of benzaldehyde in benzene medium

[$Q^+ OCl^-$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ Temperature =303K
PT Catalyst -TBAB

| $10^2$ [PhCHO] moldm$^{-3}$ | 1.0 | 1.5 | 2.0 | 2.5 |
|---|---|---|---|---|
| Time (Min.) | 1 + log (Absorbance) | | | |
| 10 | 0.8149 | 0.800 | 0.7824 | 0.7693 |
| 20 | 0.7853 | 0.752 | 0.7201 | 0.6919 |
| 30 | 0.7520 | 0.7075 | 0.6551 | 0.6148 |
| 40 | 0.7201 | 0.6570 | 0.5932 | 0.5353 |
| 50 | 0.7050 | 0.6096 | 0.5301 | 0.4579 |
| 60 | 0.6599 | 0.5658 | 0.4712 | 0.3838 |
| Slope by regression Analysis | -0.00299 | -0.00471 | -0.00625 | -.00774 |
| Corr. Coeft. | 0.9950 | 0.9998 | 0.9999 | 0.9999 |
| $10^4 k_{obs} s^{-1}$ | 1.15 | 1.81 | 2.40 | 2.97 |

### Table 3.10.3.

### Effect of substituents on the rate of oxidation of benzaldehyde in benzene

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ Temperature = 303K
[$Q^+ OCl^-$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$ PT Catalyt = TBAB

| Substrate | PMB | PhCHO | PCB | PBB | PNB |
|---|---|---|---|---|---|
| Time (min) | 1 + log (Absorbance) | | | | |
| 10 | 0.8195 | 0.8149 | 0.848 | 0.7902 | 0.7561 |
| 20 | 0.7895 | 0.7853 | 0.7626 | 0.7395 | 0.6674 |
| 30 | 0.7723 | 0.7520 | 0.7201 | 0.6972 | 0.5797 |
| 40 | 0.7497 | 0.7201 | 0.6794 | 0.6512 | 0.4927 |
| 50 | 0.7218 | 0.7050 | 0.6394 | 0.6232 | 0.4048 |
| 60 | 0.7024 | 0.6599 | 0.6031 | 0.5611 | 0.3180 |
| Slope by regr. analysis | -.00232 | -0.00299 | -0.00405 | -0.00440 | -0.00877 |
| Corr. Coeff. | 0.9978 | 0.9950 | 0.9996 | 0.9967 | 0.9999 |
| $10^4 k_{obs}$ s$^{-1}$ | 0.89 | 1.15 | 1.55 | 1.69 | 3.37 |

### Table 3.10.4

### Effect of temperature on the rate of oxidation of benzaldehyde in benzene medium

[PhCHO] = $1.0 \times 10^{-2}$ mol dm$^{-3}$ PT Catalyst = TBAB
[$Q^+ OCl^-$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$

| Temperature (K) | 303 | 306 | 309 | 312 | 315 |
|---|---|---|---|---|---|
| Time (min) | 1 + log (Absorbance) | | | | |
| 10 | 0.8149 | 0.8122 | 0.8021 | 0.7993 | 0.7875 |
| 20 | 0.7853 | 0.7774 | 0.7611 | 0.7520 | 0.7348 |
| 30 | 0.7520 | 0.7395 | 0.7193 | 0.7050 | 0.6794 |
| 40 | 0.7210 | 0.7092 | 0.6794 | 0.6599 | 0.6324 |
| 50 | 0.7050 | 0.6674 | 0.6384 | 0.6095 | 0.5775 |
| 60 | 0.6599 | 0.6324 | 0.5977 | 0.5670 | 0.5263 |
| Slope by regr. analysis | -.00299 | -0.00360 | -0.00409 | -0.00467 | -0.00521 |
| Corr. Coeff. | 0.9950 | 0.9994 | 0.9999 | 0.9998 | 0.9998 |
| $10^4 k_{obs}$ s$^{-1}$ | 1.15 | 1.38 | 1.57 | 1.79 | 2.00 |