KINETIC STUDIES ON THE OXIDATION OF SECONDARY ALCOHOLS UNDER PHASE TRANSFER CATALYSIS

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By

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CERTIFICATE

The thesis presented herewith embodies the observations on **Kinetic Studies on the Oxidation of Secondary Alcohols under Phase Transfer Catalysis**. This is an authentic record of the research work carried out by **Zuhara M.** 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.

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DECLARATION

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

M Zuhara

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Zuhara, M.

PREFACE

This thesis reports in four chapters the results of the investigation carried out independently by the author on the kinetic studies on the oxidation of secondary alcohols under phase transfer catalysis.

The first chapter gives an introduction to the principles and theories of phase transfer catalysis. An exhaustive review of the kinetics of oxidation of alcohols both in aqueous and organic media using phase transfer catalysts are included in chapter two.

Chapter three includes the experimental part of the entire work. It deals with the materials and methods employed for the kinetic investigations.

The last chapter which is the core of this thesis includes results and discussion of the work done. Mechanism and rate laws on the oxidation of the 1-phenyl ethanol and its para substituted derivatives-p-chloromethyl and methoxy derivatives – using both the methods have been discussed separately. Finally a conclusion of the work is given at the last of this chapter. This is followed by summary, references and appendix of kinetic data.

CONTENTS

LIST OF ABBREVIATIONS

BH	:	Benzhydrol
CH	:	Cyclohexanol
HOAc	:	Acetic acid
HMPT	:	Hexamethylene phosphoric triamide
PCPE	:	p-chloro-1-phenyl ethanol
PE	:	1-phenylethanol
PMEOPE	:	p-methoxy 1-phenyl ethanol
PMEPE	:	p-methyl 1-phenyl ethanol
PNPE	:	p-nitro-1-phenyl ethanol
PT	:	Phase Transfer
PTC	:	Phase Transfer Catalysis
Q^+	:	Quternary ammonium (phosphonium) cation
Q^+HCrO_4	:	Quaternary ammonium/ phosphonium monochromate
TBAB	:	Tetrabutyl ammonium bromide
TBPB	:	Tetrabutyl phosphonium bromide

Chapter 1

Introduction

1.1 PHASE TRANSFER CATALYSIS

Phase transfer catalysis permits reaction between phase transferred anionic reactant entities and organic water insoluble substrates in solvents of low polarity usually with enhanced rates. The basic function of the catalyst is to transfer the reactant anions into the organic medium in the form of ion pairs. The cationic moiety of ion pair can be a quaternary ammonium ion or phosphonium ion. In aprotic solvents these ion pairs are virtually unsolvated and unshielded and hence are very reactive.

Before introducing phase transfer technique the reaction between ionic compounds and water insoluble organic compounds were carried out using polar or dipolar organic solvents that dissolve both ionic reactant and the organic substrates. The use of dipolar aprotic solvents like dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), acetonitriles etc. are also not advisable as they are very costly and usually toxic in nature. Moreover it is quite difficult to keep such solvents in anhydrous state and difficult to recover.

Phase transfer catalysis is a relatively new field of chemistry. The origin of the phenomenon can be traced to the pioneering work of Stark and Makosza. The foundation for PTC was laid in the mid sixties by M. Makosza and E.M. Stark.[1]

However Bandstrom used the name "extractive alkylation" from a physicochemical analytical point of view based on alkylation reaction in a two phase mixture in the presence of molar amounts of the phase transfer agent. The term "Phase transfer catalysis" as coined by Starks was first used for patents in 1968. Recognition of this new technique as catalysis appeared as Stark's paper published in the Journal of the American Chemical Society in 1971.[2] Quite a large number of organic synthesis especially in pharmaceutical field have been carried out by this technique. However kinetic analysis of such reactions remained unexplored. Usually the phase transferred reagent brings in reaction at faster rate, the term catalysis is relevant.

1.2. REQUIREMENTS OF PHASE TRANSFER CATALYSTS

There are two basic requirements for a PT catalyst. One is that it must be able to transfer one of the reactants from its normal phase into the normal phase of the other viz., the substrate. The second criterion is that the transferred reagent in the new phase be available in a highly reactive form.

The phase transfer technique is usually employed for synthesis or for reaction in a non-polar medium using an inorganic anionic reactant. Some other factors in respect of the catalyst are also to be taken into consideration.

The catalyst must be cationic and must have enough organic structure so that it can remain in the non-polar medium. The effective cation-anion

bonding in the pair must be loose enough to allow enhanced anion reactivity. The stability of the ion pair under the reaction conditions, the ease of preparation, cost, ease of removal or recovery, selectivity etc. in catalytic activity are to be taken into account.

Several types of compounds are found useful as phase transfer catalysts for anion transfer from inorganic phase into organic phase. They are quaternary salts, macrocyclic ethers, N alkyl phosphoramides, etc. Crown ethers[3] are classic examples of phase transfer catalysts. During the 1960's quaternary ammonium or phosphonium salts[4] have been used as very effective catalysts. Polyethylene glycols known as "poor chemists crown" are also useful to some extent on these lines.

1.2.A. Quaternary salts

Quaternary salts (halides, phosphates, sulphides) such as those of Quaternary ammonium, phosphonium, arsonium, cations have been used as phase transfer catalysts. However in practice, only a limited number of ammonium and phosphonium salts are widely being used. This is based on the factors mentioned above in the selection of quaternary salts for effective anion transfer.

The simple notation $R_4N^+X^-$ for quaternary ammonium salts conceal a wide range of structures possible in PT catalysts. The different structural

features of the anionic moiety of the quaternary salts have to be taken into account.

a. The combination of the R groups

The primary requirement of the R groups is that they collectively should have sufficient organic structure for transfer into the organic phase. The required organic structure depends on the anion to the transferred, the polarity of the organic phase, the concentration of the inorganic reagent in aqueous phase and sometimes the presence of solvating organic compounds. It has been found that tetramethyl and tetraethyl ammonium salts do not have sufficient oleophilicity to function well as anion transfer catalysts. Such compounds are usually active in the interface and can act as micelles. Tetrabutyl ammonium slats are stable enough and are sufficiently partitioned into the organic phase. They act as good PTC catalysts for many reactions. According to A.W. Harriot and D. Picker[5] the larger R group with almost symmetric structures are the most effective both in anion transfer and reactivity. The cheapest catalyst available is "tricapryl methyl ammonium chloride sold under the name "Aliquot 336." For anions such as OH^- which are not highly nucleophilic, benzyl, alkyl and methyl substituted quaternary salts function well as phase transfer catalysts.

b. The central onium atoms

Quaternary ammonium and phosphonium salts have been successfully used as PT catalysts. Ammonium salts are more widely available and less expensive. Quaternary phosphonium salts tend to be more active catalysts and may easily be prepared if the trialkyl phosphine is available. Phosphonium salts are more thermally stable than the corresponding ammonium salts under otherwise identical conditions. The phosphonium chloride, bromide and cyanide salts are reasonably stable upto 150-170°C where as ammonium salts loose their activity rather rapidly at temperatures greater than about 110-120°C. This difference in thermal stability is not significant for application in lab but significant in an industrial scale. Phosphonium cations are exceedingly sensitive to hydroxide ion[6,7] and they undergo a reaction of the type.

$$R_4P^+OH \rightarrow R_3PO + RH$$

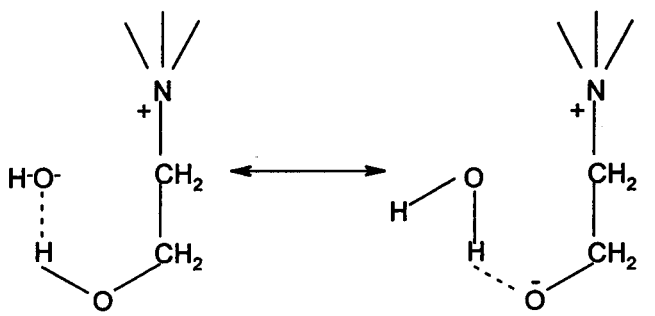
Since R_3PO is not reconvertible to $R_4P^+X^-$ under these conditions catalystic activity is irreversibly lost. Hence with strongly basic solution R_4N^+ catalysts are generally preferred over R_4P^+ compounds.

c. Functional groups on the R groups

Only a few examples of the use as catalysts of quaternary salts having one or more R groups containing a functional group have been reported and

these have mostly been concerned with cations having a hydroxyl group on carbon atoms removed from quaternary nitrogen atoms. In this position the hydroxyl group is capable of intermolecular hydrogen bonding with the anion such as OH^- and BH_4^-. Thus they enhance the transfer of the anions from aqueous to organic phase than the corresponding salts without a hydroxyl group.[8-10]

In the case of hydroxide ion, not only does intramolecular solvation of OH^- improve catalytic activity, but also Zwitter ion formation can occur according to the equation.



Formation of Zwitler ion species probably accounts for this observed increase in thermal stability of β-hydroxyl- substituted quaternary cation in strongly basic systems.[11,12]

d. Different Anions with the given catalyst cation

The activity of the quaternary salt selected for use as a phase transfer catalyst may depend markedly on the anion originally present. The

quaternary salts are useful as PT catalysts only if the anion accompanying the catalyst is distributed in the organic phase to a much lesser extent than the anion to be reacted. Quaternary salts in the iodide form are commercially available or easily prepared. But iodide ion associates strongly with quaternary cation in organic media. Hence if OH^- transfer from aqueous to organic phase is desired and 100 moles of NaOH is present for each mole of $R_4N^+I^-$ catalyst present, then only about .002% of the catalyst will be in the active $R_4N^+OH^-$ form in the organic phase. Instead, if $R_4N^+Cl^-$ is used then 50% of the catalyst will be in the active $R_4N^+OH^-$ form in the organic phase. It is found that catalysts in the iodide form perform less actively than those of the chloride and bromide form in cyanide displacement reactions.[13]

e. Effect of polarity of organic phase

PTC reactions are usually carried out in aprotic solvents of low polarity like benzene, toluene, carbon tetrachloride, chloroform, methylene chloride, etc. It is found that the solubility and partitioning behaviour of the quaternary salts are markedly affected by slight changes in the nature of the organic phase. Chloroform and methylene chloride are excellent solvents even for such smaller quaternary salts with tetraethyl and tetrapropyl ammonium as cations. The most commonly used solvent is methylene chloride which is sufficiently polar to bring almost all tetrabutyl ammonium

salt into its solution. Its low boiling point 40°C allows it to be easily removed after the reaction and is inert.

1.2.B. Crown ethers[14-16]

Crown ethers and related macrocyclic polydentate ligands, have become available as simple and efficient means for solubilizing metal salts in non polar and dipolar aprotic solvents where the solvation of anionic part is minimised. Because of the open structure crown ethers are even capable of abstracting cation from a crystalline solid. Hence they are used to carry out reactions with solid salts also.

A general comparison of quaternary salts and macrocyclic ethers as phase transfer catalysts[17] shows that ethers have high activity depending on structure. They are stable, easily recovered, can be prepared easily and available commercially. Water is not required for the reaction and presence of water sometimes inhibits reaction and have high cost.

1.3. PRINCIPLE AND MECHANISM OF PHASE TRANSFER CATALYSIS

As the hydrated anion is thermodynamically stable, the anion of inorganic salts are generally having a tendency to remain in the aqueous phase than in the organic phase. The transfer of anions takes place if the cation of phase transfer catalyst is more solvated in organic phase than the anion in the

aqueous phase. The highly effective phase transfer catalyst is one which can form a cation-anion pair that can be strongly partitioned into the organic phase.

The mechanism of ion transfer by quaternary onium salt can be summarised as follows. The reaction vessel contains two immiscible phases, one aqueous and the other organic. The aqueous phase contains the hydrophilic salt, the anion of which function as the nucleophile and the organic phase contains the water insoluble organic substrates. No reaction is observed in the absence of interfacial phenomena.[18] If a small amount of quaternary ammonium salt is added containing a lipophilic cation, rapid reaction takes place. The cation of the catalyst being soluble in both phases exchanges its anion with the anion of the salt in aqueous phase. The equilibrium state for the exchange can be represented as

$$Q^+X^-_{aq} + M^+Nu_{aq} \text{ ==== } Q^+Nu^-_{aq} + M^+X^-_{aq} \qquad 1$$

(Q^+ stands for quaternary salt)

The ion pair Q^+Nu^- is transferred into the organic phase. The phase transfer equilibrium thus formed can be represented as

$$Q^+Nu_{aq} \text{ ==== } Q^+Nu_{org} \qquad 2$$

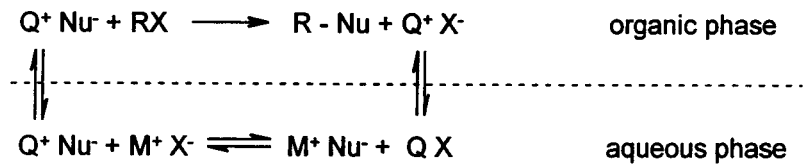
The nucleophile in the organic medium undergoes actual reaction with the organic substrate present in that phase [Eq.(3)]. In the case of

nucleophilic substitution reaction the Q^+ would ultimately be ion paired with the nucleofuge, thus generating Q^+X^- which is subjected to the further equilibrium as in(4).

$$Q^+ + Nu^-_{org} + RX_{org} \rightarrow Q^+X^- + RNu_{org} \qquad 3$$

$$Q^+X^-_{(org)} \equiv\equiv Q^+X^-_{(aq)} \qquad 4$$

Stark has offered a classic diagram of the phase transfer catalytic cycle.



Starks 'phase transfer catalytic cycle'

It is not necessary that ion pair Q^+X^- generated in the organic phase be identical to the ion pair originally added as the PT catalyst. It is only necessary that a lypophilic cation Q^+ must be present in solution and whatever be the X^-, it must be exchangeable with Nu.

The basic requirements of a PT catalyst are:

1. It must be able to transfer one of the reactants from its normal phase into the normal phase of the other reactant.

2. The transferred reagent should be highly reactive.

To be highly effective as phase transfer catalyst, the catalyst cation and the reactant anion forming the 'ion-pair' need be strongly partitioned into the organic phase. The catalyst must be associated with a cation having much 'organic structure' so that organic phase solvation is stronger than aqueous phase solvation of the anion. There are so many factors which affect the distribution of catalyst cation between aqueous and organic phases.

1. Organic structure of the catalyst cation

$$\text{The distribution ration } \alpha = \frac{\text{QX in the organic phase}}{\text{QX in the aqueous phase}}$$

is found to increase by a factor of 2 for each CH_2 group added in a given homologous series.[18] In general, the distribution ratios of this type are correlated by equation of the form.

$$\log \alpha = 0.5\ n + \text{constant}$$

where the constant is the value of log α for the first member of a given homologous series, with a particular organic phase-water mixture and at a given temperature.[20-22]

The organic structure of the catalyst cation not only affects the ability to transport an anion from aqueous to organic phase but also strongly affects the rate of organic phase reactions.

2. The anion associated with the catalyst cation

The kind of anion associated with the catalyst cation has an enormous influence on the extent to which a given cation - anion pair is extracted from the aqueous to organic phase.[23-26] Two characteristics of the anion influence its tendency to decrease or increase the ability of the catalyst cation transfer. Firstly the anion are hydrated to different extent depending on the charge to volume ratio of the anion and the more the anion hydrated, the more difficult it will be to transfer. Secondly the organic structure of the anion also influence the partitioning into the organic phase.

3. Polarity of the organic phase

The partitioning of quaternary salts depends on the polarity of the organic phase. Chloroform and methylene chloride are excellent solvents even for tetraethyl and tetrapropyl ammonium cations. By far the most commonly used solvent is CH_2Cl_2 which is sufficiently polar to bring almost all tetra butyl ammonium salts into its solution. Its low boiling point (40°C) allows it to be easily removed and it is inert in most, but not all reactions.

4. Concentration of inorganic salt in the aqueous phase

Increasing concentration of inorganic salt in the aqueous phase tends to salt out organic salts, pushing them into the organic phase. Increasing the inorganic salt concentration reduces the amount of water available for anion

hydration resulting in easy transfer of anion into the organic phase. The best phase transfer catalysis conditions are realised when the aqueous phase is saturated with inorganic reagent.

Because one or more equilibria are coupled with one or more relatively slow reaction in phase transfer catalysis, the kinetics of these systems may become extremely complicated, although in practice most systems studied have been found to be relatively simple. Most of the work published has dealt with the kinetics of anion transfer displacement reactions in which anion exchange and transfer is rapid, the slow step being the displacement reactions.

A difficult problem in the kinetics of phase transfer catalysed reaction is to sort out the rate effect due to

(a) the nature and rate of the organic phase reaction.

(b) the structure, concentration and organic phase solubility of the catalyst and

(c) the equilibria and anion transfer mechanism for transfer of anions from aqueous to the organic phase.

Ugelstand and coworkers[27] have measured rates for the reaction of potassium and tetrabutyl ammonium phenoxide with 1-chlorobutane and 1-bromobutane in various solvents and mixtures. They concluded that the high reactivity of the quaternary salt resulted from its having a greater distance of

separation between cation and anion reduces cation anion interaction energy. Litvak and Shein[28] have shown that crown ether complexes of potassium phenoxide also undergo rapid displacement reaction in non polar organic solvents.

The new branch phase transfer technique is superior to the conventional methods in the following aspects.

1. Synthetically easier to work-up.
2. Mild conditions are needed.
3. Improved reaction rates are observed
4. Cost effective as anhydrous, aprotic solvents are not required.
5. Increased yield suppressing side reactions.

These advantages throw light on the future prospects of phase transfer catalysed reaction especially in the kinetic studies of many organic compounds. Organophilicity is the main factor which determines the effectiveness of the phase transfer catalyst.

The phase transfer techniques has been found to be applicable to a wide variety of reactions like nucleophilic substitutions,[2, 29-32] elimination,[33-36] carbene rections,[37-41] alklylation,[42-47] esterification,[48-52] etherification,[53-56] condensation,[57-60], addition,[61-63] polymerisation,[64-67] hydrolysis,[68-70] isomerisation,[71-73] reduction,[74-77] rearrngement,[78,79] and oxidations,[80-83] etc.

1.4.A. Phase transfer catalysed oxidation

Phase transfer catalysis has become a pervasive and widely accepted synthetic tool, not withstanding several limitations as its commercial exploitation. Various phase transfer catalysts, such as, quaternary onium salts, crown ethers and polyethylene glycols have been used for oxidation of alkyl and aralkyl halides and also of alcohol.

Oxidation of many organic compounds are reported to be carried out by a number of inorganic oxidising agents like bromate, tribromate,[80] periodate,[84] peroxide, dichromate,[85-90] chromate, hypochlorite,[91-92] permanganate,[92] chlorate,[94] ferricyanide,[95] etc. and mild oxides like osmium tetroxide and Ruthenium tetroxide.[88] Most of the work is carried out in aqueous medium. Only a limited number of kinetics are reported using phase transferred oxidising agents given above in organic media.

1.4.B. Phase transfer catalysed dichromate oxidation

Chromic acid is one of the most versatile of the available oxidising agents reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. There exists a need for new methods which are selective and effective under wild conditions especially for highly sensitive substances. The development of new Cr(VI) reagents for the oxidation of organic substrates continues to be a subject of interest. New procedures are thus emerging

involving "non aqueous" Cr(VI) reagents and anhydrous conditions are more conducive to complexation of substrates with Cr(VI) species.

Doyamoy Dey and Mahendra K. Mahante[81] reported the oxidation of benzyl alcohol and substituted benzyl alcohol using Quinolinium dichromate in dimethyl formamide. The product was benzaldehyde and substituted benzyaldehyde with no further oxidation under their experimental conditions.

These observations suggest that the phase transferred chromate and dichromate can act as a selective oxidant.

Various phase transfer catalysts such as quaternary onium salts, crown ethers and poly ethylene glycols have been used for the oxidation of halides and alcohols.

Cardilo *et al.*[97] have suggested the usefulness of chromate ion as a nucleophile for the crown ether catalysed oxidation of alkyl halide to aldehyde in hexamethylene phosphoric triamide (HMPT) where the reaction proceeds via SN_2 displacement of the halogen atom by chromate ion to form a chromate ester which further decompose to the corresponding carbonyl compound.

$$RCH_2X + K_2CrO_4 \xrightarrow[\text{crown ether}]{\text{HMPT}} RCH_2CrO_4K \longrightarrow RCHO$$

Gopalan and Subharayan[98] have, on the basis of kinetic study, proposed a mechanism for the oxidation of benzyl chloride using chromic acid in which the reaction was found to be first order in the concentration of each of benzyl chloride, oxidant and H^+. The mechanism involves rapid formation of a chromate ester which subsequently decomposes to give benzalldehyde and Cr(IV) species. The reaction was overall third order.

In another case the oxidation of alcohol is reported with stoichiometric quantity of dichromate in 3M aqueous sulphuric acid using tetrabutyl ammonium bisulfate as the phase transfer catalyst. They have suggested that the reaction proceed via disproportionation of chromate ester in which the proton catalysed disproportionation of Cr(VI) or Cr(IV) to Cr(VI) is important. Cr(VI) in aqueous solution exists as a pH dependent mixture of several species as given below.

$$CrO_4^{2-} \xrightarrow{H^+} HCrO_4^- \xrightarrow{H^+} H_2CrO_4$$

$$HCrO_4^- + HCrO_4^- \xrightarrow{-H_2O} Cr_2O_7^{2-} \xrightarrow{H^+} HCr_2O_7^-$$

All the above species are capable of forming ion pair with the PTC cation which was partitioned into the organic phase. However the different Cr(vi) species may not be equally active for alcohol oxidation. Indeed there is an evidence that the first step of oxidation of alcohol in the absence of PTC.

$$HCrO_4^- + ROH \longrightarrow ROCrO_3^- + H_2O$$

Chromate ester has a greater solubility in organic solvent than water.[99] Hence in the presence of PTC similar mechanism is suggested.

$$HCrO_4^- + Q^+ \longrightarrow Q^+ HCrO_4^- \text{ (in aq. phase)}$$

$$(Q^+HCrO_4^-)_{org} \xrightarrow{\text{org. solvent}} (Q^+HCrO_4^-)_{org}$$

$$(Q^+HCrO_4^-)_{org} + RCH_2OH \longrightarrow (RCH_2O\ CrO_3^-Q^+)_{org} + H_2O$$

$$(RCH_2OCrO_3^-\ Q^+)_{org} \longrightarrow RCHO + Cr(IV) + Q^+ + H^+$$

$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$$

The bracketed quantities denote ion pair.

A thorough and systematic study of the mechanism and kinetics of the oxidation of benzyl chloride by dichromate in L-L phase transfer catalysis has been provided to throw light on the course of reaction. The rate of reaction depends on the pH of the aqueous phase in view of the fact that chromium exists as dichromate, perchromate or chromate depending on pH. It was observed that $Q^+HCrO^-_4$ was the active species.

Chapter 2

Review and Scope

2.1. REVIEW OF THE PRESENT WORK

2.1.A. Kinetics of Oxidation of Secondary Carbinols in aqueous and non polar media

Kinetic studies on oxidation of secondary carbinols using phase transferred monochromate is quite interesting. The studies intended to be undertaken have selectivity of the oxidation process. More over the fact that the inorganic oxidant is transferred into non-polar solvents where it takes part in the reaction under homogeneous condition. A brief review of the oxidation studies relevant to the one undertaken are reviewed here. It may be mentioned, however, that such studies in non-polar media are quite a few.

There have been detailed investigation on the kinetics and mechanism of oxidation of alcohols using various inorganic agents such as permanganate, dichromate, hypochlorite, tribromides, bromate, Cr^{+4} ion etc. in the aqueous media and these are well documented in the chemical literature. Review of such investigations are not given in this chapter. But some cases involving PTC for oxidation in aqueous media are worth mentioning in this context.

The oxidation of aliphatic alcohols using tetrabutylammonium tribromide in aqueous acetic acid leads to the formation of the corresponding aldehydes. The reaction is first order with respect to the carbinol. However polymerisation sets in during the reaction.[80] Catalyst concentration had no effect on the rate. The oxidising species is reported as tribromide ion and rate

increased with increase in polarity of the solvent and a hydride ion transfer mechanism control the rate determining step.

Oxidation of benzyl and some ortho, para, and meta monosubstituted benzyl alcohols by benzyl trimethyl ammonium chlorobromate (BTMACB) in aqueous acetic acid were studied.[100] The corresponding benzaldehydes were formed as products. The reaction is first order each in BTMACB and alcohol concentrations. The reaction rate increases with increase in polarity of the medium.

A report on the kinetics and mechanism of the oxidation of carbinols in non polar medium appeared in 1978.[101] Banerji and Venketa Subrahmanian *et al.* reported the oxidation of alcohol by pyridinium chlorobromate in 1:1 (v/v) dichloromethane and nitro benzene solution. The reaction was found to be first order both in the respect to the PCC and alcohol. The oxidation of deuterated benzyl alcohol and ethanol showed the presence of substantial kinetic isotopic effects with respect to the alpha hydrogen. The cleavage of an α C–H bond controlled the rate determining step. It was suggested that the oxidation proceeded with hydride ion transfer either directly or via a chromate ester formation.

Nair *et* al.[83] studied the kinetics of oxidation of some aryl ethanols in benzene, toluene, carbon tetra chloride and dichloromethane using permanganate ion under phase transfer catalysis. The corresponding ketones

have been formed almost in quantitative yield. The reaction is first order each in the (oxidant) as well as the carbinol concentration. A unique substituent effect of enhancing the rate was observed by both electron donating and electron withdrawing groups. The Hammett plot resolve into two separate linear relations. Mechanism involving α CH bond cleavage subsequent to formation of permanganate ester has been proposed.

Dayamoy Day and Mahendra K. Mehanta reported the oxidation of benzyl alcohol and substituted benzyl alcohols in dimethyl formamide[81]. First order dependence both on the (alcohol) and Quinolinium dichromates has been observed. Electron releasing substituents accelerate the reaction where as withdrawing groups retard the reaction rate and rate data fitted with the Hammett relationship. The reaction constant ρ was -1.67 $\pm$ 0.08 at 313 K. The kinetic isotopic effect was 5.89 at 313 K. No induced polymerisation is observed. The experimental data is in accordance with the hydride ion transfer in the rate determining step.

Kinetics of oxidation of benzyl alcohol using potassium dichromate in non polar media under phase transfer catalysis was reported.[102] The reaction was found to be first order each in alcohol and chromate ion concentration. The oxidation is selective giving benzaldehyde as the only product with no indication of benzoic acid. No polymerisation reaction is observed to be

induced in the reaction. The energy of activation being a low value of 29 - 31 $KJmol^{-1}$.

Derek Pletcher[103] reported the PT catalysed oxidation of twelve primary alcohols and two secondary alcohols giving aldehydes and ketones respectively. The oxidation was carried out using potassium dichromate in presence of sulphuric acid and tetrabutyl ammonium sulphate to PTC. Methylene chloride was used as solvent, the rate constant was determined by GLC and NMR. In the absence of an alcohol, the methylene chloride phase becomes strongly orange yellow when shaken with acid dichromate and tetrabutyl ammonium bisulphate. Only alcohols are oxidised in the presence of tetrabutyl ammonium ion inferring the reaction between alcohol and dichromate in organic phase.

Robert and Hutchins[104] reported the resistance of solubilization of dichromate anion in typical organic solvents using a wide variety of available crown ether, tetra alkyl ammonium and phosphonium salts. The only successful reagent was found to be Adogen (464) a liquid commercial mixture and methyl trialkyl ammonium chloride. Using this, fascile solubilization of potassium dichromate was carried out in several organic solvents including methylene chloride, chloroform, carbon tetrachloride and benzene. A 2:1 ratio of Adogen (464) to dichromate was used. The resulting orange solution was fairly stable at ambient temperature but slowly darkened after several

days. The oxidation utility of dichromate in benzene, orange benzene reveals it to be a mild, effective and selective in oxidation of alcohols to aldehydes and ketones. They observed that benzyl alcohol is converted into benzaldehyde within 15 hours giving a yield of 82% and 1 phenyl ethanol and 2 octanols to corresponding ketones within 15 to 24 hours respectively with a yield of 80% and 33% respectively.

A new and highly efficient combination for the conversion of secondary alcohols to ketones was reported.[105] The reagent consisted of peroxy acetic acid in the presence of catalytic amounts of 2,4-dimethyl pentano-2,4-diol cyclic chromate using a solvent mixture of carbon tetrachloride and methylene chloride. It was observed that longer reaction time was required for hindered secondary alcohols. Oxidation of borneol to camphor, which suggested that sterically screened hydroxyls form the chromate outer only slowly and that the chromate ester formation may be the rate determining step in the overall reaction.

Tabushi and Koga[106] have investigated a synergic action of the electron transfer catalyst in the presence of a common PT catalyst, trioctyl methyl ammonium chloride to promote the oxidation of alcohols. Results revealed that the direct oxidation with sodium hypochlorite was very slow, but in the presence of catalysts the oxidation was very fast.

Ishi and Kishi[107] studied the oxidation of alkyl and aryl substituted hydroquinones with aqueous sodium hypochorite in various organic solvents in the presence of catalytic amounts of tetrabutyl ammonium hydrogen sulphate. For the oxidation of mono-substituted hydroquinones, dichloro methane and chloroform were found to be suitable solvents compared to ethyl acetate and benzene.

A rapid and selective method for the oxidation of primary alcohols to aldehydes and polynuclear aromatic hydrocarbons to quinones based on phase transfer catalysis was discribed.[108] Several papers[93,102,103,109-111] described methods which employ Cr(VI) species as the oxidising agent for the oxidation of primary alcohol and reported effects of variations in the reaction conditions and showed that lower acid concentrations may be employed with advantage.

Mahendra K. Mahanta and Kalyan K. Banerji reported[112] the synthetic mechanistic studies of the oxidation of alcohol using complexed Cr(VI) compounds. So many complexed Cr(VI) compounds like bipyridinium dichromate, pyridinium fluorochromate, naphthyridinium chlorochromate were synthesised and characterised.[113] They were found to be selective oxidants for alcohols giving corresponding carbonyl compounds .

Halosilanes[114], chromium tetroxide and imidazolinium dichromate[115] were found to be mild selective reagents for the oxidation of alcohols to the corresponding carbonyl compounds.

Jaya Gosani and Pradeep, K. Shama reported[116] the use of tetrabutyl ammonium tribromide for the kinetic studies of oxidation of aliphatic secondary alcohols, 1-phenyl ethanols and benzhydrol in aqueous acetic acid medium. The oxidation results in the formation of corresponding ketones. Reactions are first order with respect to TBATB and alcohol. No polymerisation reaction is induced. No significant isokinetic relationship between entropy and enthalpy of oxidation. The mechanism involving transfer of a hydride ion from alcohol to oxidant is suggested as the rate determining step. The observed negative entropy of activation is in confirmity with the phenomenon.

Shweta Vyas & Pradeep K. Sharma reported[117] the kinetics of oxidation of some diols and their monoethers by quinolinium bromochromate (QBC) in dimethyl sulphoxide. The main product of oxidation is corresponding hydroxy carbonyl compound. The reaction was first order each in QBC and the diods. Gelband *et al.*[118] have demonstrated the use of onium salts as PT catalysts to get complex chromate salts which is soluble in aprotic organic solvents such as dichloromethane. This complex chromate was used for the oxidation of several alcohols.

Complex of chromium and 3,5-dimethyl pyrazole have been employed for the oxidation of alcohol.[109] This was prompted by the fact that a complex[119] is involved in the reaction and that formation of ester complex

proceeds to oxidation involving a cyclic intramolecular intermediate as the transition state.

Kalyan K Banerji *et al.*[120] reported the oxidation of benzyl alcohol and some ortho, meta and para mono substituted ones by quinolinium fluorochromate in dimethyl sulphoxide leading to the formation corresponding benzaldehyde. A few reports[121-123] on the oxidation by QFC have already been emanated.

Kinetic and mechanism of oxidation of secondary alcohols by bis-(2,2'-bipyridyl) copper(II) permanganate in aqueous acetic acid medium was reported.[124] The oxidation lead to the corresponding ketones. The reaction was found to be first order with respect to BBCP and alcohol. The reaction rate increases with increase in concentration of H^+ ions. The oxidation of benzhydrol exhibited substantial kinetic isotopic effect (KH/KD = 5.34) with increase in the amount of acetic acid in the solvent mixture of acetic acid and water, the rate increases.

Alexander Mckillop and Lester S. Mills[95] reported the oxidation of aryl methanols with $KMnO_4$ using Trans (2-(2-methoxyethoxy) ethyl anion (TDA-1) as phase transfer catalyst. The product benzaldehyde is obtained in excellent yield. The catalyst TDA-1 is introduced as a cheap, stable, non toxic and non-cation specific phase transfer catalyst.

J. Mohammedpoor Baltork *et al.* reported[125] oxidation of alcohols to carboxyl compounds, thiols to disulfides and aromatic amines to azo compounds, efficiently by n-butyl triphenyl phosphorium dichromate. Primary and secondary benzylic and saturated alcohols were converted to their corresponding aldehydes and ketones in high yields. Further oxidation to their carboxylic acids were not observed.

Kinetics of oxidation of aliphatic aldehydes by quaternary ammonium permanganate in dichloromethane was reported with special reference to the formation of colloidal manganese(IV).[126]

Primary amines are oxidised by permanganate under PTC to corresponding azo compounds in good yield.[127]

Phase transfer catalysed oxidation of organic substrate by triphenyl methyl arsonium permanganate in chloroform solution was demonstrated by Gibson and Hosking.[84] Permanganate ion transferred into the organic layer oxidises olefinic alcohols, nitroalkanes and nitriles. It does not oxidise 1-butanol, benzene, toluene, ethyl acetate, dimethyl ether, acetone or 4-heptanone.

Durst have solubilised potassium permanganate in methylene chloride using 18-crown-6 and has shown that substituted catechols have been converted to the corresponding O-quinones in high yield.[128]

Permanganate solubilised in methylene chloride with the aid of TDA-1 as phase transfer agent, oxidises benzyl alcohol to benzaldehyde.[129]

Kinetics and mechanism of the oxidation of unsaturated carboxylic acids by methyl tributyl ammonium permanganate in methylene chloride solution has been investigated.[130] The involvement of a free radical is indicated during the oxidation of acetic and methacrylic acid due to polymer formation.

Freeman and Koppus[131] investigated the use of cetyl trimethyl ammonium permanganate (CTAP) for the oxidation of cycloalkanes in dichloremethane. The order of reaction is unity with respect to permanganate ion concentration as well as cyclo alkane concentration.

Holba *et al.* investigated the oxidation of higher aliphatic alcohols with tetra butyl ammonium permanganate. The oxidation proceeds with involvement of autocatalysis.

Nair *et al.* studied the kinetics of the oxidation benzaldehyde, 1-phenyl ethanol, and benzylalcohols using phase transferred permanganate[83] monochromate[102] hypochloride, etc in non polar media. Tricapryl methyl ammonium chloride and tetrabutyl ammonium bromide were used as phase transfer catalysts. The reaction showed first order dependence both on [substrate] and [permanganate ion].

Lee and Freedmann[134] reported that hypochlorite anion can be transferred into organic solvents by quaternary cations for the oxidation of alcohols and amines. In the absence of a catalyst no reaction occurs. Benzene, carbon tetrachloride and methylene chloride function well as solvents. Ethyl acetate appears to be the solvent of choice for these reactions.

Oxidation of benzyl alcohol by the phase transferred hypochlorite ion in presence of tetrabutyl ammonium chloride as PT catalyst was studied[135]. The results showed that the rate of oxidation of benzyl alcohol in immiscible aqueous/dichloromethane system was controlled stirring rate at speeds of 500 rpm. The results showed first order dependence both on oxidant and benzyl alcohol.

Oxidation of benzyl alcohol using hypochlorite under phase transfer catalysis was investigated in a heterogeneous liquid-liquid system.[136] Cetyl trimethyl ammonium bromide and toluene were chosen as the best catalyst and solvent respectively. The rate was found to be proportional to the concentration of cetyl trimethyl ammonium hypochlorite in organic phase.

A new triphasic solid-solid-liquid catalytic system for the inexpensive and selective oxidation of secondary alcohols by calcium hypochlorite is reported.[137] In contrast with the results under homogeneous phase, steric and geometry factors were found to effect rate constants. The catalyst is

recovered without any regeneration process and it could be used several times with no loss of activity.

Oxidation of benzhydrol to benzophenone using bleach as an oxidant in ethyl acetate solvent by tetrabutyl ammonium hydrogen sulphate as PT catalyst was employed.[138]

Aromatic aldehydes were oxidised to carboxylic acid in high yield using sodium hypochlorite as oxidant in a PTC system.[139] The medium was strongly influenced by the pH of the aqueous phase with a maximum reaction rate at pH 9-11. The maxima are attributed to co-extraction of hypochlorite anion and hypochloric acid into the organic phase, the latter increasing the reaction rate.

The kinetics of anodic oxidation of benzyl alcohol in the two phase systems involving both the redox indicator OCI/CI and a PT catalyst were studied.[140]

As the strong oxidant RuO_4 is soluble in organic solvents, a catalyst system consisting of hypochlorite, a phase transfer catalyst and $RuCl_3$ or RuO_3 can be developed. It was found to oxidise various ortho, para substituted toluene derivatives in methylene chloride at room temperature.[141] Similarly alkenes are oxidised to yield carboxylic acids.[142]

In the presence of quaternary ammonium PT agents copper salts catalyse the selective oxidative dehydrogenation of alcohols and hydroxy acids by tert-butyl hydroperoxide in aqueous organic two phase system.[143]

Use of catalysts derived from heavy metals together with a PT catalyst for the oxidation of several typical olefin with H_2O_2 has been described in patents[144,145] with cyclohexene, an epoxide of cyclohexane and cyclohexane diol were formed exclusively with OsO_4, MoO_3 or H_2WO_4

The selective oxidation of primary alcohols to carboxylic acid (60 to 70% selectivity) secondary alcohols to ketones (100% selectivity) primary benzylic alcohols to aldehydes (95-100% selectivity) and allylic alcohols to ketones (80% selectivity) was performed in a H_2O_2-$RuCl_3 3H_2O$ PT catalyst system[146] at a high substrate - $RuCl_3$ ratio. It has been found that PT catalyst has the dual role of extraction of $RuCl_3$ and H_2O_2 with the organic phase and also to protect the metallic catalyst against reduction.

Quaternary ammonium salts assist the extraction of both hydrogen peroxide and metal salts like ruthenium or palladium chloride from the aqueous to the non-aqueous component of a two-phase system. The system has been used for the oxidation of styrene[147] with H_2O_2 in H_2O-dichloromethane containing both $RuCl_3$ and a PT catalyst to give mainly PhCHO. Similar oxidation of styrene in the presence of $PdCl_2$ gave PhCOMe.

A phase transfer procedure for the oxidation of terminal alkynes under mild conditions was reported.[148] The catalytic system involves dilute H_2O_2, Na_2MO_4 salt (M=Mo, W) and Hg $(OAc)_2$. In the absence of mercuric derivative no oxidation takes place. By changing the pH of the aqueous phase and nature of the PT catalyst either cationic or neutral as well as metal (Mo or W) carboxylic acids or 2-keto aldehydes may be selectively obtained in good yields.

2.1.B. Dichromate oxidation

It was showed that a coloured chromate derivative can be extracted into non polar organic solvents in presence of phase transfer catalysis[84,149] from an aqueous acidic solution of dichromate. The resulting yellow-orange liquid is found to be a selective oxidant for alcohols giving the corresponding adehyde.

Kinetic oxidation of lactic acid, mandelic acid and its nine substituted derivatives by butyl triphenyl phosphorium dichromate in dimethyl sulphoxide is reported.[150]

A method for the oxidation of alcohols by a complex of chromium oxide and 3,5-dimethyl pyrazole in CH_2Cl_2 at room temperature is reported.[109]

A rapid and selective method for the oxidation of primary alcohols to aldehydes and polynuclear hydrocarbon to quinone is described.[108] Substrate

in organic solvent is shaken with aqueous acidic dichromate and a phase transfer agent and the effect of the reaction condition on the selectivity and rate of reaction is discussed.

Interesting results are obtained in the oxidation of primary and secondary alcohols to carboxyl compounds in good yield using $HCrO_4$[151] ion.

The kinetics of oxidation of allyl alcohol by chromium(VI) in acetone solution was reported.[152] Variation of substrate, oxidant and acid concentration in kinetic studies showed a first order dependence in each of them. The activation energy and entropy of activation were respectively 11.4 Kcal mol^{-1} and -26 eu.

Kinetics of oxidation of secondary alcohols by Cr(VI) have been investigated in aqueous medium in presence of oxalic acid.[153] Hexavalent chromium is known to function both as a one and two electron oxidant depending on the substrate. Rocek and Hasan[154] showed that the system involving alcohol-oxalic acid Cr(VI) behaved in a different way in that the Cr(VI) get directly reduced to Cr(III) a reaction that involved a three electron transfer.

Mahendra K. Mahanti *et al.*[112] reported mechanistic studies of the reaction of the complexed Cr(VI) reagent soluble in organic solvent and convenient to use. A number of Cr(VI) compounds like 2,2'-bipyridinium chlorochromate, pyridinium fluorochromate, 4-(dimethylamine) pyridinium,

chlorochromate, etc. are found to be effective and selective oxidants for alcohols to corresponding carbonyl compounds.

Oxidation of benzyl alcohol and substituted benzyl alcohols are reported[81] to take place smoothly in dimethyl formamide in presence of acid by Quinolinium dichromate. The reaction has unit dependence each on (alcohol), (QDC) and (acid). Electron releasing group accelerate while electron withdrawing groups retard the rates and rate data obey Hammett relationship. Hydride ion transfer is proposed in the rate determining step.

Yadev G.D. and Haldawanbar B.V. reported[99] the kinetics and mechanism of liquid-liquid phase transfer catalysed oxidation of benzyl chloride with chromate to throw light on the selectivity of reaction giving benzaldehyde as the product.

A very recent paper reported the kinetics of oxidation of benzyl alcohol in non polar medium using potassium dichromate under phase transfer catalysis.[102] Tetrabutyl ammonium bromide and tetrabutyl phosphorium bromide are used as phase transfer catalysts. The reaction is first order each in (benzyl alcohol) and (chromate). The oxidation is selective forming benzaldehyde only.

Dodwad & Archana reported[155] the oxidation of alcohols, using chromium trioxide to corresponding carbonyl compound in excellent yield

under mild condition using tricapryl ammonium chloride as PT catalyst in dichloro methane.

The use of onium salt as PT catalyst to get complex chromate salt soluble in aprotic solvents has been reported[156] by Gelbard *et al.* The complex chromate was used for the oxidation of several alcohols.

2.2. SCOPE AND OBJECTIVE OF THE PRESENT STUDY

Phase transfer catalysis has become a pervasive and convenient synthetic tool for many organic reactions in organic media. However the studies on the kinetics and mechanism of oxidation of secondary alcohol using potassium dichromate as an oxidising agent in non polar media is limited. The dichromate divalent anion can be transferred into organic solvents by extraction with Adogen 464 in the ratio of 1:2. Onium salts and crown ethers are not effective to transfer dichromate in the organic solvents in the absence of acid medium. The resulting orange solution is effective for the selective oxidation of alchols to carbonyl compounds.

In the present work the monochromate ion, which is transferred from acidic aqueous medium to organic solvents using phase transfer catalysts, tetrabutyl ammonium bromide and tetrabutyl phosphonium bromide is used as the oxidising agent for the oxidation of the secondary alcohol, 1-phenyl ethanol and its some para substituted derivatives. The work is carried out in different solvents like benzene, toluene, chloroform and methylene chloride.

The oxidation of secondary alcohol to ketone is important theoretically and synthetically.

The following are the chief objectives of the present investigation:

1. To study the kinetics and mechanism of oxidation of 1-phenyl ethanol using phase transferred monochromate.

2. To compare the rate of oxidation of 1-phenyl ethanol and some of its derivatives in organic medium with those in aqueous acetic acid medium.

3. To study the temperature effect on the oxidation of cyclohexanol and benzhydrol in benzene using the phase transferred monochromate.

4. To evaluate the kinetic and related thermodynamic parameters like $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$.

5. To find the effect of dielectric constant of the medium on the rate of oxidation.

6. To evaluate the substituent effect at the para position of aryl ring on the rate of oxidation of 1-phenyl ethanol.

7. To formulate the mechanism consistent with the observations of the kinetic study.

Chapter 3

Experimental

The materials employed and methods adopted for the studies are included in this chapter. The contents are presented as follows.

1. Extraction of dichromate into non polar media.

2. Kinetic studies of the oxidation of 1-phenyl ethanol and other secondary carbinols in non polar solvents using phase transferred monochromate.

3. Kinetic studies of the oxidation of 1-phenyl ethanol and other secondary alcohols in aqueous acetic acid medium using aqueous potassium dichromate for purpose of comparison.

3.1. EXTRACTION OF DICHROMATE ION FROM AQUEOUS TO ORGANIC MEDIUM

The oxidation of organic compounds in organic media by potassium dichromate has to be carried out by transferring the oxidant into organic medium from aqueous phase or solid phase by means of phase transfer catalysts. The extraction was carried out using different concentrations of different phase transfer catalysts, using different solvents. While carrying out the phase transferring of the oxidant from an aqueous solution, its acidity was controlled using mineral acids.

Materials

Materials used for the extraction studies includes, potassium dichromate, water, sulphuric acid, phase transfer catalysts such as (tetrabutyl ammonium bromide (TBAB), tetrabutyl phosphorium bromide (TBPB) and aliquot, etc. and various organic solvents. Dichromate solutions were prepared using AR potassium dichromate in double distilled water. Phase transfer catalysts were of SISCO quality and hence used as such. Solvents employed are benzene, toluene, chloroform and methylene chlorides and were purified according to the standard procedures.[157,158] The solvents purified were subsequently refluxed with potassium dichromate crystals and phase transfer catalysts for about ten hours and then distilled for use.

Methods

A known volume of aqueous potassium dichromate solution (0.1 M) which is 2M with respect to sulphuric acid was stirred and equilibrated with an equal volume of the organic solvent containing PT catalyst. The organic layer was then separated and made anhydrous over anhydrous sodium sulphate. The concentration of extracted $HCrO_4^-$ ion was estimated spectrophotometrically using a Shimadzu 1601-uv-vis spectrophotometer. The extracts made accordingly were used for oxidation and kinetics investigation.

3.2. KINETIC STUDIES OF THE OXIDATION USING PHASE TRANSFERRED MONOCHROMATE

Kinetic studies on the oxidation using phase transferred monochromate were carried out using 1-phenyl ethanol, benzhydrol and cyclohexanol as substrates. Chloroform, methylene chloride, toluene and benzene were used as solvents. Phenyl methyl carbinol used was of E. Merck (German) quality. It was purified by vacuum distillation. Cyclohexanol was purified by vacuum distillation. The p-chloro, p-methyl and p-methoxy 1-phenyl ethanol [Lancaster England] were used as such.

3.2.(a) Methods

A known volume of the extract ($Q^+HCrO^-_4$) in known volume of the organic solvent and a solution of the substrate were thermostated for about 20 minutes. After attaining temperature equilibrium a known volume of the substrate solution is pipetted out into a known volume of the oxidant solution. The reaction was carried out keeping [alcohol] >> ($Q^+HCrO_4^-$). A definite amount of the reaction mixture was withdrawn at regular intervals of time and progress of the reaction was noted after immediately chilling the reaction from the absorbance values obtained at 364 nm using a Shimadzu 1601 uv-vis spectrophotometer.

The experiments were carried out in all the solvents with different oxidant concentrations, substrate concentrations and at various temperatures using TBAB and TBPB as catalysts.

Substituent effects were studied using some para substituted 1-phenyl ethanol as per the above procedure at various temperatures with TBAB and TBPP.

Temperature coefficient studies were carried out for these secondary alcohols, cyclohexanol and benzhydrol with the catalyst TBAB and TBPB at four different temperatures.

3.2. (b) Stoichiometry

The stoichiometry of the reaction between oxidant and substrate was determined by taking excess of chromate ion over alcohol concentration and allowing the reaction for completion. The absorbance of ($Q^+HCrO_4^-$) was measured initially and after completing the reaction. From the values the stoichiometry was determined and found to be 3:2.

3.2.(c) Product Analysis

Product analysis was carried out using a mixture containing excess of ($Q^+HCr^-O_4^-$) over 1-phenyl ethanol concentration in benzene. The mixture was stirred for 6 hours using magnetic stirrer. The resulting solution was extracted repeatedly with ether. The ether layers were collected and treated

with sodium bicarbonate solution. Organic layer was separated and ether was evaporated off. A saturated solution of 2,4-dinitrophenylhydrazine in methanol was added to the organic layer and the precipitated 2,4-dinitrophenylhydrazone was filtered, dried and weighed. Yield was found to be > 85%.

3.2.(d) Effect of addition of acrylonitrile

To the reaction mixture containing $2x10^{-1}$ mol dm^{-3} of 1-phenyl ethanol and $5x10^{-4}$ mol dm^{-3} extract in benzene, 5 ml of acrylonitrile was added and kept for 5 hours. No polymerisation was observed indicating the absence of any free radical formation during the course of the reaction.

3.3. KINETIC STUDIES IN AQUEOUS ACETIC ACID MEDIUM

3.3.(a) Materials

Potassium dichromate, water, H_2SO_4, acetic acid, alcohols, potassium iodide, starch, sodium thiosulphate and hydrochloric acid were used for the studies.

Potassium dichromate was of Merck quality, water used were of doubly distilled, acetic acid purified by refluxing with dichromate for 2 hours and then distilling. Alcohols of pure quality were used as such and other distilled, potassium iodide starch, and sodium thiosulphate were of pure quality.

3.3.(b) Methods

An aqueous solution of the reaction mixture containing definite concentration of dichromate, H_2SO_4, and acetic acid was thermostated and after attaining equilibrium, previously thermostated acetic acid solution of alcohol was added. Then the progress of the reaction was measured iodometrically by titrating a definite volume against standardised sodium thiosulphate solution. This procedure was repeated for investigating the effect of changing the oxidant concentration, substrate concentration, H_2SO_4 concentration, HOAc concentration, temperatures and sodium chloride concentration. Kinetics were studied keeping the concentration of alcohol excess over oxidant concentration.

The rate of oxidation of secondary alcohols benzhydrol and cyclohexanol was studied at a temperature range of 303 to 318 under identical kinetic conditions.

3.3.(c) Effect of addition of acrylonitrile

To the reaction mixture containing 4 x 10^{-2} mol dm^{-3} of 1-phenyl ethanol and 1 x 10^{-3} mol dm^{-3} of $K_2Cr_2O_7$ in 10% acetic acid, 5 ml of acrylonitrile was added and kept overnight. The absence of white precipitate ruled out the possibility of polymerisation.

3.3.(d) Stoichiometry

Stoichiometry was determined by allowing the reaction mixture containing acetic acid, definite concentration of potassium dichromate and alcohol, sulphuric acid, and double distilled water for completion of the reaction. The concentration of dichromate was estimated iodometrically at the initial and final stages of the reaction. The concentration of dichromate was taken in excess over alcohol. From the titre values and concentration of alcohol, stoichiometry was calculated.

3.3.(e) Product analysis

Product analysis was carried out in aqueous acetic acid medium using a mixture of known concentration of acetic acid, sulphuric acid, alcohol, potassium dichromate and double distilled water. This mixture was stirred for 6 hours using a magnetic stirrer. The product was identified using 2,4-dinitrophyenyl hydrazine. The product mixture extracted with ether and treated the ether layer with 2,4-dinitrophenyl hydrazine, the ppt is filtered, dried and weighed.

3.4. Calculation of rate constants[59-162]

Rate constants are calculated knowing the slope of the line obtained from the linear plots of log absorbance of chromate ion versus time in the case of non aqueous reaction. In aqueous medium linear plots of log concentration

of chromate versus time were made and rate constants calculated from the slope of their linear plots. The slope was calculated by linear regression analysis.

3.5. Thermodynamic Parameters[162-165-]

The thermodynamic parameters, energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta G^{\#}$) and free energy of activation ($\Delta G^{\#}$) were calculated using standard equations.

The energy of activation was calculated by using Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

where k is the rate constant, Ea the energy of activation, A is frequency factor, R is universal gas constant, T absolute temperature.

A plot of log k Vs 1/T gave a straight line with a slope of Ea/2.303 R. From the slope Ea was calculated.

According to transition state theory the rate constant k is related to $\Delta H^{\#}$ and $\Delta S^{\#}$ by the equation

$$k = \frac{k_b T}{h} e^{\Delta S\#/R} e^{\Delta H\#/}RT$$

$$\log \frac{k}{T} = \log \frac{k_b}{h} + \frac{\Delta S^{\#}}{2.303R} - \frac{\Delta H^{\#}}{2.303RT}$$

Where k_b is the Boltzmann constant and h Planck's constant.

Plot of log k/T Vs 1/T should be linear with slope equal to $\Delta H^{\#}/2.303$ R from which $\Delta H^{\#}$ can be calculated.

The value of $\Delta S^{\#}$ can be calculated by applying the values of k_b, h, R and $\Delta H^{\#}$ in the above equation.

The free energy of activation $\Delta G^{\#}$ can be calculated using the relation.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Chapter 4

Results and Discussion

The results obtained under the investigation studies are presented in this chapter. It is divided into 3 sections. They are

1. Extraction studies of dichromate using phase transfer catalysts.
2. Kinetic studies on the oxidation of 1-phenyl ethanol and some secondary alcohols with phase transferred chromate ion.
3. Kinetic studies of the same substrates in aqueous acetic acid medium.

4.1. EXTRACTION STUDIES OF DICHROMTE FROM AQUEOUS TO ORGANIC MEDIA USING TBAB, TBPB AND TCMAC.

To investigate the oxidation of organic compound with the inorganic reagent, potassium dichromate, in organic solvents, this reagent has to be transferred from aqueous acidic solution of it into the organic solvents by means of phase transfer catalysts. The extraction studies were carried out with respect to

1. Concentration of PT catalyst.
2. Concentration of H_2SO_4
3. Structure of PT catalyst
4. Nature of solvents

4.1.1. Effect of concentration and structure of PT catalyst on extraction

The partition was studied by equlibrating a definite volume of brown concentration of aqueous acidic potassium dichromate with an equal volume of organic solvents containing a definite concentration of PT catalysts followed by stirring for 30 minutes. The extraction was almost complete after 30 minutes. The amount extracted was estimated by the titration of aqueous layer iodometrically. This procedure was repeated varying the concentration of different PT catalysts.

It was reported[17] that the ion that is transferred when the aqueous phase is acidic is mainly $HCrO_4^-$ or $HCr_2O^-_7$. The results are presented in the table 4.1.1.1.

TABLE 4.1.1

Effect of Concentration and Structure of PT Catalysts on Extraction

Time : 30 minutes $[K_2Cr_2O_7]x10^2$: 1 M
Temperature : 303° Solvent : Bezene $[H_2SO_4]$: 2 M

Concentration of PT catalyst	Percentage of extraction		
	TBAB	TBPB	TCMAC
.005	48	65	68
.01	55	76	77
.015	68	87	88
.02	76	92	98

The extent of extraction of dichromate from aqueous to organic phase in a given solvent increased with increasing the concentration of PT catalyst. The extraction was almost complete and attained a steady state with the catalytic concentration twice that of the given dichromate. The percentage of extraction with respect to the different catalysts is in the order TBAB<TBPB<TCMAC. The increase in the extraction power of the catalysts is due to the greater organophilicity of larger catalyst cation.

4.1.2. Effect of H_2SO_4 concentration on the extraction

The extent of extraction of $HCrO_4^-$ from aqueous acidic solution to organic solvent benzene using 3 different phase transfer catalysts were studied varying the concentration of H_2SO_4 in aqueous medium. It was found that percentage of extraction increases with increasing concentration of H_2SO_4. Results are shown in table 4.1.2.

TABLE 4.1.2

Effect of H_2SO_4 Concentration on Extraction

Time : 30 minutes $[K_2Cr_2O_7]x10^2$: 1 M
Temperature : 303° Solvent : Bezene [PTC] x 10^2 : 2M

Concentration of H_2SO_4	Percentage of extraction		
	TBAB	TBPB	TCMAC
0.5	68	79	80
1.0	70	83	84
1.5	73	88	89
2	76	92	98

4.1.3. Effect of nature of solvents on extraction

Extraction studies were carried out using different organic solvents with the phase transfer catalysts TBAB and TBPB. The effect of solvent on extraction is shown in Table 4.1.3. A very little correlation was observed between extractability and dielectric constant of the medium. From these values it is found that $CHCl_3$ and CH_2Cl_2 are better solvents for extraction.

TABLE 4.1.3

Effect of nature of solvents on extraction

Time : 30 minutes $[K_2Cr_2O_7]x10^2$: 1 M
Temperature : 303° [PTC] x 10^2 : 2 M $[H_2SO_4]$: 2 M

Solvents	Percentage of extraction		
	TBAB	TBPB	Dielectric constant
C_6H_6	76	92	2.27
$C_6H_5CH_3$	35	65	2.40
$CHCl_3$	80	96	4.7
CH_2Cl_2	96	98	9.08

4.1.4. Stability of extract

The stability of chromate ion extracted into various solvents was studied by measuring the absorbance at λ_{max} of 364 nm for a period of 3 hours. It was found that there is a negligible change in the absorbance after

about a period of 3 hours. This shows that the chromate ion extracted into the organic medium is fairly stable for studying the kinetics of oxidation.

4.2. KINETICS OF OXIDATION OF 1-PHENYL ETHANOL BY MEANS OF PHASE TRANSFERRED MONOCHROMATE ION

4.2.1. Stoichiometry and product analysis

The stoichiometry of the reaction was investigated by equilibrating known amount of 1-phenyl ethanol and extract containing known excess amounts of oxidant in benzene medium. The absorbance is measured initially and after completing the reaction. From these values the stoichiometry was determined and found that [alcohol] : [monochromate] is 3:2.

Product analysis was carried out as mentioned in the experimental part and the product was identified as acetophenone.

4.2.2. Kinetic studies

The results of kinetic studies of phase transfer catalysed oxidation of 1-phenyl ethanol with potassium dichromate using TBAB and TBPB as phase transfer catalysts are given below.

4.2.2.1. Effect of changing oxidant concentration

The kinetics of oxidation of 1-phenyl ethanol using phase transferred chromate was studied fixing substrate concentration and varying oxidant

concentration. Pseudo first order condition was maintained keeping the concentration of alcohol higher than the oxidant concentration. The progress of the reaction was followed spectrophotometrically, measuring the absorbance at various intervals of time. The pseudo first order rate constant k_{obs} was calculated from the linear least square plot of log absorbance Vs time. Duplicate runs showed that the values are reproducible. The values are presented in the tables 4.2.1 and 4.2.2. Results showed a first order dependence on oxidant concentration.

TABLE 4.2.1

Effect of changing oxidant concentration on the rate of oxidation of 1-phenyl ethanol

Solvent : Benzene
[Substrate] x 10 : 2 mol dm^{-3}

Temperature : 308
PTC : TBAB

(oxidant) x 10^4 mol dm^{-3}	k_{obs} x 10^5 S^{-1}	k_2 x 10^5 k_{obs}/[substrate] mol^{-1} dm^3 sec^{-1}	Correlation coefficient
5	3.26	16.3	.9992
6.25	3.26	16.3	.9997
7.5	3.14	15.7	.9994
8.75	3.26	16.3	.9999

TABLE 4.2.2

Effect of oxidant concentration change on the rate of oxidation of 1-phenyl ethanol

Solvent : Benzene
[Substrate] x 10 : 2 mol dm^{-3}

Temperature : 308
PTC : TBPB

(oxidant) x 10^4 mol dm^{-3}	k_{obs} x 10^5 S^{-1}	k_2 x 10^5 k_{obs}/[substrate] mol^{-1} dm^3 sec^{-1}	Correlation coefficient
5	1.9575	9.787	.9994
6.25	2.226	11.13	.9998
7.5	2.03	10.15	.9995
8.75	2.14	10.7	.9997

The effects are shown graphically in Fig. 4.2.2(a) and 4.2.2(b).

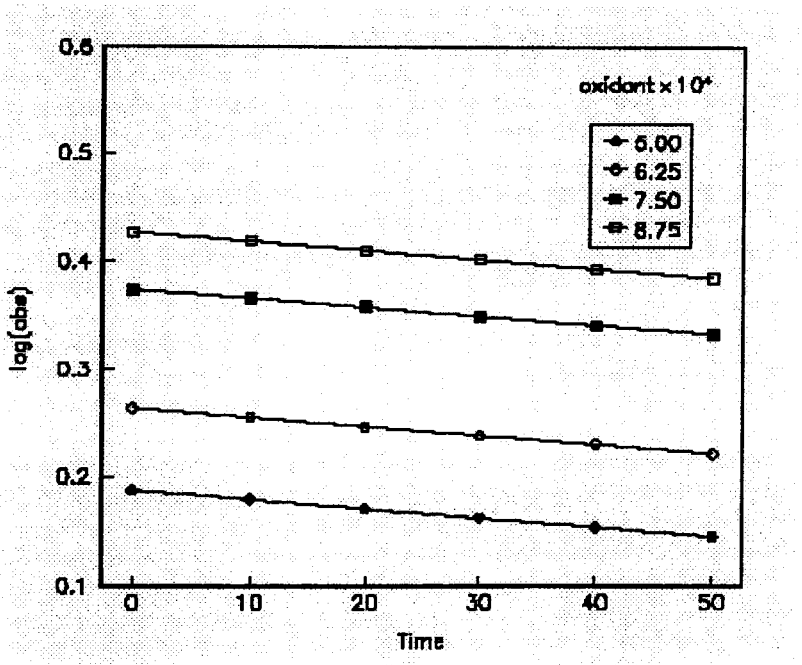


Fig. 4.2.2(a) Effect of [oxidant] on the rate of oxdn of PE in benzene (TBAB)

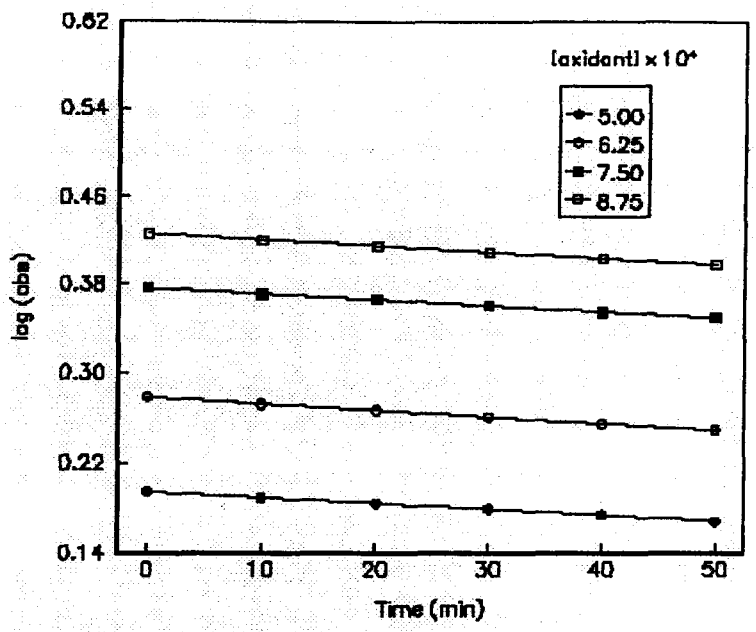


Fig. 4.2.2(b) Effect of [oxidant] on the rate of oxdn of PE in benzene (TBPB)

4.2.2.2. Effect of substrate concentration change on the rate of oxidation

Effect of substrate concentration on the rate of oxidation was studied keeping the oxidant concentration and other conditions same but varying the initial concentration of substrate using catalysts TBAB and TBPB. The observed rate constant is increased linearly with increase in the concentration of substrate. The second order rate constant k_2 obtained, dividing the k_{obs} values by the respective substrate concentrations, practically remained constant for the same catalyst and showed first order dependence with respect to substrate concentration. The results are given in the tables 4.2.3 and 4.2.4.

TABLE 4.2.3

Effect of substrate concentration on the rate of oxidation

Solvent : benzene — Temperature : 308

[Oxidant] x 10^4 : 5 moldm^{-3} — PTC :TBAB

[Substrate] x 10 mol dm^{-3}	k_{obs} x 10^5 S^{-1}	k_2 x 10^5 k_{obs}/[substrate] mol^{-1} dm^3 s^{-1}	Correlation coefficient
2	3.26	16.3	.9998
2.5	3.876	15.48	.9992
3	5.6	18.66	.9995
3.5	6.9	19.7	.9988

TABLE 4.2.4

Effect of substrate concentration on the rate of oxidation

Solvent : benzene — Temperature 308

(Oxidant) x 10^4 : 5 moldm^{-3} — PTC : TBPB

(Substrate) x 10 moldm^{-3}	k_{obs} x 10^5 S^{-1}	k_2 x 10^5 k_{obs}/[substrate] mol^{-1} dm^3 s^{-1}	Correlation coefficient
2.0	1.9575	9.787	.9994
2.5	2.418	9.67	.9991
3.0	3.22	10.74	.9994
3.5	3.416	9.76	.9998

The effect of changing substrate concentration are shown graphically in Fig. 4.2.3(a) and 4.2.3(b) for the catalysts TBAB and TBPB respectively.

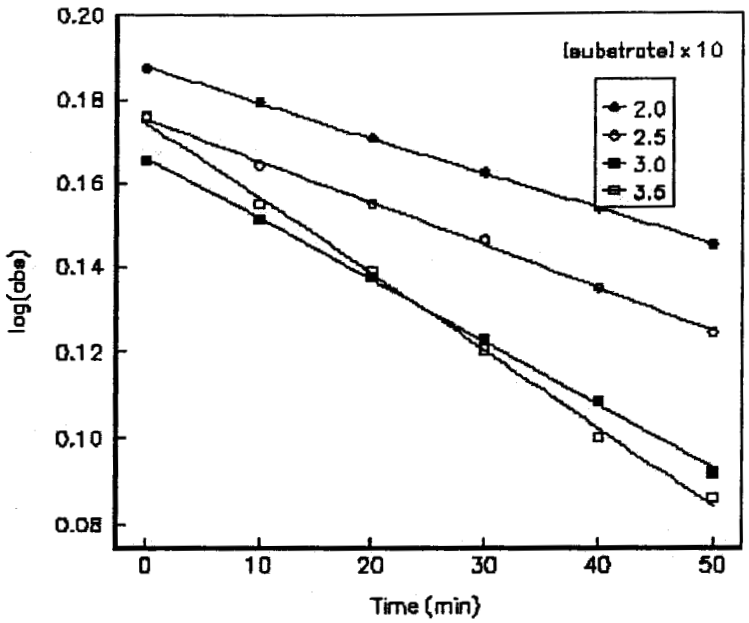


Fig. 4.2.3(a) Effect of [substrate] on the rate of oxdn of PE in benzene (TBAB)

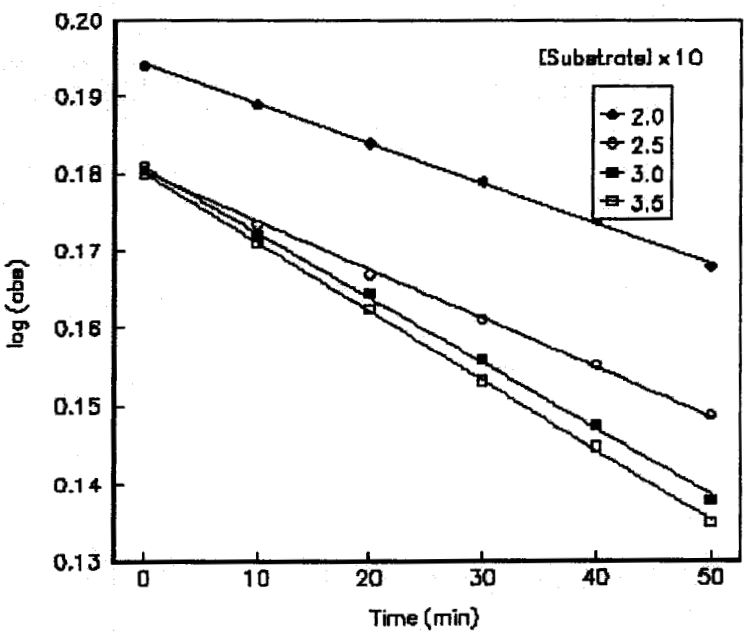


Fig. 4.2.3(b) Effect of [substrate] on the rate of oxdn of PE in benzene (TBPB)

The effect of substrate concentration was further confirmed by double logarithemic plot of log k_{obs} Vs log(substrate) shown in Fig. 4.2.3(c) and 4.2.3(d).

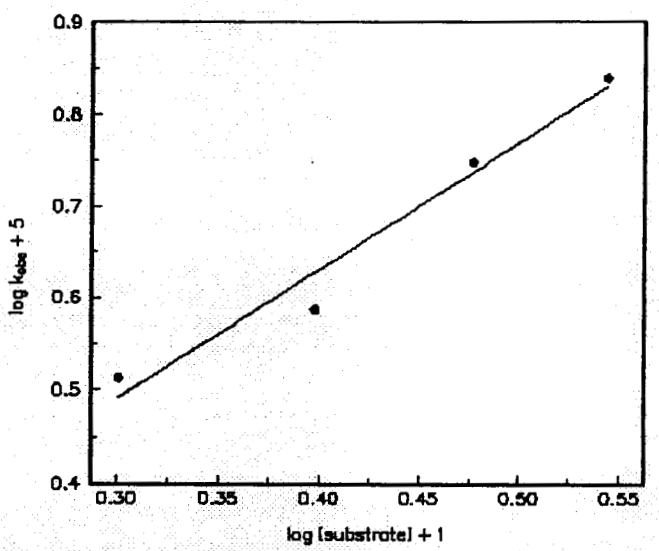


Fig. 4.2.3(c) Order with respect to PE (TBAB)

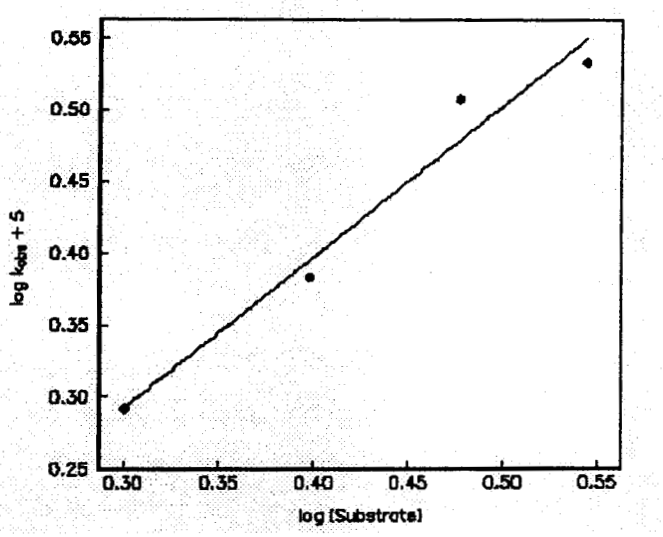


Fig. 4.2.3(d) Order with respect to PE (TBPB)

The double reciprocal plots, Plots of $\frac{1}{k_{obs}}$ Vs $\frac{1}{[\text{Substrate}]}$ are shown in Fig. 4.2.3(e) and 4.2.3(f). The plots are linear not passing through the origin.

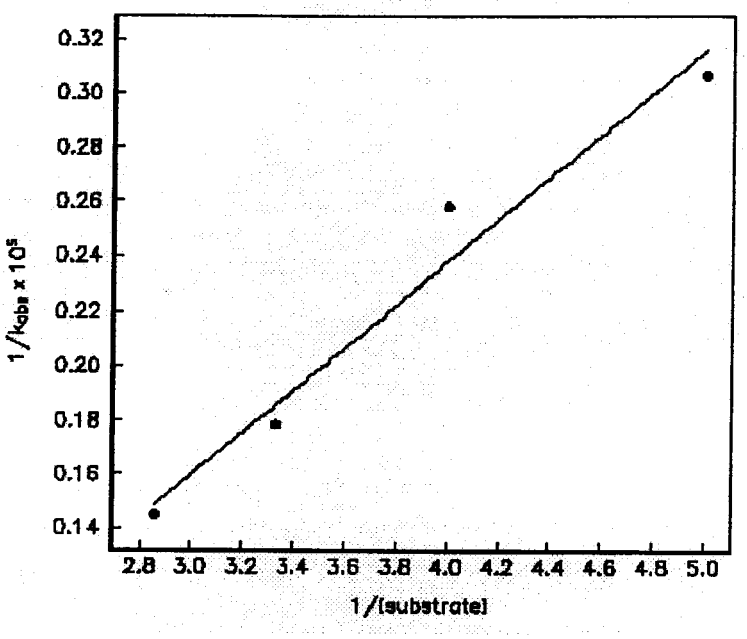


Fig. 4.2.3.(e) $1/k_{obs}$ Vs. 1/[Substrate] Plot (TBAB)

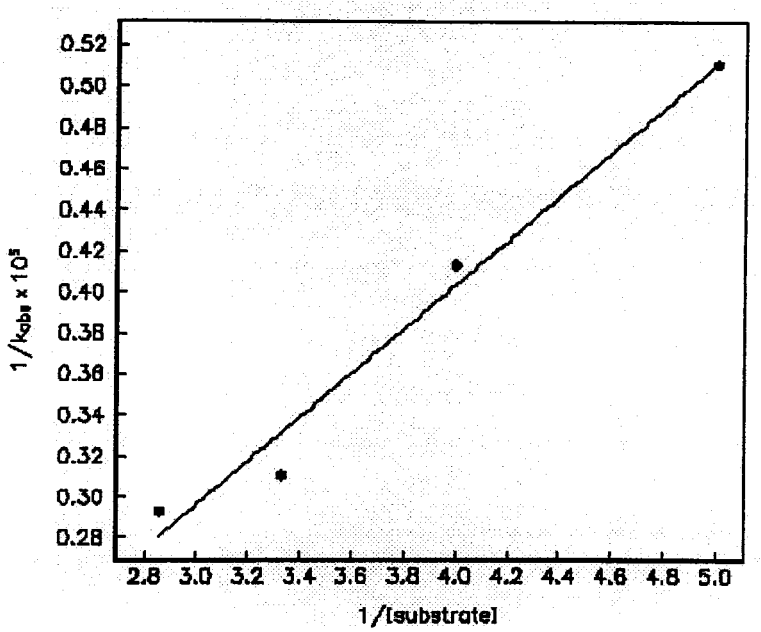


Fig. 4.2.3.(f) $1/k_{obs}$ Vs. 1/[Substrate] Plot (TBPB)

4.2.2.3. Effect of polarity of the medium on the rate of oxidation

The experiment was carried out in various organic solvents at 308 by keeping all other kinetic conditions the same. The values are tabulated in tables 4.2.5 and 4.2.6. The results showed that the rate of oxidation increased with increasing dielectric constant of the medium indicating the interaction between an anion and a dipole (Fig. 4.2.4(a) and 4.2.4(b)).

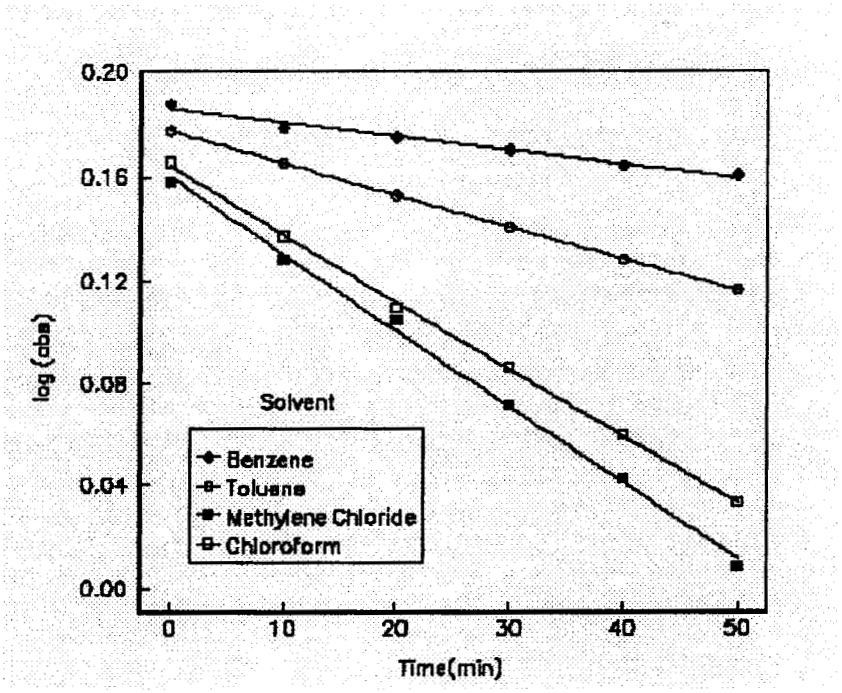


Fig. 4.2.4(a) Effect of solvent polarity on the rate of oxdn of PE (TBAB)

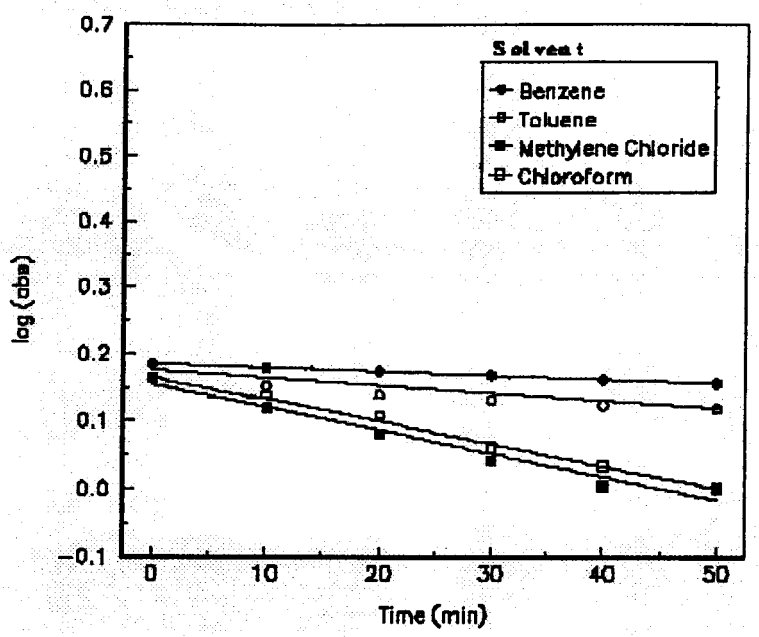


Fig. 4.2.4(b) Effect of solvent polarity on the rate of oxdn of PE (TBPB)

The reactivity is found to be in the order $CH_2Cl_2 > CHCl_3 > C_6H_5CH_3 > C_6H_6$.

TABLE 4.2.5

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

[Substrate] x 10 : 2 moldm^{-3} Temperature : 308
[Oxidant] x 10^4 : 5 moldm^{-3} PTC : TBAB

Solvent	Dielectric constant D	k_{obs} x 10^5 s^{-1}	k_2 x 10^5 mol^{-1} dm^3 s^{-1}	Correlation coefficient
Benzene	2.27	3.26	16.3	.9998
Toluene	2.4	4.644	23.22	.9997
Chloroform	4.7	10.05	50.25	.9997
Methylene chloride	9.08	11.39	56.95	.9988

TABLE 4.2.6

Effect of Polarity of the medium in the rate of oxidation

[Substrate] x 10 : 2 moldm^{-3} Temperature : 308

[Oxidant] x 10^4 : 5 moldm^{-3} PTC : TBPB

Solvent	Dielectric constant D	k_{obs} x 10^5 s^{-1}	k_2 x 10^5 mol^{-1} dm^3 s^{-1}	Correlation coefficient
Benzene	2.27	1.9575	9.78	.9962
Toluene	2.4	2.33	16.66	.9914
Chloroform	4.7	12.55	62.75	.9977
Methylene chloride	9.08	13.16	65.82	.9835

The plots of log k_2 Vs 1/D of the solvent is a curve with negative slope indicating the interaction between an anion and a dipole and not linear as according to Amis equation[165] (Fig. 4.2.4.c and 4.2.4.d).

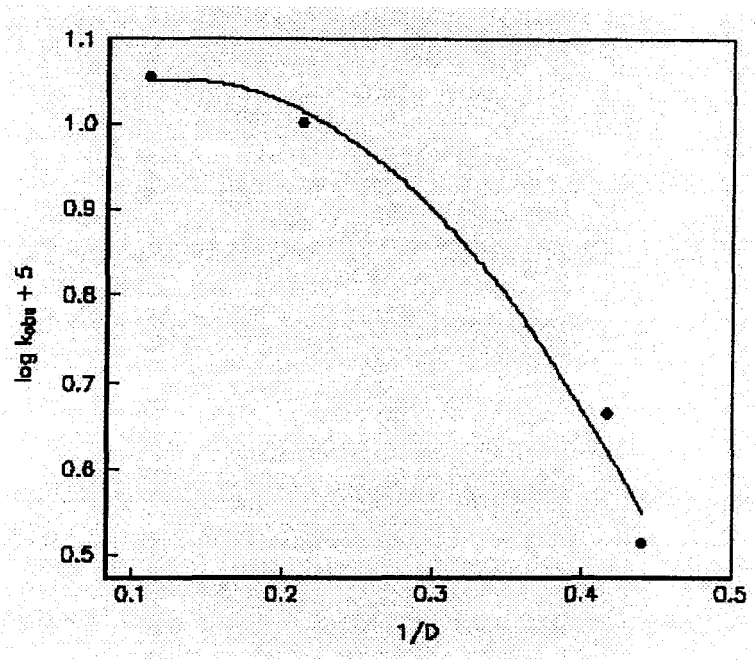


Fig. 4.2.4(c). Log k_2 Vs. 1/D plot (TBAB)

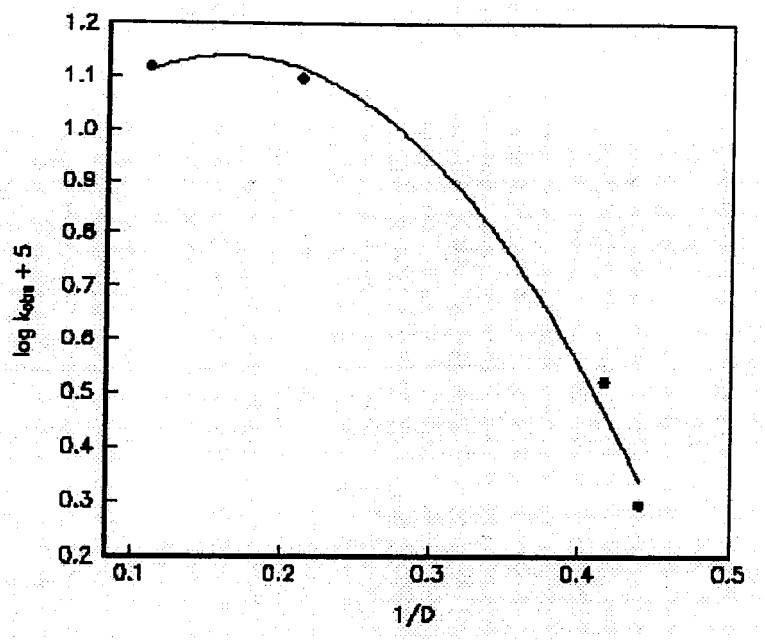


Fig. 4.2.4(d). log k_2 Vs. 1/D plot (TBPB)

4.2.2.4. Effect of adding acrylonitrite

The reaction system containing 0.2 M of 1 phenyl ethanol, 5 x 10^{-4} M of $Q^+HCrO_4^-$ in benzene and 5 ml acrylonitrile was kept for 5 hours. No polymerisation was observed indicating the absence of free radical formation during the course of the reaction.

4.2.2.5. Effect of substituents on the rate of oxidation of 1 phenyl ethanol

The experiments were carried out to study the effect of substituents on the rate of oxidation of 1 phenyl ethanol using p-chloro, p-methyl and p-methoxy substituted compounds in benzene medium. The results are presented in table 4.2.7 & 4.2.8. The rate of oxidation is found to be in the

order p-methoxy > p-methyl > 1 phenyl ethanol > p-chloro 1-phenyl ethanol. This showed that the electron releasing groups accelerate the rate of reaction where as electron withdrawing groups retard the rate of reaction. The plots are given in Fig. 4.2.5(a) and 4.2.5(b).

TABLE 4.2.7

Effect of substituent on the rate of oxidation of 1-phenyl ethanol

[Substrate] x 10 = 2 mol dm^{-3} Temperature : 308
[Oxidant] x 10^4 = 5 $moldm^{-3}$ PTC : TBAB
[Solvent]: Benzene

Substrate	k_2 x 10^5 mol^{-1} dm^3 s^{-1}	Correlation coefficient
p-methoxy 1-phenyl ethanol	29.17	.997
p-methyl 1-phenyl ethanol	25.71	.9946
p-chloro1-phenyl ethanol	12.47	.9998
1-phenyl ethanol	16.3	.9998

TABLE 4.2.8

Effect of substituent on the rate of oxidation of 1-phenyl ethanol

[Substrate] x 10 = 2 mol dm^{-3} Temperature : 303
[Oxidant] x 10^4 = 5 $moldm^{-3}$ PTC : TBPB
[Solvent]: Benzene

Substrate	k_2 x 10^5 mol^{-1} dm^3 s^{-1}	Correlation coefficient
p-methoxy 1-phenyl ethanol	21.68	.9997
p-methyl 1-phenyl ethanol	17.08	.9998
p-chloro 1-phenyl ethanol	5.565	.994
1-phenyl ethanol	9.787	.9994

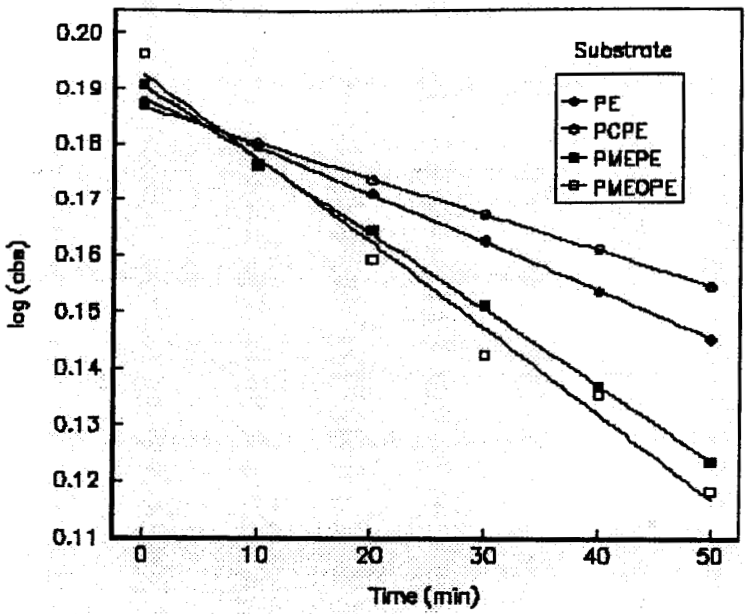


Fig. 4.2.5(a). Effect of substituents on the rate of oxdn of PE in benzene (TBAB)

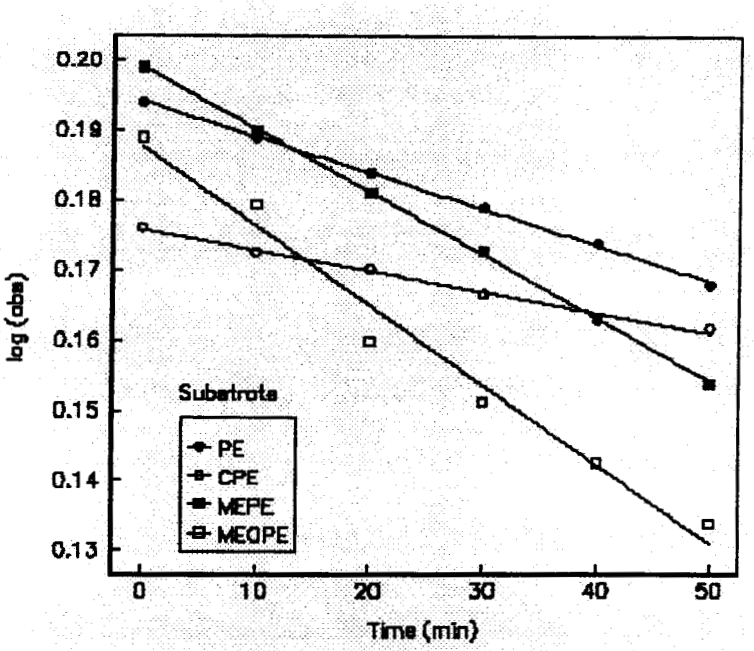


Fig. 4.2.5(b). Effect of substituents on the rate of oxdn of PE in benzene (TBPB)

The Hammett plot[166] of log k_2 Vs σ (Fig. 4.2.6a & 4.2.6b) were found to be linear with negative values of reaction constants for the two catalysts TBAB and TBPB. The negative values confirm the above observed fact of electron withdrawing groups retard the rate of reaction. The reaction constant $\rho = -0.7749$ and $r = 0.993$ using the catalyst TBPB.

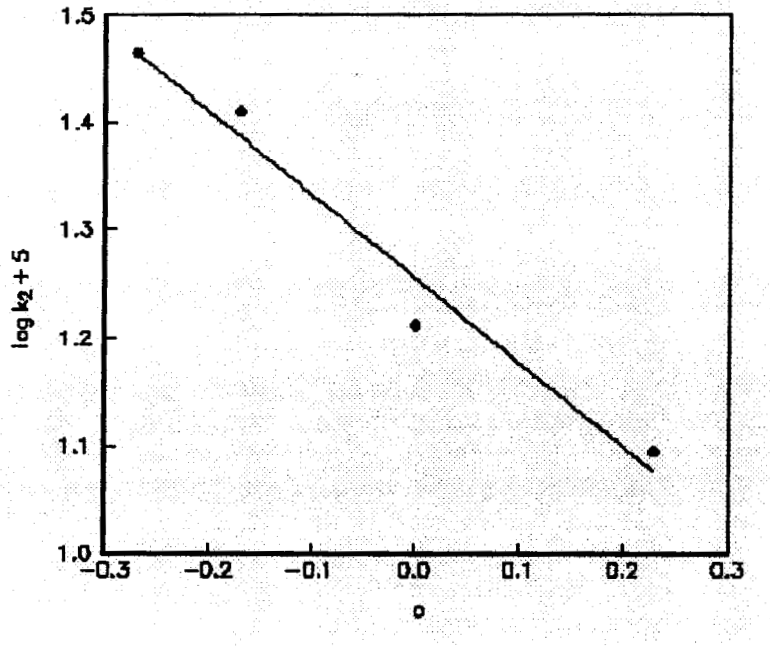


Fig. 4.2.6.(a) Hammett plot for the oxdn of PE in benzene (TBAB)

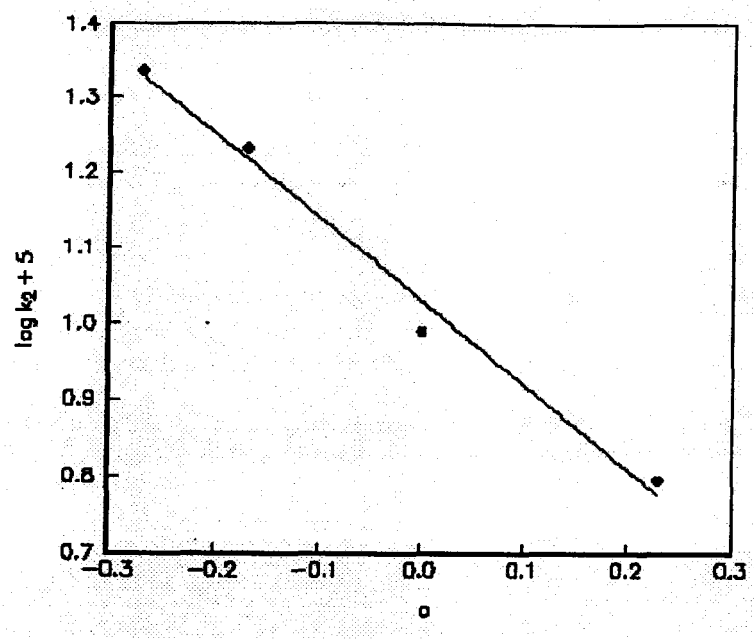


Fig. 4.2.6.(b) Hammett plot for the oxdn of PE in benzene (TBPB)

4.2.2.6. Effect of temperature on the rate of oxidation of 1-phenyl ethanol and its substituents

The effect of temperature on the rate of oxidation of 1-phenyl ethanol and some of its para substituted derivatives-p-methoxy, p-methyl and p-chloro derivatives were studied at temperatures ranging from 303 to 318 K under identical kinetic conditions. The results obtained using the two phase transfer catalysts are presented in table 4.2.9 to 4.2.12 and the corresponding plots in Fig. 4.2.7(a) to Fig. 4.2.7(h).

TABLE 4.2.9

Effect of temperature on the rate of oxidation of 1-phenyl ethanol

[Substrate] x 10 = 2 mol dm^{-3} Solvent : Benzene
[Oxidant] x 10^4 = 5 $moldm^{-3}$

Temperature	TBAB			TBPB		
	$k_{obs}\ 10^5$ S^{-1}	$k_2 \times 10^5$ mol^{-1} $dm^3\ S^{-1}$	corre. coeffi.	$k_{obs}\ 10^5$ S^{-1}	$k_2 \times 10^5$ mol^{-1} $dm^3\ S^{-1}$	corr. coeff.
303	2.45	12.25	.9996	1.42	7.1	.9989
308	3.26	16.3	.9998	1.9575	9.787	.9994
313	3.56	17.8	.9993	2.68	13.4	.9992
318	4.29	21.45	.9998	4.145	20.225	.998

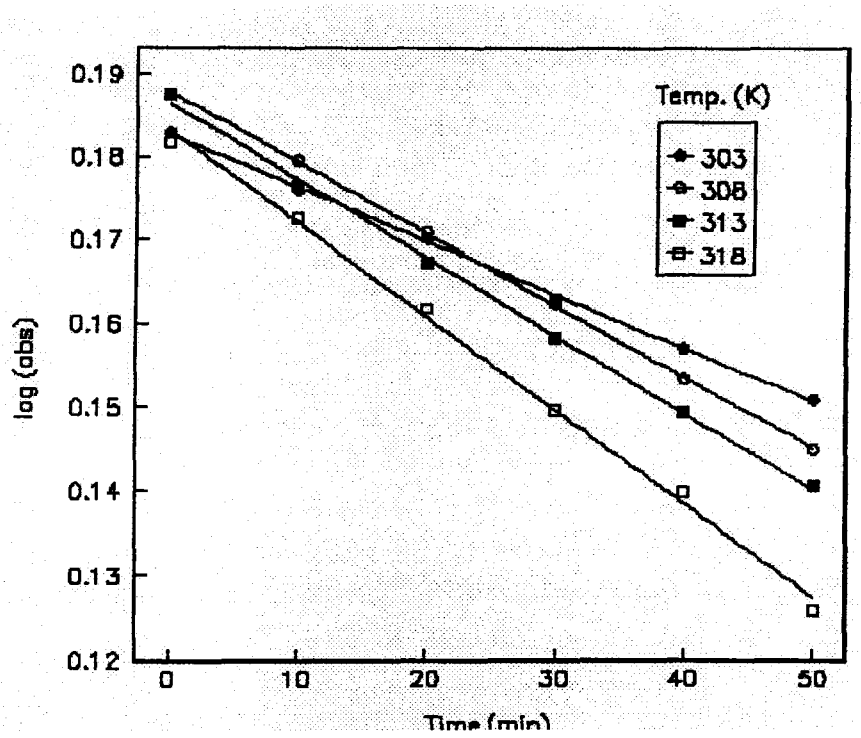


Fig. 4.2.7(a) Effect of temp on the rate of oxdn of PE in benzene (TBAB)

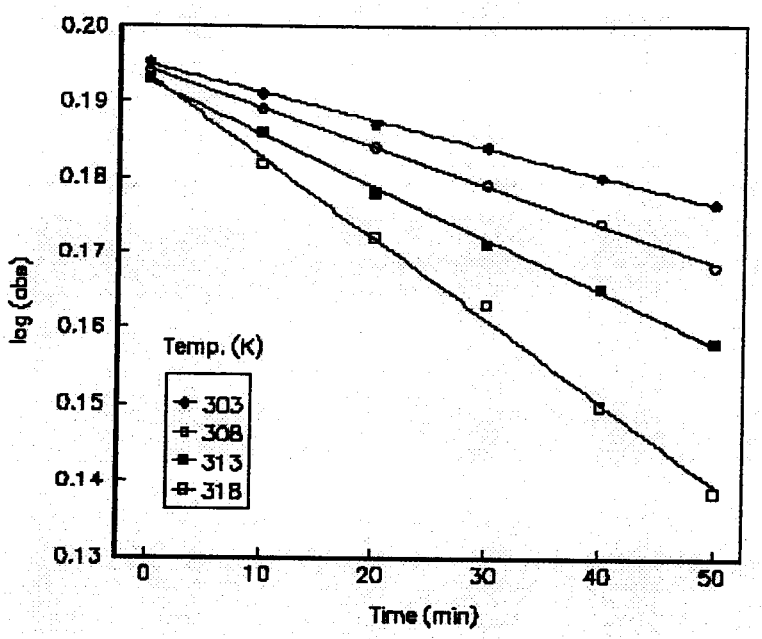


Fig. 4.2.7(b) Effect of temp on the rate of oxdn of PE in benzene (TBPB)

TABLE 4.2.10

Effect of temperature on the rate of oxidation of p-chloro 1-phenyl ethanol

[Substrate] x 10 = 2 mol dm^{-3}
[Oxidant] x 10^4 = 5 mol dm^{-3} Solvent : Benzene

Temperature	TBAB			TBPB		
	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corre. coeffi.	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corr. coeff.
303	2.034	10.17	.9998	0.959	4.795	.992
308	2.494	12.47	.9998	1.113	5.565	.994
313	3.07	15.35	.9996	1.458	7.29	.998
318	3.492	17.46	.999	1.957	9.785	.999

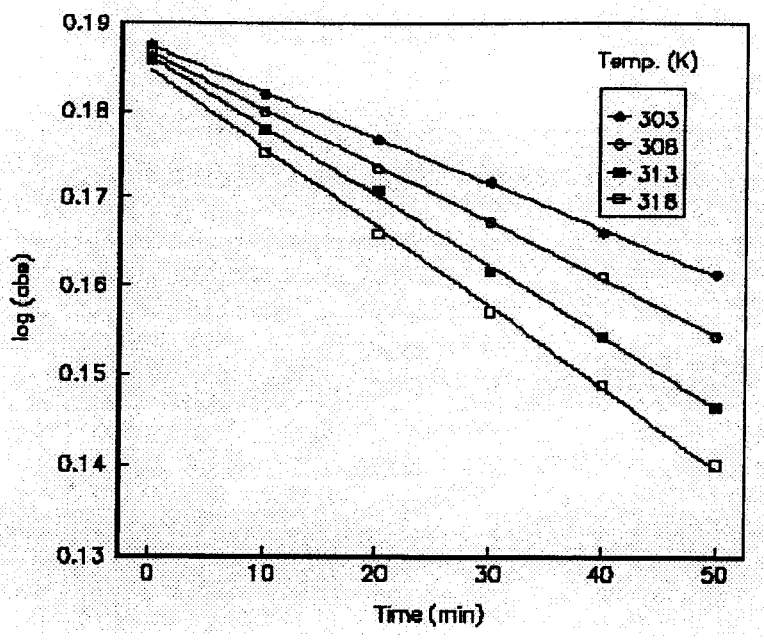


Fig. 4.2.7(c) Effect of temperature on the rate of oxdn of PCPE in benzene (TBAB)

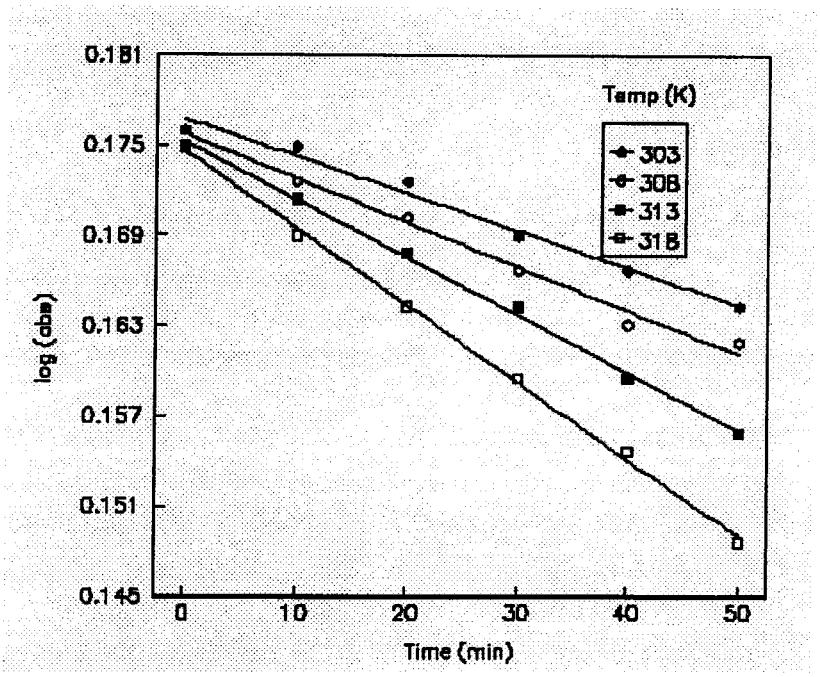


Fig. 4.2.7(d) Effect of temperature on the rate of oxdn of PCPE in benzene (TBPB)

TABLE 4.2.11

Effect of temperature on the rate of oxidation of p-methyl 1-phenyl ethanol

[Substrate] x 10 : 2 mol dm^{-3}
[Oxidant] x 10^4 = 5 $moldm^{-3}$ Solvent : Benzene

Temperature	TBAB			TBPB		
	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corre. coeffi.	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corr. coeff.
303	3.876	19.38	.9997	2.763	13.81	.9998
308	5.143	25.71	.9996	3.416	17.08	.9998
313	5.9494	29.74	.9996	3.991	19.95	.9999
318	7.216	36.08	.9992	4.644	23.22	.9999

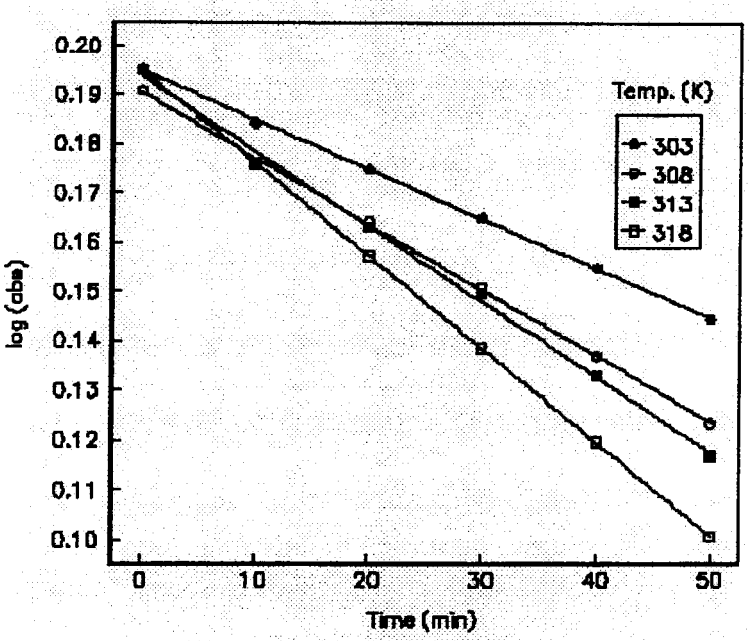


Fig. 4.2.7(e) Effect of temp on the rate of oxdn of PMEPE in benzene (TBAB)

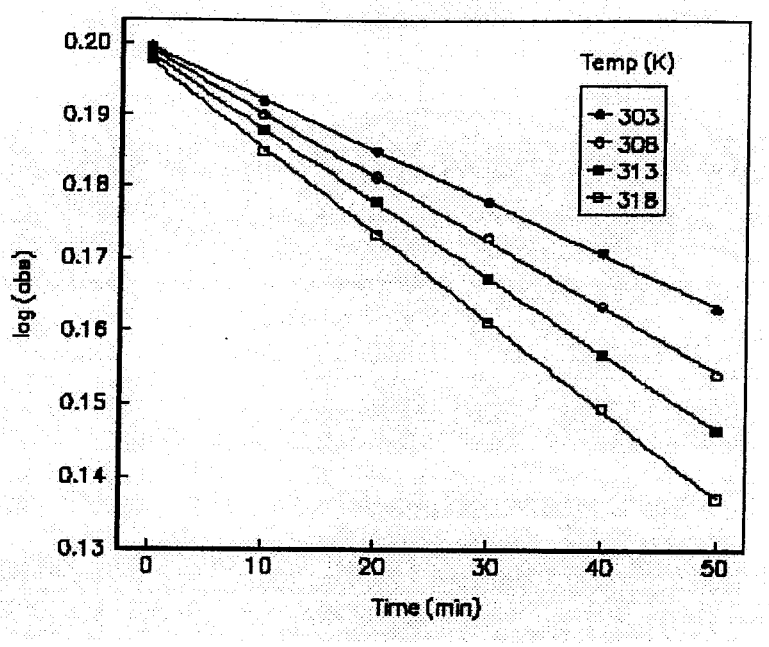


Fig. 4.2.7(f) Effect of temp on the rate of oxdn of PMEPE in benzene (TBPB)

TABLE 4.2.12

Effect of temperature on the rate of oxidation of p-methoxy 1-phenyl ethanol

[Substrate] x 10 : 2 moldm^{-3}
[Oxidant] x 10^{4} : 5 moldm^{-3} Solvent : Benzene

Temperature	TBAB			TBPB		
	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corre. coeffi.	k_{obs} 10^5 S^{-1}	k_2 x 10^5 mol^{-1} dm^3 S^{-1}	corr. coeff.
303	4.145	20.72	.998	4.145	20.72	.9998
308	5.834	29.17	.997	4.337	21.68	.9888
313	8.597	42.98	.9988	4.452	22.26	.9996
318	12.51	62.5	.998	4.9898	24.94	.9997

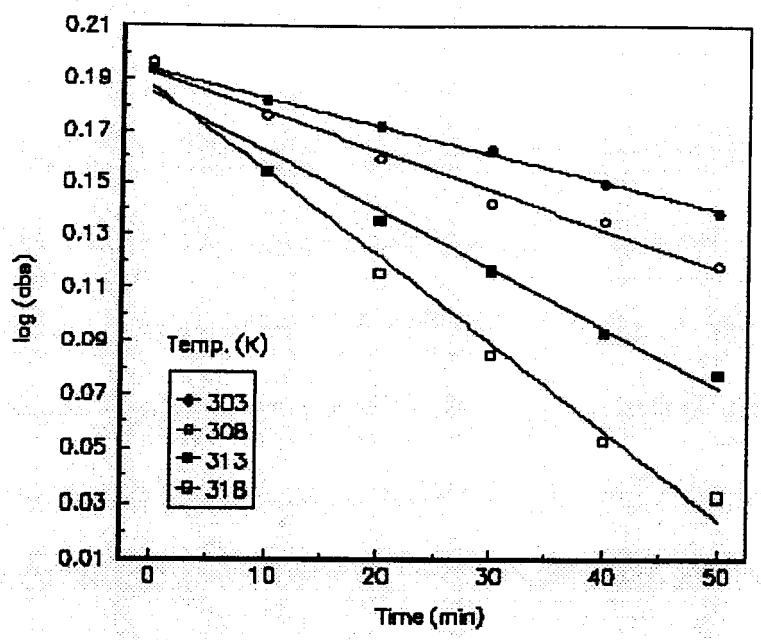


Fig. 4.2.7(g) Effect of temp on the rate of oxdn of PMEOPE in benzene (TBAB)

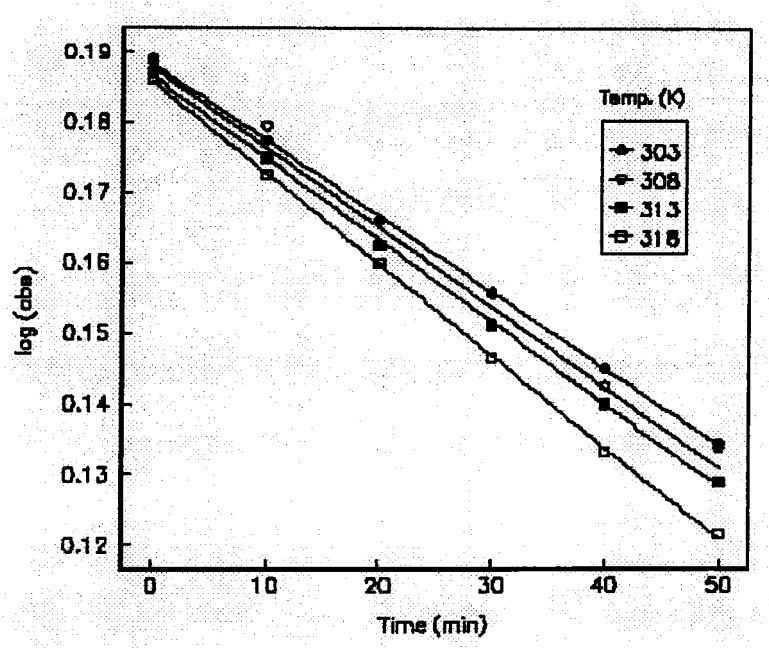


Fig. 4.2.7(h) Effect of temp on the rate of oxdn of PMEOPE in benzene (TBPB)

The results obtained by the investigations on the temperature effects show that rate is sensitive to temperature changes. The second order rate constant for 1-phenyl ethanol and the three para substituted 1-phenyl ethanols increased when the temperature is varied from 303 to 318 K.

4.2.2.7. Calculation of thermodynamic parameters

The values of various thermodynamic parameters are calculated from the plots of log k_2 Vs 1/T and log k_2/T Vs $1/T$[167] and presented in the table 4.2.13 and 4.2.14 and the plots in Fig. 4.2.8(a) to 4.2.8(d).

TABLE 4.2.13

Activation parameters for the oxidation of 1-phenyl ethanol and its para substituted derivatives

Solvent : Benzene Catalyst : TBAB

Substrate	$k_2 \times 10^5$ mol^{-1} dm^3 s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
1-phenyl ethanol	12.25	27.41	24.92	-103.99	56.43
p-chloro 1-phenyl ethanol	10.17	28.42	25.93	-102.38	56.958
p-methyl 1-phenyl ethanol	19.38	31.17	28.67	-96.143	57.83
p-methoxy 1-phenyl ethanol	20.72	57.41	54.8	-58.355	72.54

TABLE 4.2.14

Activation parameters for the oxidation of 1-phenyl ethanol and para-substituents of 1-phenyl ethanol

Solvent : Benzene Catalyst : TBPB

Substrate	$k_2 \times 10^5$ $mol^{-1}\ dm^3\ s^{-1}$	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-}	$\Delta S^{\#}$ $JK^{-1}\ mol^{-1}$	$\Delta G^{\#}$ kJ mol^{-1}
1-phenyl ethanol	7.1	53.49	50.98	.67.78	71.518
p-chloro 1-phenyl ethanol	4.795	37.31	34.79	-92.39	62.784
p-methyl 1-phenyl ethanol	13.818	26.52	24.06	-103.94	55.55
p-methoxy 1-phenyl ethanol	20.727	43.88	41.38	-77.63	64.90

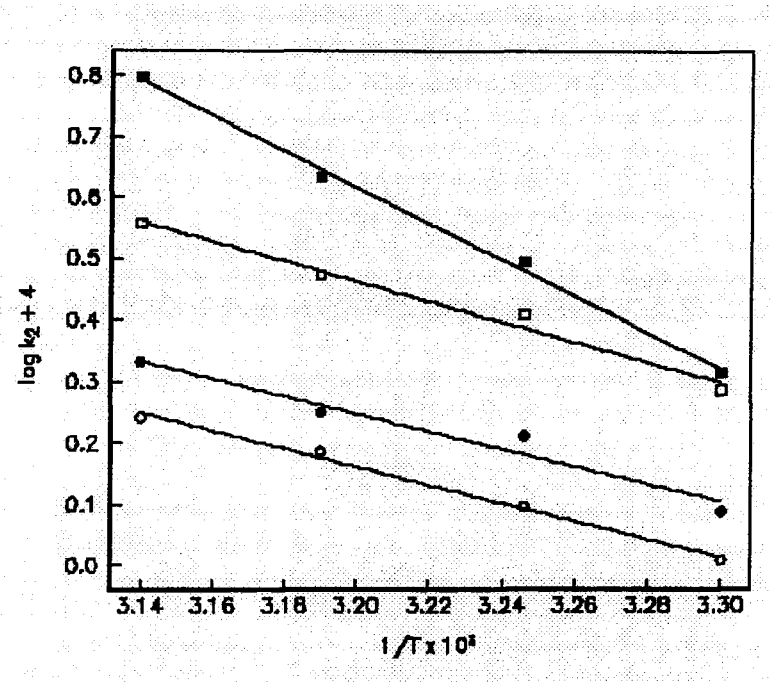


Fig. 4.2.8(a) Plot of log k_2 Vs 1/T for oxdn of PE in benzene (TBAB)

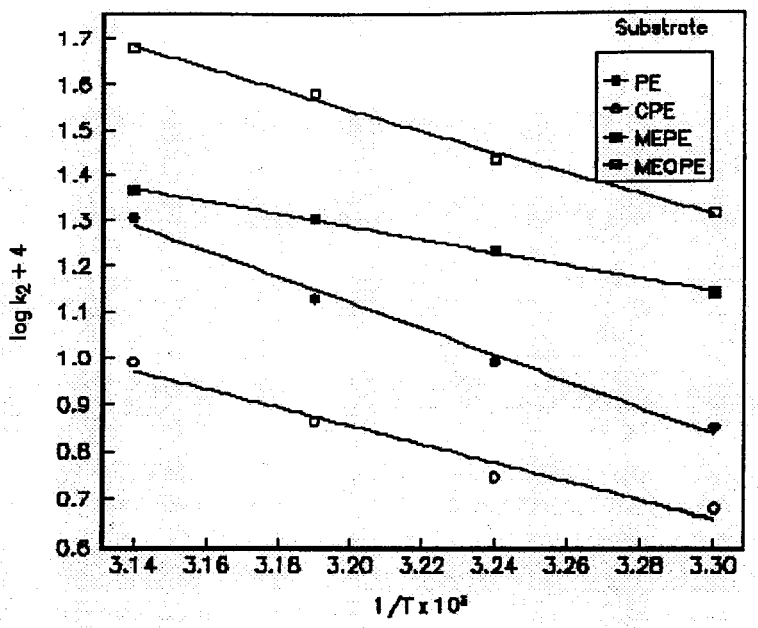


Fig. 4.2.8(b) Plot of log k_2 Vs 1/T for oxdn of PE in benzene (TBPB)

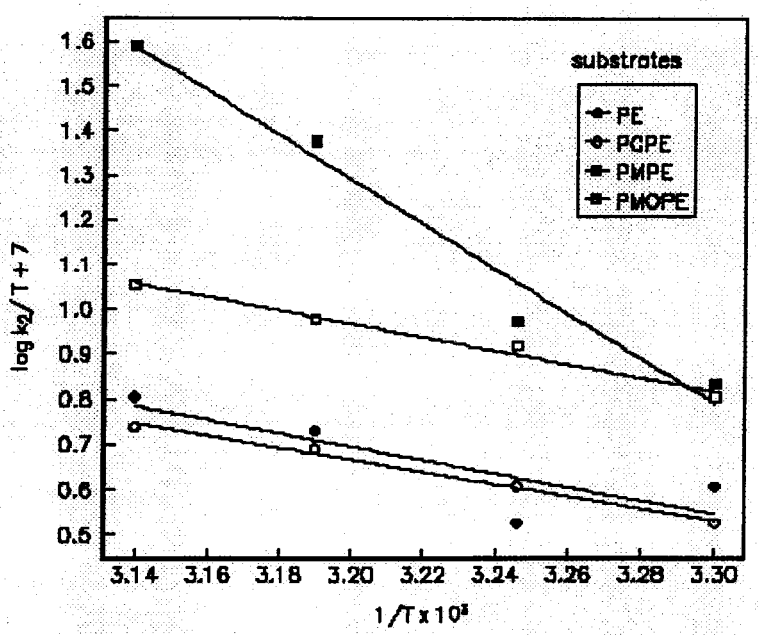


Fig. 4.2.8(c) Plot of log k_2/T Vs 1/T for oxdn of PE in benzene (TBAB)

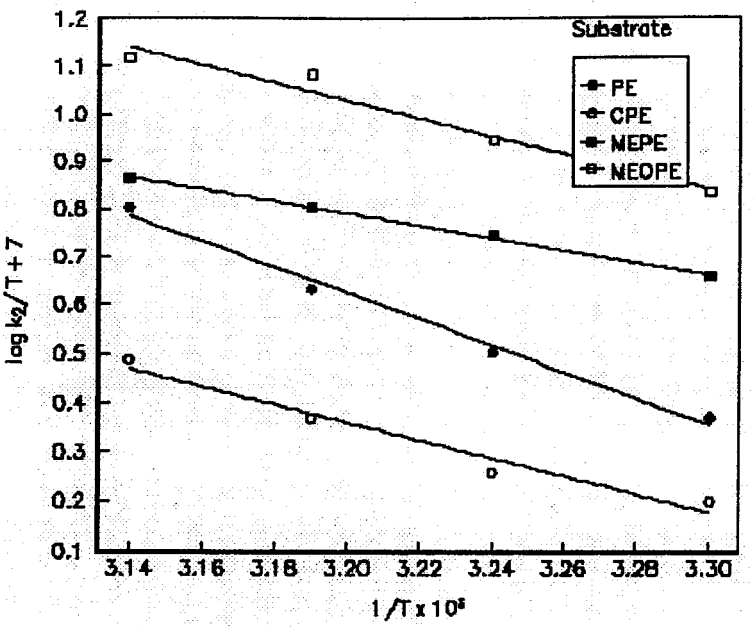


Fig. 4.2.8(d) Plot of log k_2/T Vs 1/T for oxdn of PE in benzene (TBPB)

The free energy of activation is nearly the same indicating that a similar mechanism is operating in the case of 1-phenyl ethanol and its substituents during the oxidation. The plot of $\Delta H^{\#}$ Vs $\Delta S^{\#}$ was found to be linear which further confirm the above fact. The isokinetic temperature β was calculated using the isokinetic relationship suggested by Leffler and Grunwald.[168] $\Delta H^{\#} = C + \beta \Delta H^{\#}$ Fig. 4.2.8(e) and 4.2.8(f).

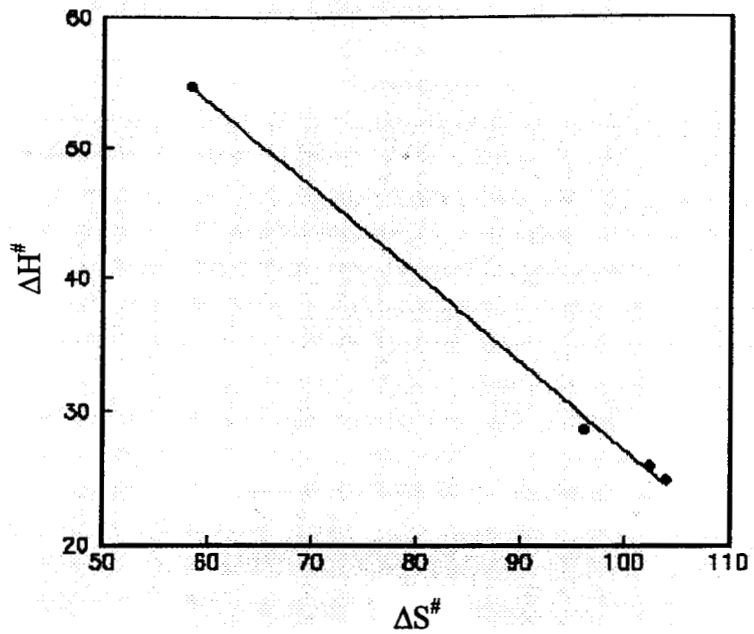


Fig. 4.2.8(e) Isokinetic plot for the oxdn of PE in benzene (TBAB)

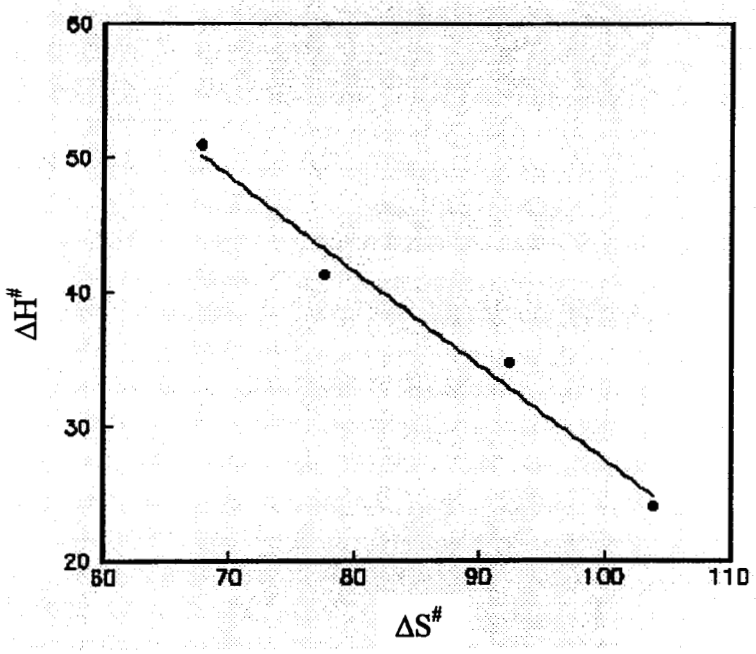


Fig. 4.2.8(f) Isokinetic plot for the oxdn of PE in benzene (TBPB)

The Exner's plot[169] of log k_2 at 318 Vs log k_2 at 303 K was also linear (Fig. 4.2.8(g) and Fig. 4.2.8(h)).

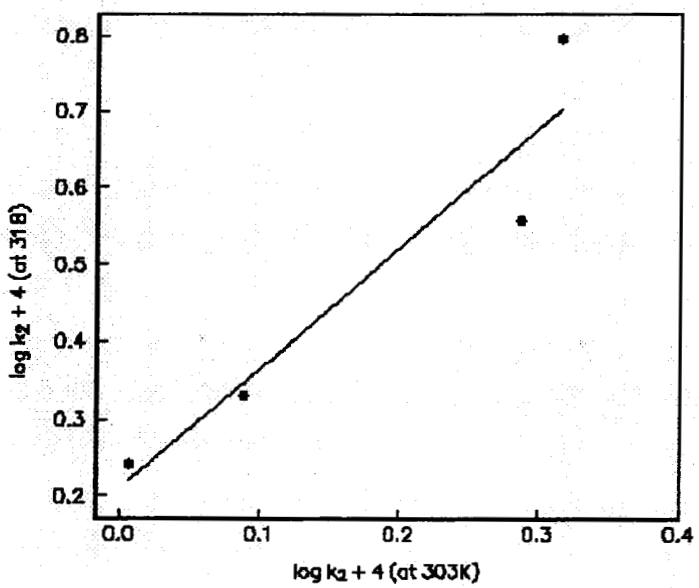


Fig. 4.2.8(g). Exner's plot (TBAB)

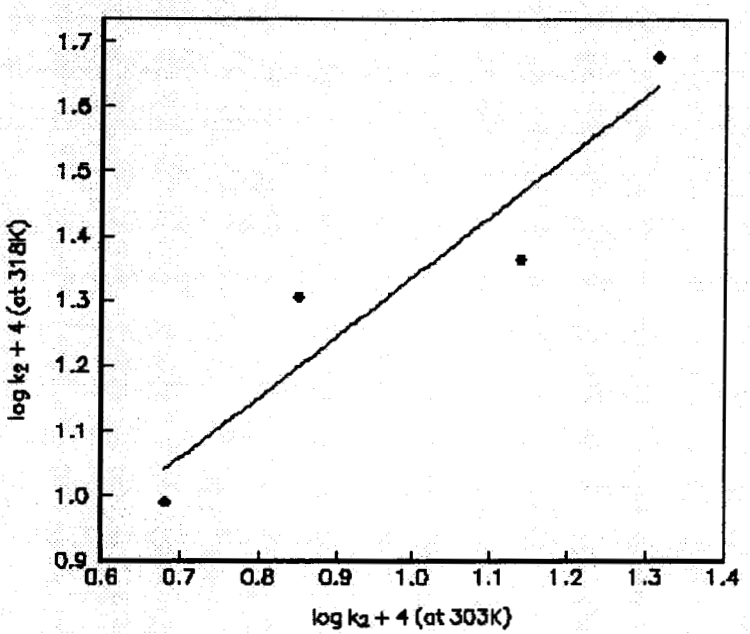


Fig. 4.2.8(h). Exner's plot (TBPB)

4.2.2.8. Effect of temperature on the rate of oxidation of benzhydrol in organic solvent

The effect of temperature on the rate of oxidation of benzhydrol in benzene as solvent using potassium dichromate with the catalysts TBAB and TBPB was studied in the temperature range of 303 to 318 K. The values are tabulated in table 4.2.15 and plots in Fig. 4.2.9(a) and 4.2.9(b).

TABLE 4.2.15

Effect of temperature on the rate of oxidation of benzhydrol

TBAB			TBPB		
Temp	$k_2 \times 10^5$	corr. coeff.	Temp	$k_2 \times 10^5$	corr. coeff.
303	10.15	.9997	303	10.7	.9997
308	14.2	.9997	308	15.73	.9989
313	17.25	.9999	313	19.5	.9998
318	22.8	.9997	318	25.3	.9999

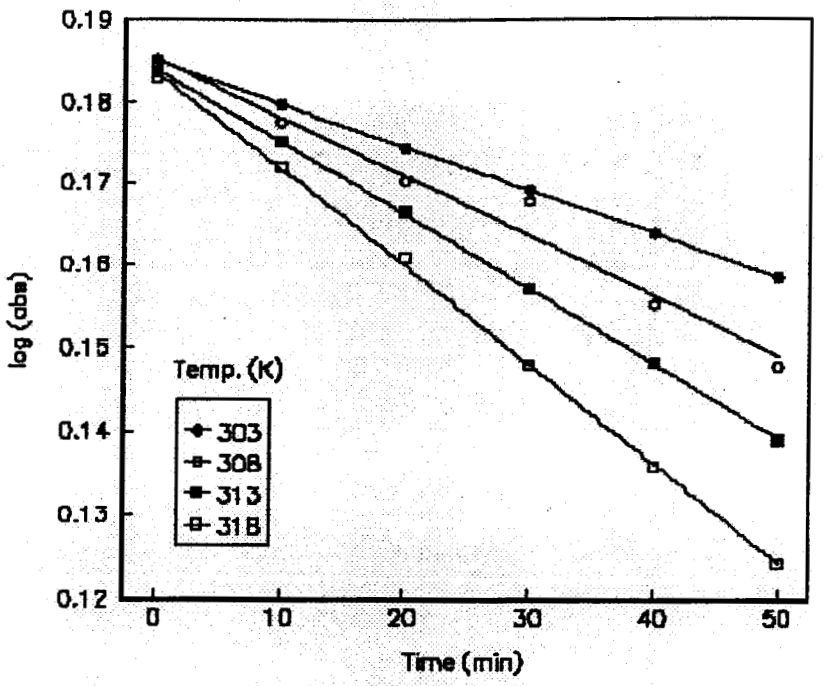


Fig. 4.2.9(a) Effect of temp on the rate of oxdn of BH in benzene (TBAB)

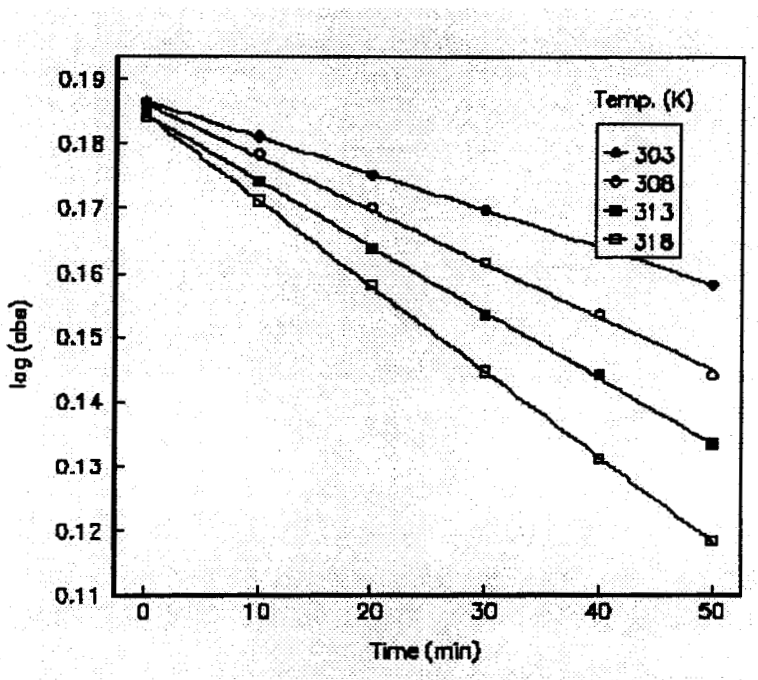


Fig. 4.2.9(b) Effect of temp on the rate of oxdn of BH in benzene (TBPB)

The corresponding log k_2 Vs 1/T and log k_2/T Vs. 1/T plots are given in Fig. 4.2.9(c) and 4.2.9(d).

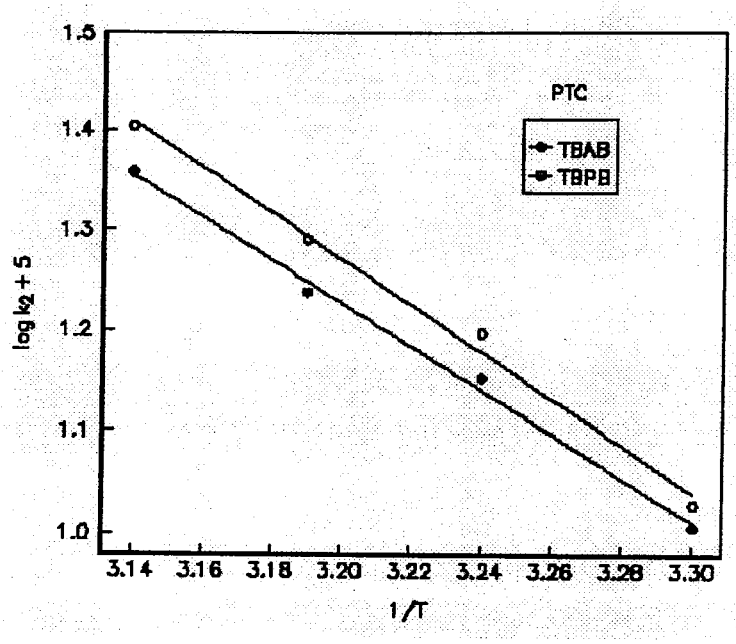


Fig. 4.2.9(c). Plot of log k_2 Vs. 1/T for the oxdn of BH in benzene

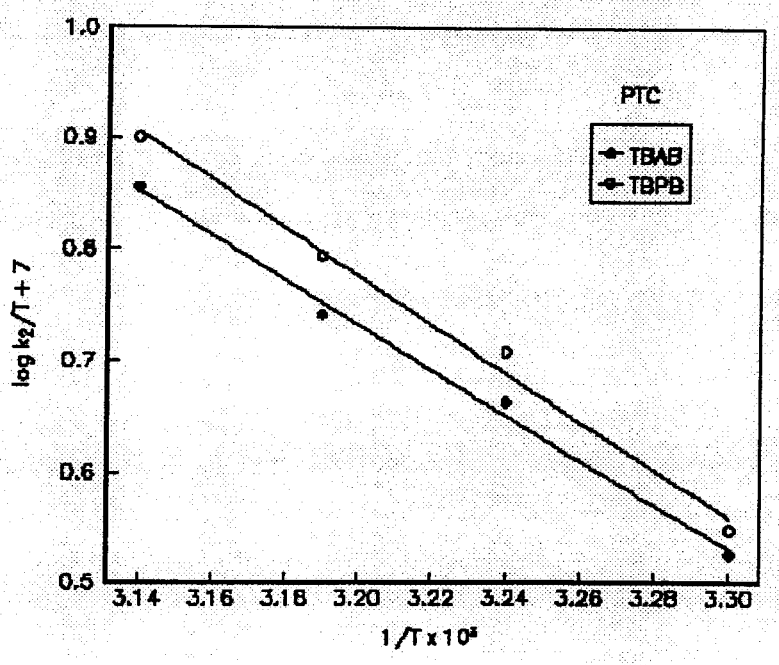


Fig. 4.2.9(d). Plot of log k_2/T Vs. 1/T for the oxdn of BH in benzene (TBPB)

The results show that the rate of oxidation increased with increasing the temperature.

4.2.2.9 Effect of temperature on the rate of oxidation of cyclohexanol

The rate of oxidation of cyclohexanol by phase transferred potassium dichromate in benzene was studied using the catalysts. TBAB and TBPB at various temperature ranging from 303 to 318 K. The values are tabulated in table 4.2.16 and the plots in Fig. 4.2.10(a) and 4.2.10(b).

TABLE 4.2.16

Effect of temperature on the rate of oxidation of cyclohexanol

TBAB			TBPB		
Temp	$k_2 \times 10^5$ mol^{-1} dm^3 S^{-1}	corr. coeff.	Temp	$k_2 \times 10^5$ mol^{-1} dm^3 S^{-1}	corr. coeff.
303	17.25	.9997	303	11.51	.9999
308	19.75	.9991	308	15.5	.9991
313	23.03	.9998	313	17.25	.9996
318	28.0	.9983	318	20.7	.9906

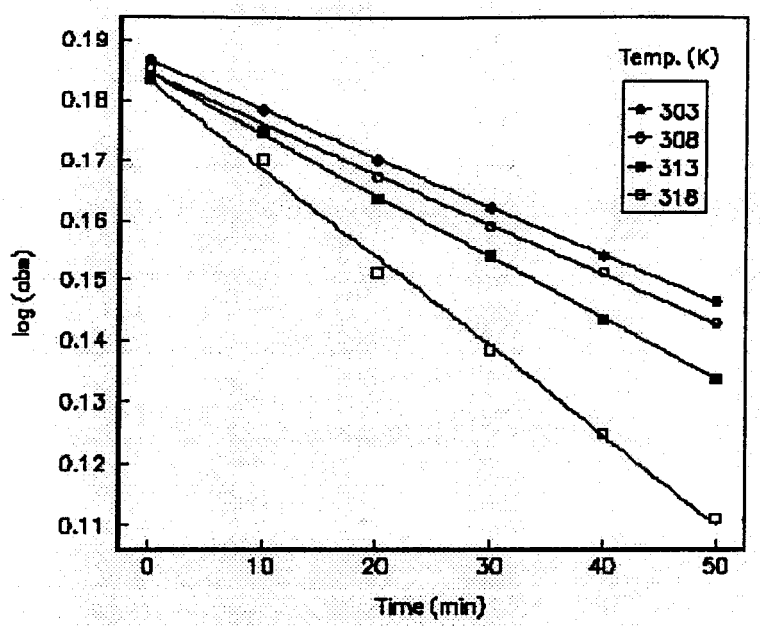


Fig.4.2.10(a) Effect of temp on the oxdn of CH in benzene (TBAB)

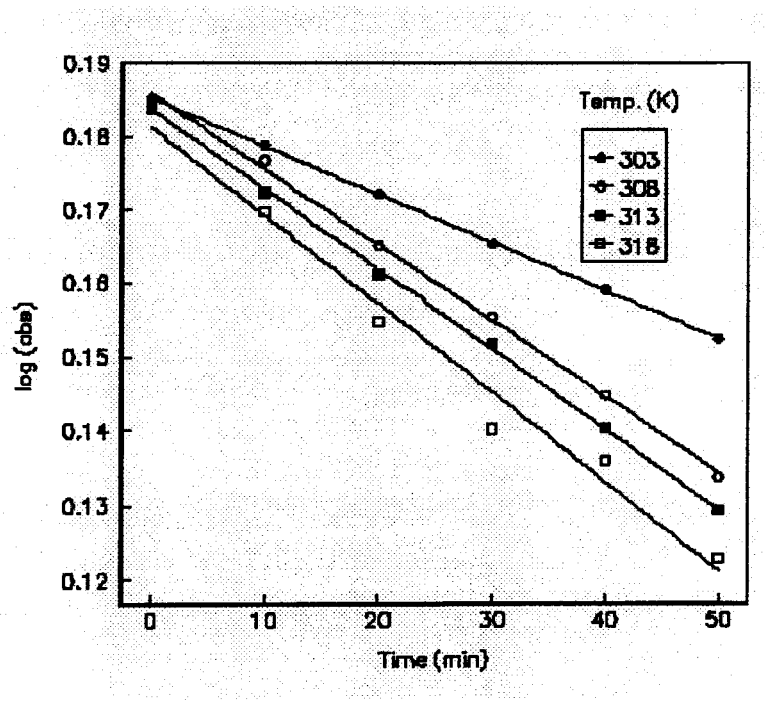


Fig.4.2.10(b) Effect of temp on the oxdn of CH in benzene (TBPB)

The plot of log k_2 Vs. 1/T is given in Fig. 4.2.10(c).

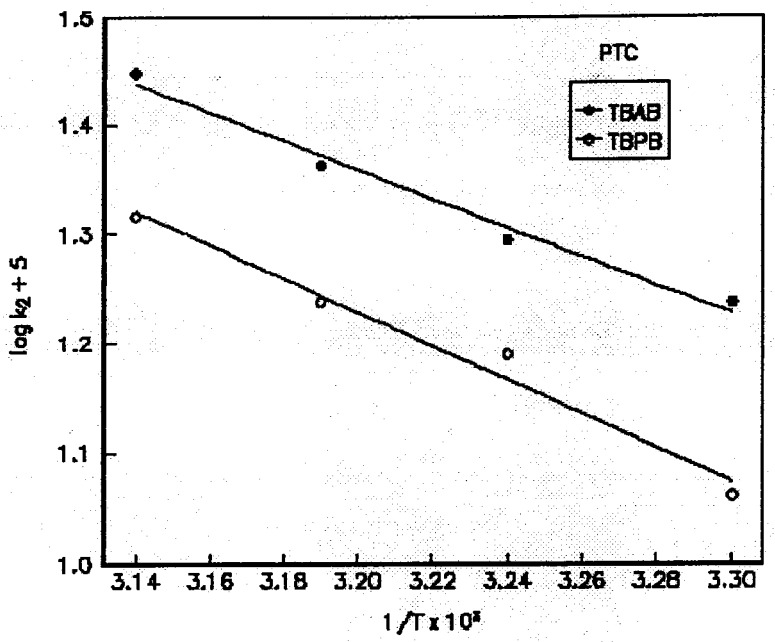


Fig. 4.2.10(c). Plot of log k_2 Vs. 1/T of CH in Benzene

Activation parameters were calculated from the log k_2 Vs. 1/T and log k_2/T Vs. 1/T plots.

TABLE 4.2.17

Activation parameters for the oxidation of benzhydrol and cyclohexanol in benzene

Catalyst : TBAB

Substrate	$k_2 \times 10^5$ mol^{-1} dm^3 s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
CH	17.25	25.07	22.55	-117.88	58.26
BH	10.15	41.16	38.61	-92.95	66.77

TABLE 4.2.18

Activation parameters for the oxidation of benzhydrol and cyclohexanol in benzene

Catalyst : TBPB

Substrate	$k_2 \times 10^5$ $mol^{-1}\ dm^3\ s^{-1}$	Ea $kJ\ mol^{-1}$	$\Delta H^{\#}$ $kJ\ mol^{-}$	$\Delta S^{\#}$ $JK^{-1}\ mol^{-1}$	$\Delta G^{\#}$ $kJ\ mol^{-1}$
CH	11.51	28.944	26.95	-110.11	60.31
BH	10.7	44.07	41.48	-89.02	68.45

Almost constant value of free energy of activation is obtained for cyclohexanol and benzhydrol using the two catalysts.

DISCUSSION

Stoichiometric analysis under the kinetic investigation showed a 3:2 ratio between [alcohol] and [oxidant]. Hence the overall reaction for the oxidation of 1-phenyl ethanol can be written as

$$3PhCHOHCH_3 + 2Cr(VI) \rightarrow 3PhCOCH_3 + 6H^+ + 2Cr(III)$$

The product of oxidation in organic media was confirmed to be acetophenone by DNP test and obtained almost in good yield.

For oxidations under PTC, the peak height at 364 nm in the absorption spectrum of the reaction mixture, was used to calculate the rate of reaction. The sequential scan of the absorption spectrum obtained for the oxidation of 1-phenyl ethanol with $HCrO_4^-$ under PTC in benzene at 303 K is as shown in

Fig. 4.4.1. The presence of isobestic point at 325 nm and 382 nm ruled out any complicated mechanism in the reaction.[130,174,176]

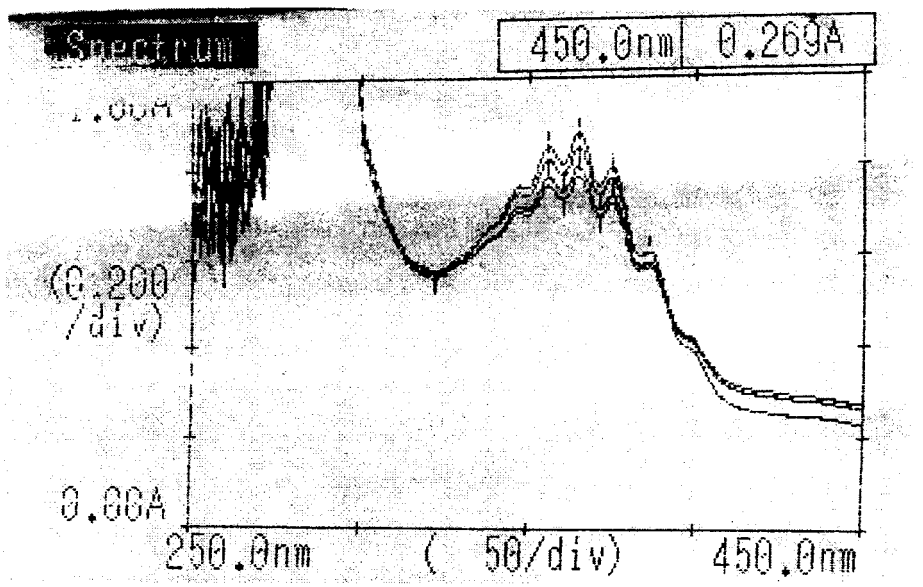


Figure 4.4.1. Sequential scan of the absorption spectrum of the kinetics of the oxidation of 1-phenyl ethanol by $HCrO_4^-$ in benzene at 35°C

The rate data obtained for the effect of [oxidant] and [substrate] in organic medium shows that the rate is first order with respect to both [oxidant] and [substrate].

The effect of solvent polarity shows that the rate increased with increasing polarity of the solvent. This suggests the possibility of interaction between an anion and a dipole and also shows the cation solvating power of the polar solvents.

The reaction mixture failed to induce polymerisation of acrylonitrile which in turn confirms that no free radicals are formed during the reaction.

The substitution effect shows that the rate is accelerated by electron donating groups whereas the rate is retarded by the electron withdrawing groups. The Hammett plot with a negative reaction constant explains the above phenomena.

The effect of temperature shows that the rate increases with increasing temperature. The activation parameters are calculated by plotting log k_2 Vs 1/T and log k_2/T Vs 1/T. The negative value of entropy of activation confirms the existence of a degree of orderness in the transition state. The free energy of activation is found to be almost constant. This shows that the same mechanism is operating in 1-phenyl ethanol and its para-substituted derivatives under investigation. The plot of $\Delta H^{\#}$ Vs. $\Delta S^{\#}$ is linear and the isokinetic temperature calculated are 777 K and 750 K using TBAB and TBPB respectively.

The effect of temperature in the range of 303 to 318 was studied in the case of Benzhydrol and cyclohexanol also. The rate is found to be increasing with increasing temperature in the case of benzhydrol and cyclohexanol using TBAB and TBPB.

Mechanism

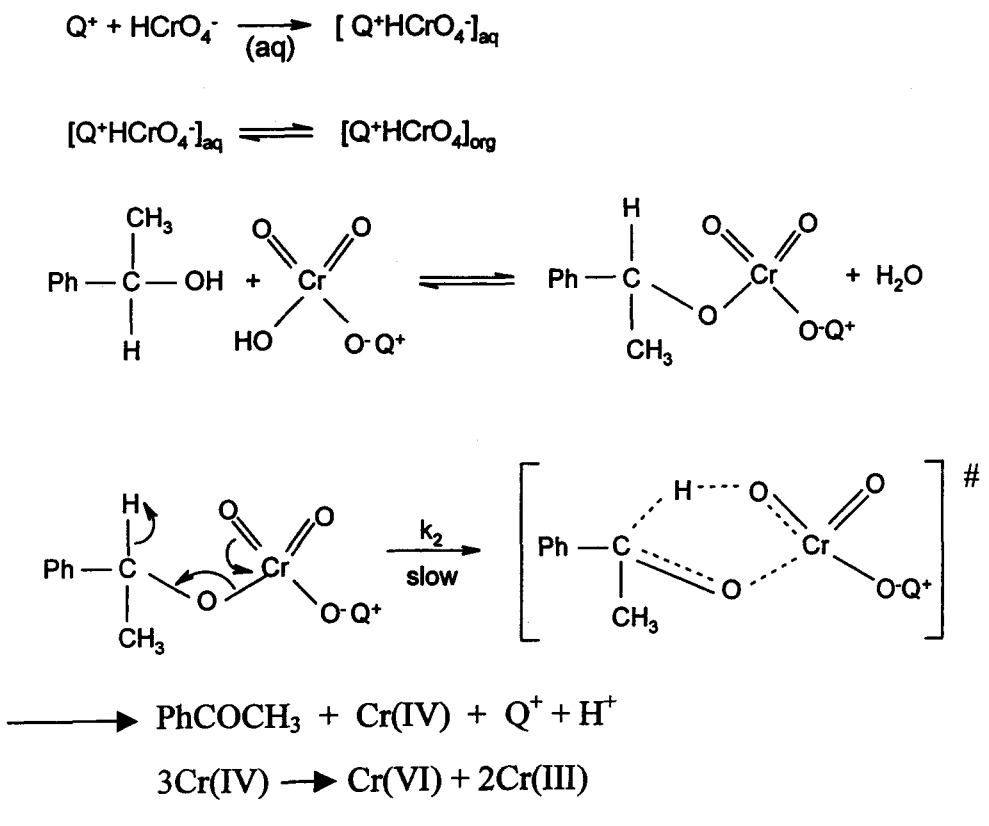
The cation of the phase transfer catalyst form the ion pair with the oxidant $HCrO_4^-$ formed in aqueous medium and is transferred into the organic medium. The negative value of entropy of activation suggests a route through the interaction of oxidant and substrate forming a complex which disproportionates to form the product. In the case of primary alcohol, existence of a substantial primary kinetic isotope effect is established.[177,178] Thus an αC–H bond cleavage was suggested in the rate determining step of primary alcohol. The negative value of reaction constant suggests the formation of a carbocation in the transition state. Hence the transfer of hydride ion from alcohol to oxidant can be suggested. This hydride ion transfer mechanism is further confirmed by the high cation solvating power of the solvents which resulted in an increase in the rate of oxidation with increase in dielectric constant of the medium.

The hydride ion transfer can proceed by a cyclic intermediate formation process or by an acyclic one step bimolecular process.

It has been reported that the chromate ester formed during the reaction has greater stability in organic solvents than in water.[89,99,179] The negative values of entropy of activation are in agreement with the degree of orderness supporting the formation of a cyclic intermediate formation. Bordwell has reported[172] a cogent evidence against the occurrence of concerted one step

bimolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterised by transfer of hydrogen in a cyclic transition state are the only truly symmetrical process involving linear hydrogen transfer.[187] Litter has also shown that a cyclic hydride transfer in the oxidation of alcohols by Cr(VI) involves six electrons and being Huckel type system, is an allowed process.[181] Then the overall mechanism is proposed to involve the formation of a chromate ester in the fast step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state to form the product (Scheme 1).

The suggested mechanism can be presented as:



Scheme I

A suitable rate equation for the oxidation of the 1-phenyl ethanol using phase transferred monochromate can be written as

$$\frac{-d[HCrO_4^-]}{dt} = k_2 \text{ (complex)}$$

$$= K k_2 [PhCHOHCH_3] [HCrO_4^-]$$

4.3. KINETICS OF OXIDATION OF 1-PHENYL ETHANOL IN 10% AQUEOUS ACETIC ACID MEDIUM USING POTASSIUM DICHROMATE

4.3.1. Stoichiometry and product analysis

Stoichiometry of the reaction has been investigated by equilibrating known amounts of 1-phenyl ethanol and potassium dichromate at room temperature in presence of acetic acid and mineral acid - sulphuric acid. Potassium dichromate is taken in excess. The system is kept for 2 days. A blank without the carbinol is taken and the initial concentration of potassium dichromate is determined iodometricaly by titrating a known volume of mixture against standard thiosulphate. The amount of potassium dichromate remaining is determined at regular intervals of time till a constant value is obtained indicating completion of the reaction. From these titre values stoichiometry was calculated and [carbinol] : [potassium dichromate] is found to be 3:2.

The reaction mixture containing known amounts of alcohol, potassium dichromate, acetic acid and water was stirred using magnetic stirrer for six hours. The product treated with ether and the ether layer evaporated and the product was identified as acetphenone by DNP test. This product is dried and weighed. The yield was above 85%.

4.3.2.1. Effect of oxidant concentration on the rate of oxidation of 1-phenyl ethanol in 10% HOAc

The influence of oxidant on the rate of oxidation was followed iodometrically by isolating dichromate taking alcohol in excess. The variation of oxidant concentration with time is shown in Fig. 4.3.1 and tabulated in table 4.3.1. The log oxidant Vs. time plot was found to be linear indicating first order dependence of rate on oxidant concentration.

TABLE 4.3.1

Effect of oxidant concentration on the rate of oxidation of 1-phenylethanol in 10% Acetic acid medium

[Substrate] x 10^2: 4 mol dm^{-3} Temp: 308K
[HOAc] : 10% $[H_2SO_4]$ x 10 : 5 mol dm^{-3}

$[K_2Cr_2O_7)x10^2$	1	2	3	4
k_{ob} 10^4 S^{-1}	2.698	2.682	2.752	2.706
Correlation coefficient	0.9999	0.9991	0.9999	0.9997

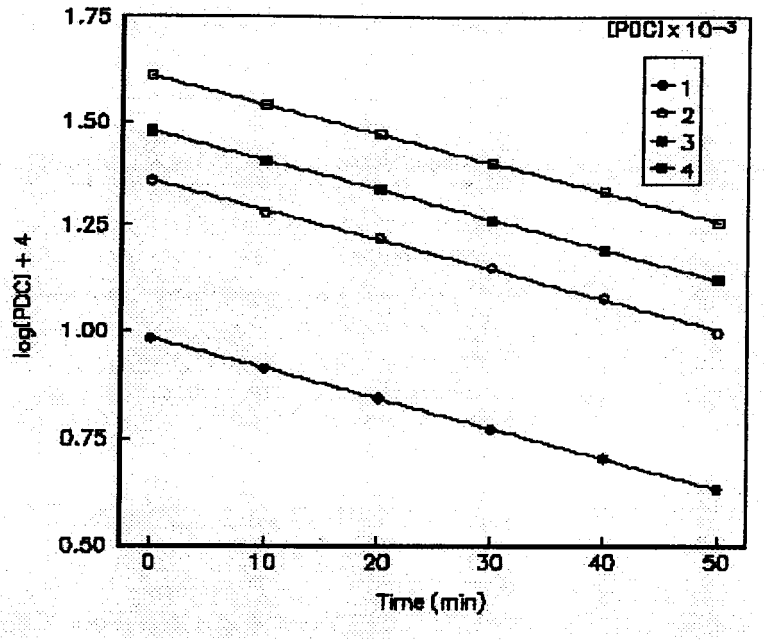


Fig. 4.3.1 Effect of [oxidant] on the rate of oxdn of PE in 10% aq HOAc

4.3.2.2. Effect of substrate concentration on the rate of oxidation of 1- phenyl ethanol in 10% aq. acetic acid medium

The effect of varying substrate concentration on the rate of oxidation was studied by changing the concentration of 1-phenyl ethanol from 2 x 10^3 to 5 x 10^{-2} moldm^{-3} keeping all other conditions the same. The pot of log [oxidant] Vs. time was linear and presented in Fig. 4.3.2 and values are tabulated in Table 4.3.2.

TABLE 4.3.2

Effect of substrate concentration on the rate of oxidation of 1-phenylethanol in 10% Acetic acid medium

$[K_2Cr_2O_7] \times 10^3$: 1 mol dm^{-3} Temp: 308K

[HOAc] = 10% $[H_2SO_4] \times 10$: 5 mol dm^{-3}

[Substrate] x 10^2	2	3	4	5
k_{ob} 10^4 S^{-1}	1.305	1.949	2.698	3.197
Correlation coefficient	0.9991	0.9999	0.9999	0.9999

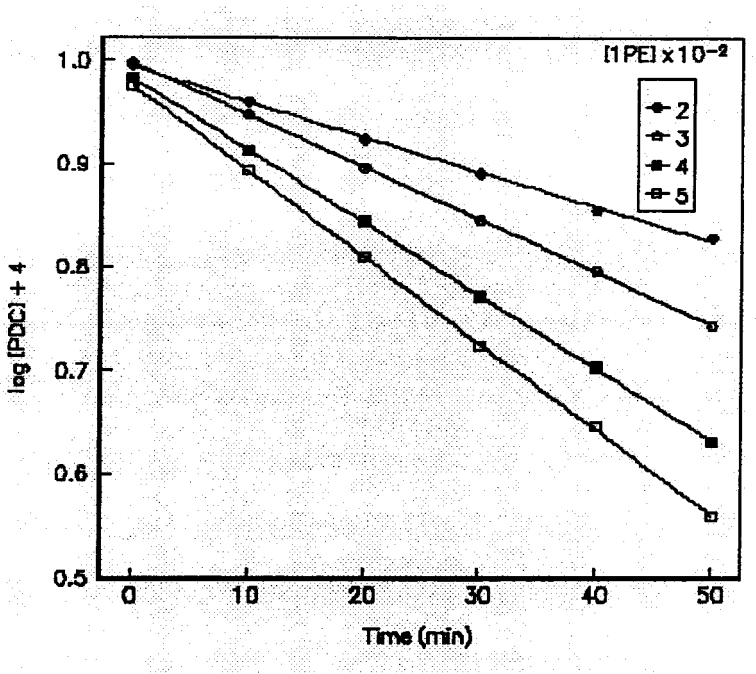


Fig. 4.3.2 Effect of [substrate] on the rate of oxdn of PE in 10% aq HOAc

The rate constant k_{obs} was found to be directly proportional to the alcohol concentration. The second order rate constant k_2 obtained dividing k_{obs} by (alcohol) are almost constant. The first order dependence of the alcohol concentration was further confirmed by the plot of log k_{obs} Vs.

log[alcohol] which is linear with a slope approximately equal to one Fig. 4.3.3.

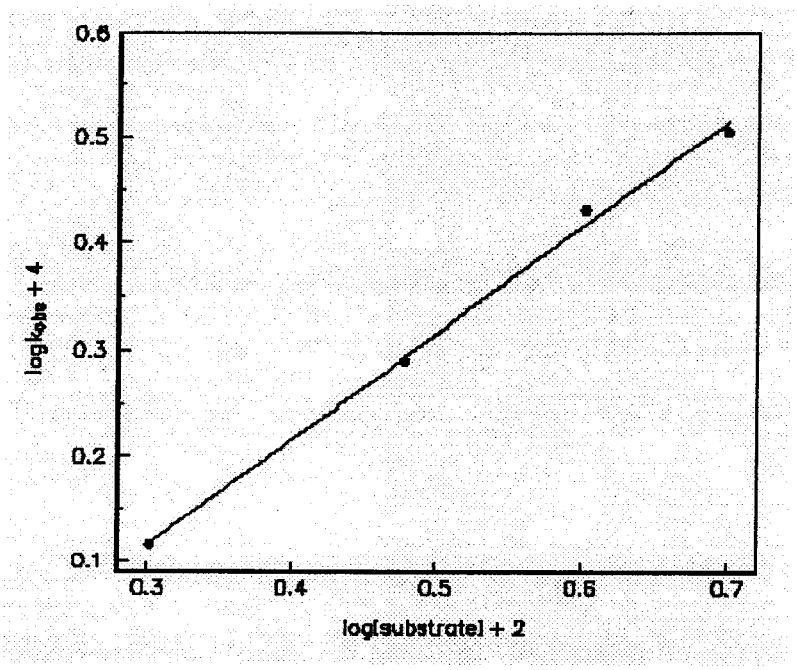


Fig. 4.3.3 Order with respect to PE

Double reciprocal plot of $1/k_{obs}$ Vs.1/[substrate] is also found to be linear (Fig. 4.3.3a).

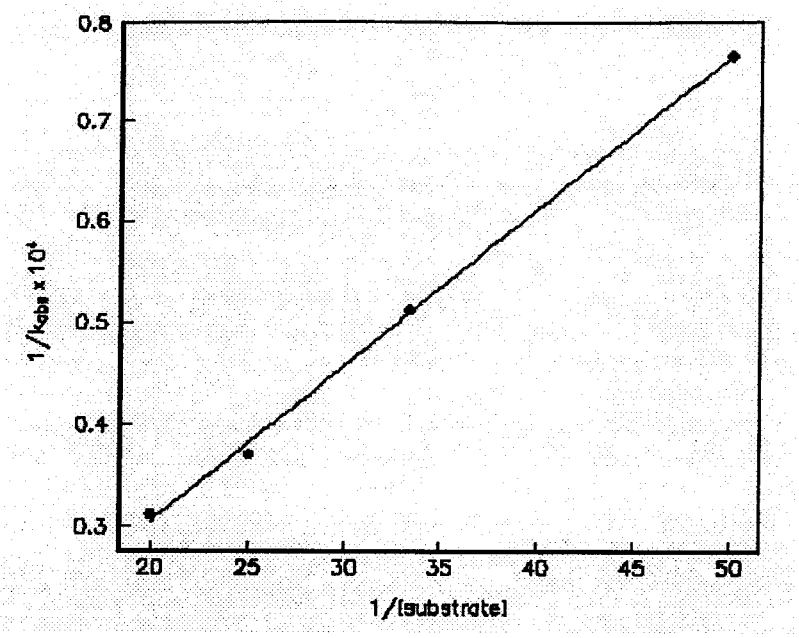


Fig. 4.3.3a. Lineweaver-Burke plot of $1/k_{obs}$ Vs 1/[PE]

4.3.2.3. Effect of added mineral acid

The investigations on the effect of added sulphuric acid on the rate of oxidation of 1-phenyl ethanol by potassium dichromate in 10% aq. acetic acid medium showed that the rate increased with increase in concentration of sulphuric acid (Table 4.3.3, Fig. 4.3.4). The plot of log k_{obs} vs. log (H_2SO_4) Fig. 4.3.5. showed that the acceleration of rate is low by small increase in concentration of H_2SO_4 and then approaches a linear variation at higher concentration of the added acid. This shows that the reaction is acid catalysed and follows a path involving singly and doubly protonated form of the reaction species at moderate and higher concentrations of the acid

respectively. A similar observation is made in the case of permanganate oxidation of 1-phenyl ethanol in aqueous acetic acid medium.[83]

TABLE 4.3.3

Effect of $[H_2SO_4]$ on the rate of oxidation of 1-phenylethanol in 10% Acetic acid medium

$[Substrate] \times 10^2$: 4 mol dm^{-3} Temp : 308K
$[K_2Cr_2O_7] \times 10^3$: 1 moldm^{-3} [HOAc] : 10%

$[H_2SO_4]\ 10^{-1}$	2.5	5	7.5	10
$k_{ob}\ 10^4\ S^{-1}$	2.322	2.698	3.18	4.414
Correlation coefficient	0.9999	0.9999	0.9994	0.9999

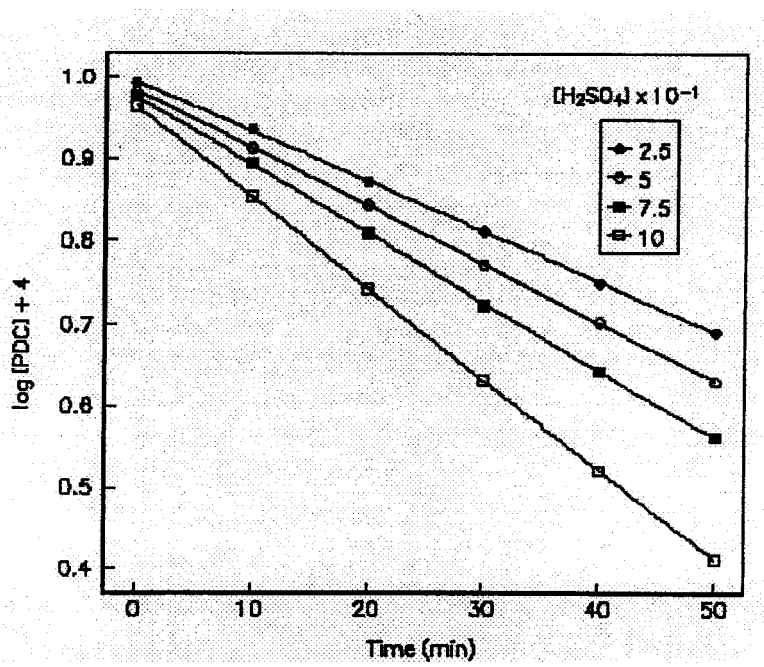


Fig. 4.3.4 Effect of $[H_2SO_4]$ on the rate of oxdn of PE in 10% aq HOAc

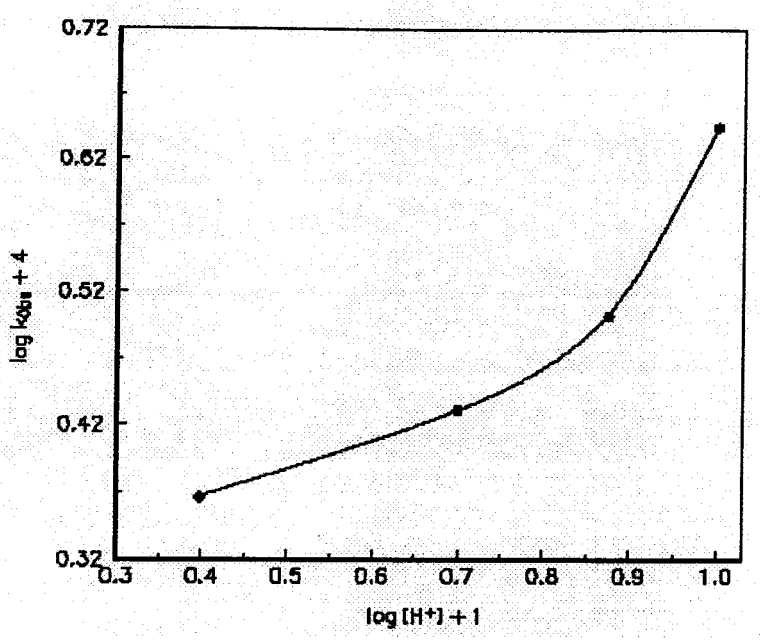


Fig. 4.3.5 Order with respect to acid

4.3.2.4. Effect of added salt

No primary kinetic salt effect was observed by increasing the addition of NaCl to the reaction system under similar kinetic conditions. The rate constant was found to be a constant suggesting the absence of ion-ion type interaction and hence possibility of interaction between ion-dipole and dipole-dipole entities.[164, 170, 171] Tabulation in table 4.3.4 and Fig. 4.3.6.

TABLE 4.3.4

Effect of ion strength on the rate of oxidation of 1-phenylethanol in 10% Acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp : 308K
$[K_2Cr_2O_7]$ x 10^3 : 1 mol dm^{-3} $[H_2SO_4]$ x 10 : 5 mol dm^{-3}
[HOAc] : 10%

[NaCl] x 10^2 moldm^{-3}	2	3	4	5
k_{ob} 10^4 S^{-1}	2.698	2.506	2.579	2.602
Correlation coefficient	0.9997	0.9971	0.9998	0.9998

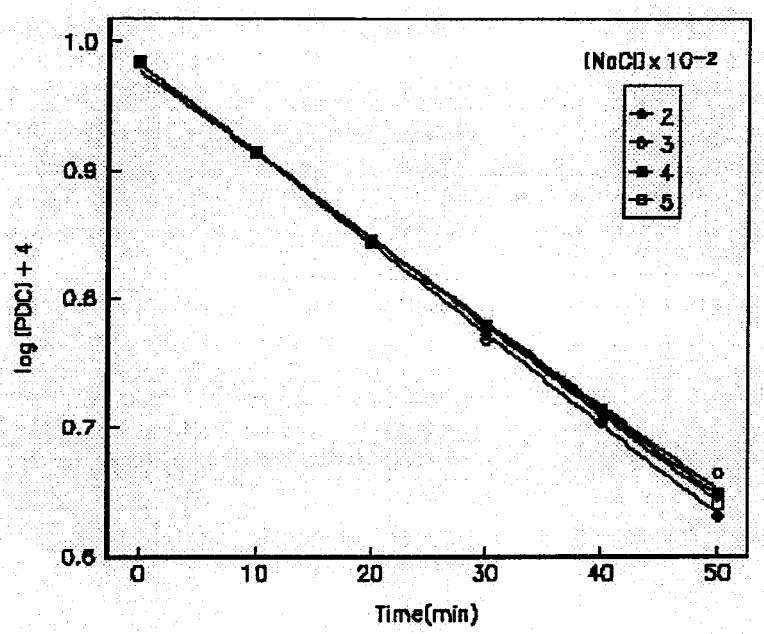


Fig. 4.3.6 Effect of [NaCl] on the rate of oxdn of PE in 10% aq HOAc

4.3.2.5. Effect of polarity of the medium

The results obtained by changing the percentage of acetic acid in the medium showed that the rate of oxidation increased considerably with increase in the percentage of acetic acid in the medium (Table 4.3.5. Fig. 4.3.7). The plot of log k_{obs} Vs. 1/D (Fig. 4.3.7a) suggests a mechanism involving an ion-dipole interaction. Increase in % acetic acid lowers the dielectric constant of the medium which favours reactions involving protonation. The dielectric constant values used were obtained according to the literature.[172]

TABLE 4.3.5

Effect of Solvent polarity on the rate of oxidation of 1-phenylethanol

[Substrate] x 10^2 : 4 mol dm^{-3} Temp : 308 K
$[K_2Cr_2O_3]$ x 10^3 : 1 mol dm^{-3} $[H_2SO_4]$ x 10 : 5 mol dm^{-3}

[HOAc] %	10	20	30	40
Dielectric constant	68	61	54	47
k_{ob} 10^4 S^{-1}	2.698	4.713	9.7007	14.43
Correlation coefficient	0.9999	0.9997	0.9976	0.9967

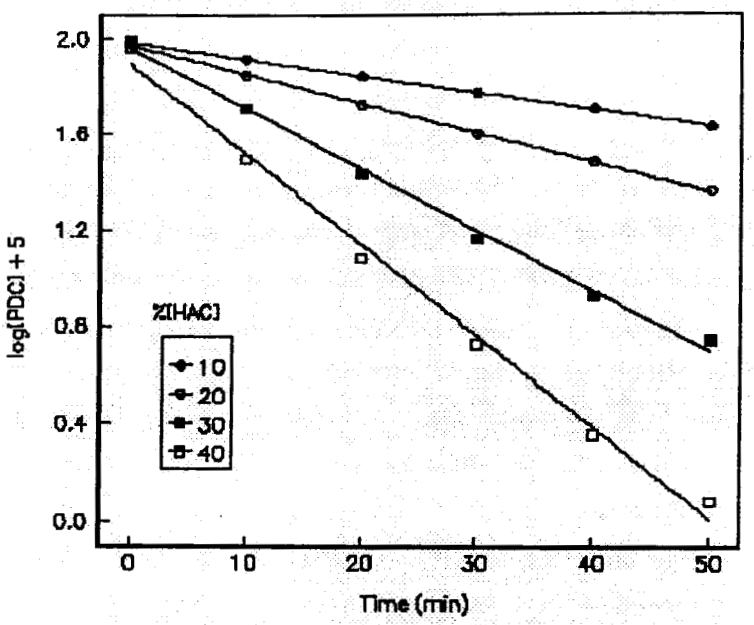


Fig. 4.3.7 Effect of solvent polarity on the rate of oxdn of PE in 10% aq HOAc

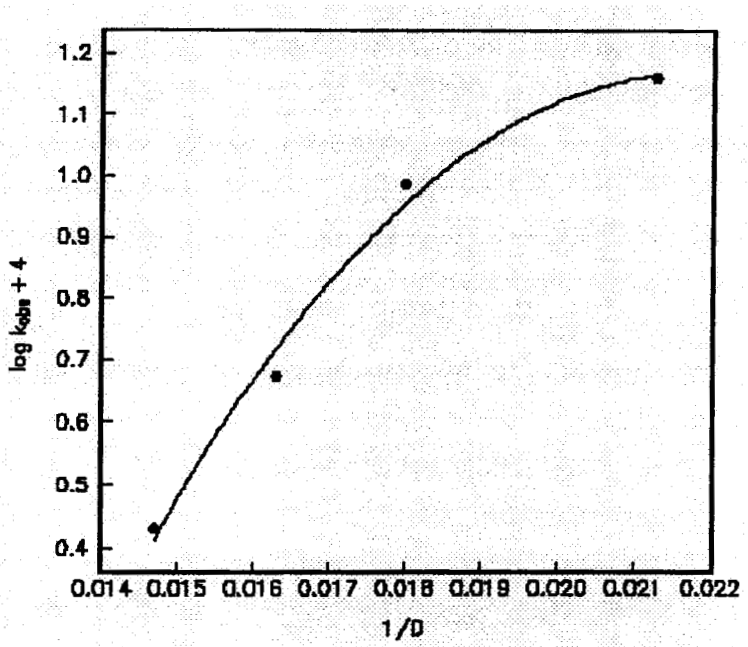


Fig. 4.3.7(a). Plot of log k_{obs} Vs. 1/D for the oxdn of PE in 10% aq. HOAc

4.3.2.6. Effect of temperature on the rate of oxidation of 1-phenyl ethanol in 10% aqueous acetic acid medium

The effect of temperature on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid medium was studied in the temperature range of 303 to 318 under identical kinetic conditions. The rate was accelerated by increase in temperature and the results tabulated in table 4.3.6 and Fig. 4.3.8.

TABLE 4.3.6

Effect of temperature on the rate of oxidation of 1-phenylethanol in aqueous acetic acid medium

[Substrate] 10^2 : 4 mol dm^{-3} $[K_2Cr_2O_7] \times 10^3$: 1 mol dm^{-3}
[HOAc] : 10% $[H_2SO_4] \times 10$: 5 mol dm^{-3}

Temp. K	303	308	313	318
k_{ob} 10^4 S^{-1}	2.652	2.698	4.337	5.957
Correlation coefficient	0.9997	0.9999	0.9998	0.9994

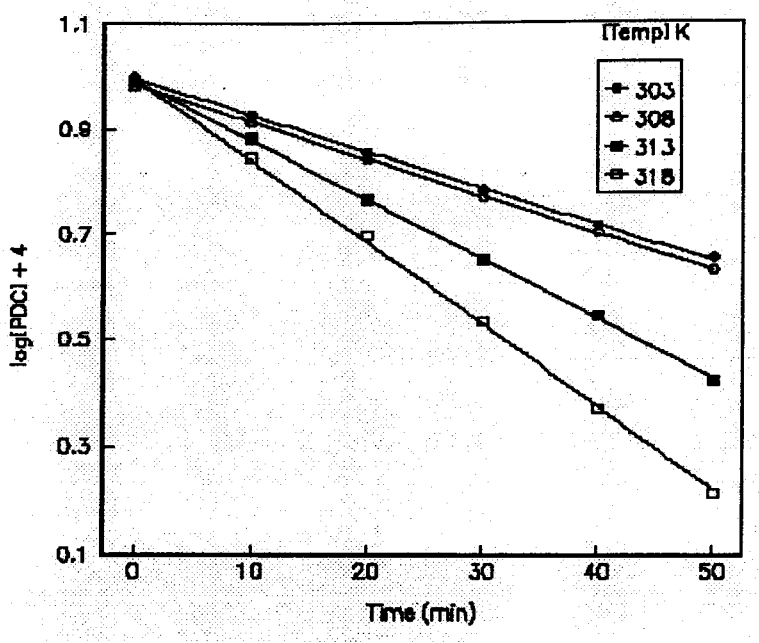


Fig. 4.3.8 Effect of temp on the rate of oxdn of PE in 10% aq HOAc

4.3.2.7. Effect of substituents on the rate of oxidation of 1-phenylethanol in aq. acetic acid medium

The effect of substituents was studied using some para substituted 1-phenyl ethanols like chloro, nitro, methyl and methoxy derivatives (Table 4.3.7. Fig. 4.3.9).

TABLE 4.3.7

Effect of substituents on the rate of oxidation of 1-phenylethanol in aq. acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp : 303 K
$[K_2Cr_2O_7]$ x 10^3 : 1 mol dm^{-3} $[H_2SO_4]$ x 10: 1 mol dm^{-3}
[HOAc] = 10%

Carbinols	PCPE	PNPE	PMPE	PMEOPE	PE
k_{ob} 10^4	2.23	0.725	5.949	13.65	2.652
Correlation coefficient	0.9996	0.9987	0.9998	0.9988	0.9999

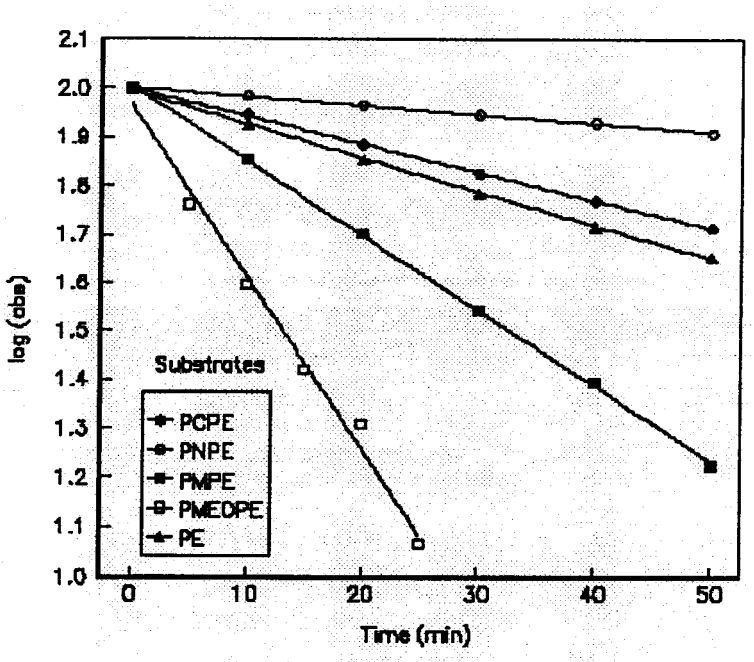


Fig. 4.3.9. Effect of substituents on the rate of oxdn of PE in 10% aq HOAc

The order of reactivity was found to be PMOPE > PMPE > PE > PCPE > PNPE. The electron withdrawing group retards the rate of oxidation and the electron donating group accelerates the rate of oxidation. The Hammett

plot of log k_{obs} Vs. σ (Fig. 4.3.10) was found to be linear. A similar case is observed in most reactions which are considered to be acid catalysed.[173]

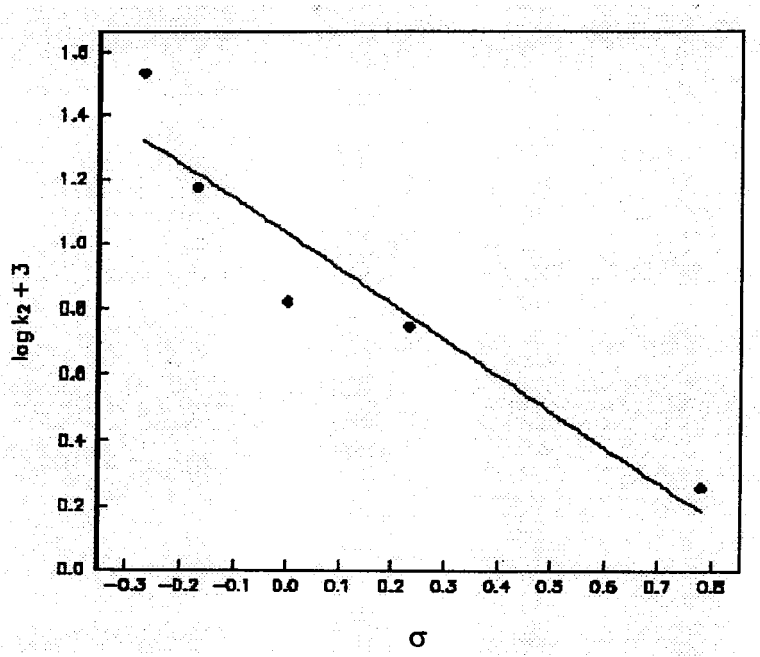


Fig. 4.3.10. Hammett plot for the oxidation of PE in 10% aq. HOAc

4.3.2.8. Effect of temperature on the rate of oxidation of 1-phenyl ethanol and its substituted derivatives

The influence of temperature on the rate of oxidation of 1-phenyl ethanol and its parasubstituted chloro, nitro, methyl and methoxy derivatives using potassium dichromate was studied for a temperature range of 303 to 318 K. The values are tabulated in Table 4.3.8 and Fig. 4.3.11 to 4.3.14.

TABLE 4.3.8

Effect of temperature on the rate of oxidation of 1-phenylethanol and its substituents in aq. acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc] = 10%
[$K_2Cr_2O_7$] x 10^3 : 1 mol dm^{-3} [H_2SO_4] x 10 : 5 mol dm^{-3}

Carbinols	k_2 x 10^3 at temp. K dm^3 mol^{-1} sec^{-1}			
	303	308	313	318
PE	6.63	6.745	10.84	14.89
PCPE	5.57	6.7	9.13	11.05
PNPE	1.813	2.98	5.76	8.43
PMPE	14.87	19.35	29.57	39.41
PMEOPE	34.14	49.17	58.69	63.22

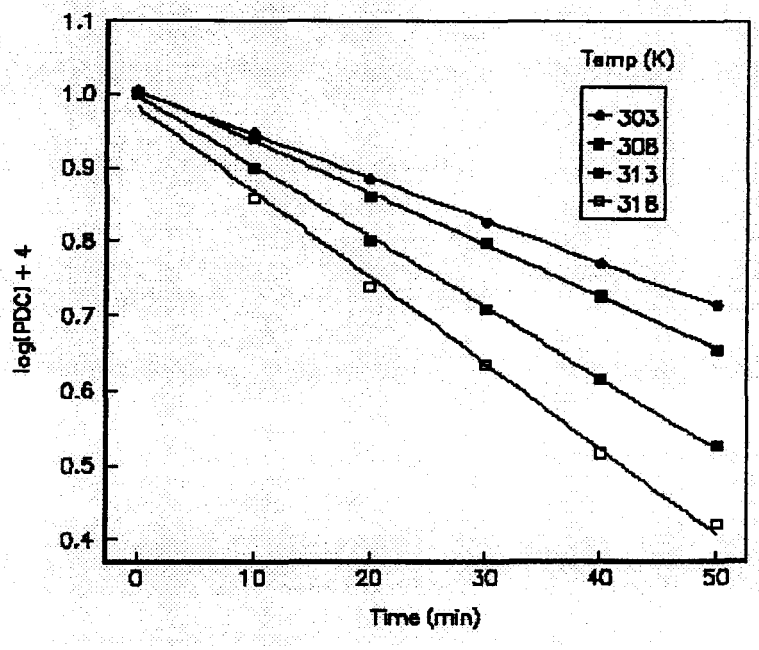


Fig. 4.3.11 Effect of temp on the oxdn of PCPE in 10% aq HOAc

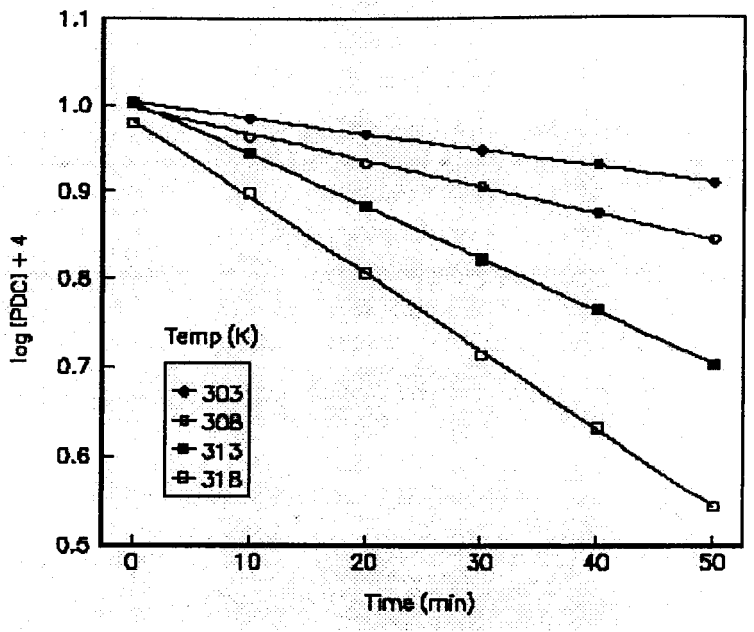


Fig. 4.3.12 Effect of temp on the oxdn of PNPE in 10% aq HOAc

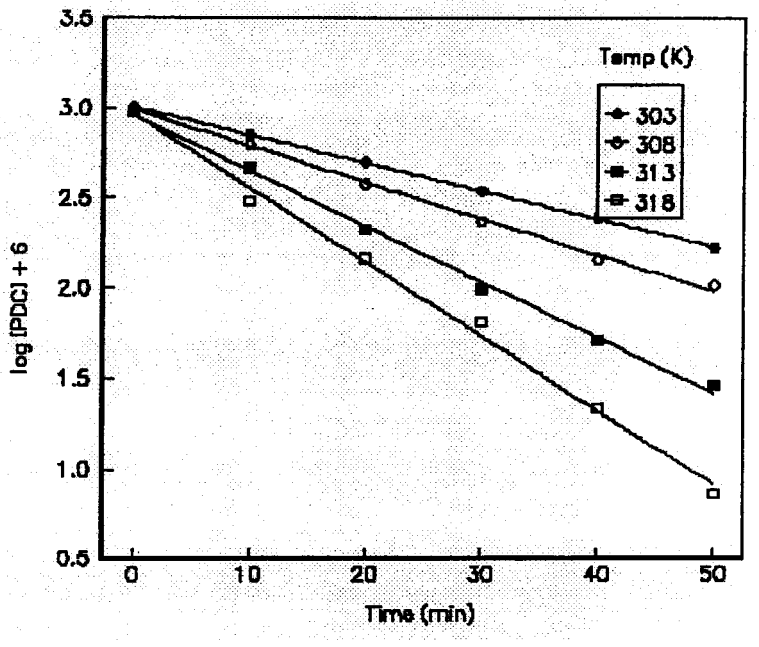


Fig. 4.3.13 Effect of temp on the oxdn of PMEPE in 10% aq HOAc

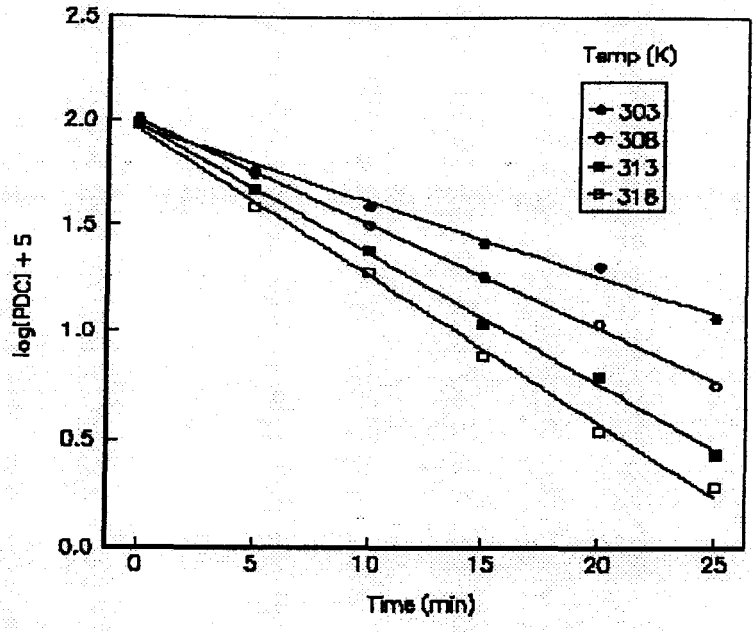


Fig. 4.3.14 Effect of temp on the oxdn of PMEOPE in 10% aq HOAc

The activation parameters computed from the plots of log k_2. Vs. 1/T and log k_2/TVs. 1/T (Fig. 4.3.15 and Fig. 4.3.16) and presented in Table 4.3.9.

TABLE 4.3.9

Activation parameters for the oxidation of 1-phenylethanol and its substituents derivatives in aq. acetic acid medium

Carbinols	$k_2 x 10^3$ at 303 K dm^3 $mol^{-1}s^{-1}$	Ea $kJmol^{-1}$	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J $mol^{-1}K$	$\Delta G^{\#}$ $kJmol^{-3}$
PE	6.63	44.87	42.46	63.53	61.709
PCPE	5.57	36.67	34.21	76.02	51.244
PNPE	1.813	82.114	74.374	15.73	69.607
PMPE	14.87	51.93	49.46	50.63	64.8
PMEOPE	34.14	31.47	29.10	76.82	52.376

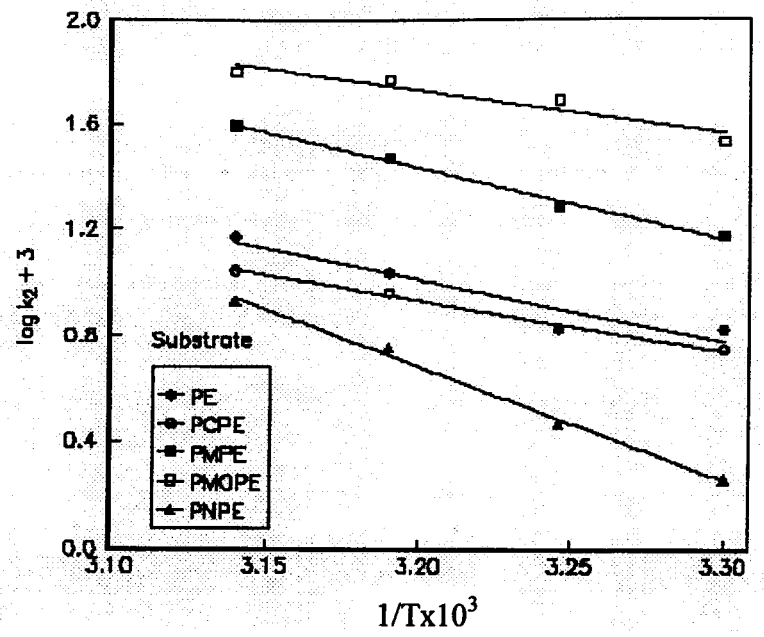


Fig. 4.3.15 Log k_2 Vs 1/T plot for the oxdn of PE in 10% aq HOAc

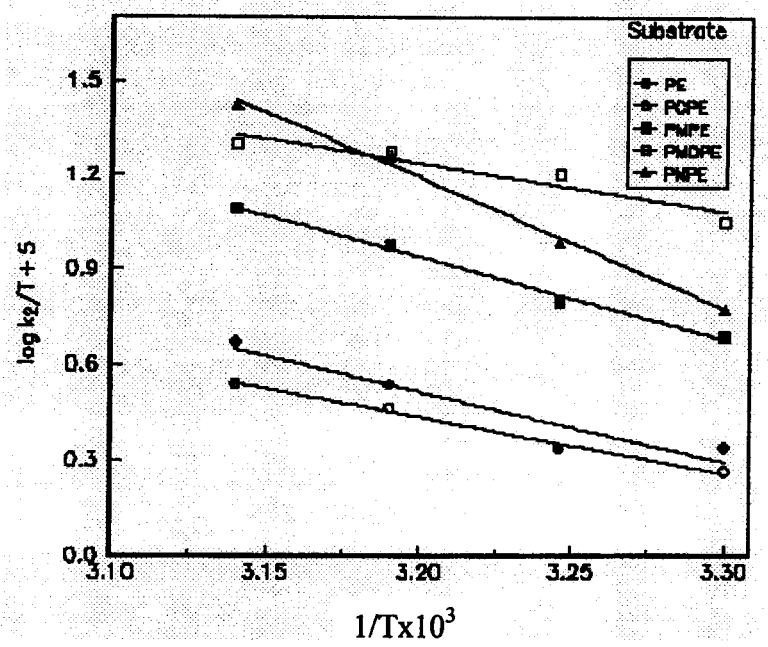


Fig. 4.3.16 Log k_2/T Vs 1/T plot for the oxdn of PE in 10% aq HOAc

A constancy of free energy of activation $\Delta G^{\#} \approx 60$ KJmol^{-1} in all the phenyl ethanols suggests that similar mechanism is operating in all cases. It was further confirmed by linear plot of $\Delta H^{\#}$ Vs. $\Delta S^{\#}$ Fig. 4.3.17.

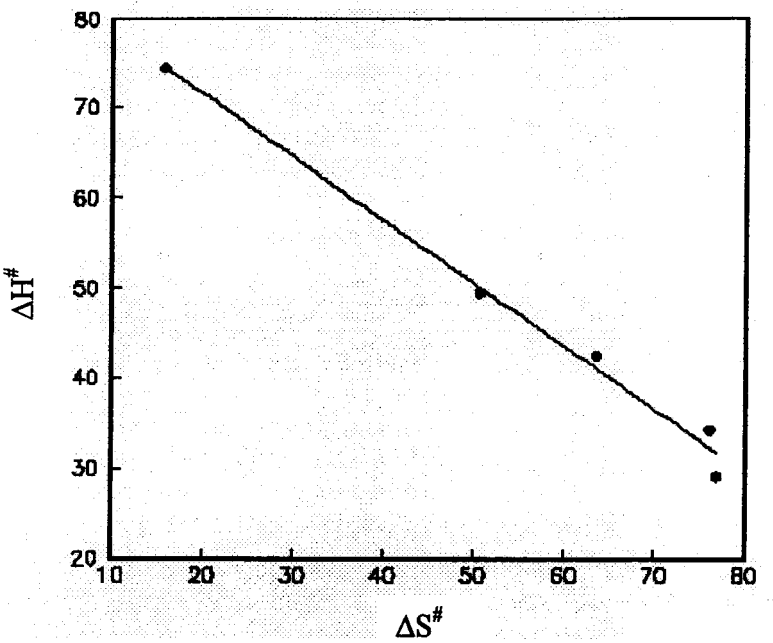


Fig. 4.3.17. Plot of $\Delta H^{\#}$ Vs. $\Delta S^{\#}$ for the oxidation of PE in 10% aq. HOAc

4.3.2.9. Effect of addition of Acrylonitrile to the reaction mixture

To the reaction mixture containing 4 x 10^{-2} moldm^{-3} of 1-phenyl ethanol, 1 x 10^{-3} moldm^{-3} $K_2Cr_2O_7$ in 10% acetic acid system, 5 ml of acrylonitrile was added and kept overnight in the dark. The absence of white precipitate shows the absence of polymerisation reaction, indicating the absence of any free radical formation during the course of the reaction.

4.3.2.10. Effect of temperature on the rate of oxidation of benzhydrol in 10% aq. acetic acid medium

Effect of temperature on the rate of oxidation of benzhydrol in 10% aq. acetic acid medium was studied in the temperature range of 303 to 318 K under the same kinetic conditions. The results are represented in table 4.3.10 and Fig. 4.3.18.

TABLE 4.3.10

Effect of temperature on the oxidation of BH in 10% aq. HOAc

$[BH] \times 10^2$: 4 mol/dm^3 [HOAc] : 10%
$[K_2Cr_2O_3] \times 10^3$: 1 mol dm^3 $[H_2SO_4] \times 10$: 5 mol/dm^3

Temp.	303	308	313	318
$k_2 \times 10^3$	3.502	4.62	5.49	7.07
Correlation	0.993	0.9987	0.9990	0.9987

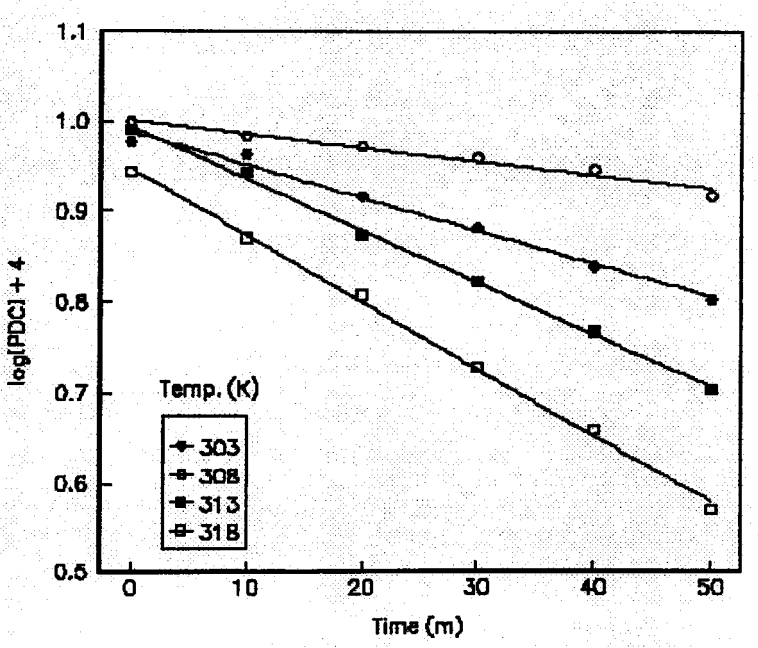


Fig. 4.3.18. Effect of temp on the rate of oxdn of BH in 10% aq. HOAc

4.3.2.11. Effect of temperature on the rate of oxidation of cyclohexanol in 10% aq. acetic acid medium

Effect of temperature on the rate of oxidation of cyclohexanol was studied in 10% aq. acetic acid medium in the temperature range of 303 to 318. The results are tabulated in table 4.3.11 and Fig. 4.3.19.

TABLE 4.3.11

Effect of temperature on the rate of oxidation of CH in 10% aq. HOAc

$[CH] \times 10^2$: 4 mol/dm^3 [HOAc] : 10%
$[K_2Cr_2O_3] \times 10^3$: 1 mol dm^3 $[H_2SO_4] \times 10$: 5 mol/dm^3

Temp.	303	308	313	318
$k_2 \times 10^3$	5.81	8.64	11.44	12.59
Correlation	0.9998	0.9999	0.9998	0.9998

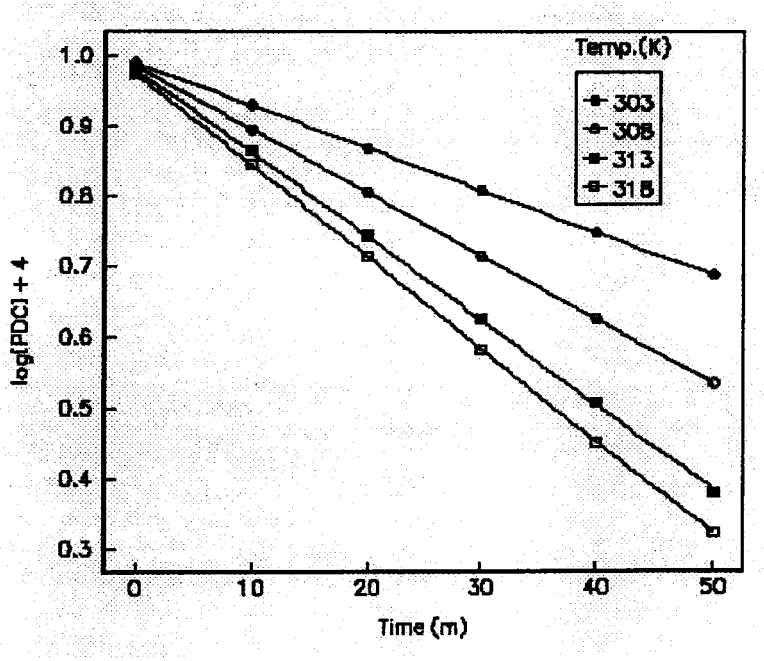


Fig. 4.3.19. Effect of temp on the rate of oxdn of CH in 10% aq. HOAc

The energy of activation Ea and the other activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are calculated from the plots of log k_2 Vs. 1/T and log k_2/T Vs. 1/T (Table 4.3.12; Fig. 4.3.20 and 4.3.21).

TABLE 4.3.12

Activation parameters for the oxidation of cyclohexanol and benzhydrol in 10% aq. acetic acid medium

Substrate	$k_2 \times 10^5$ mol^{-1} dm^3 s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
CH	5.81	41.13	38.55	-73.96	60.95
BH	3.502	35.78	33.26	-84.3	58.80

Free energy of activation of cyclohexanol and benzhydrol in aqueous acetic medium is found to be comparable with that of 1-phenyl ethanol and its substituents in organic medium.

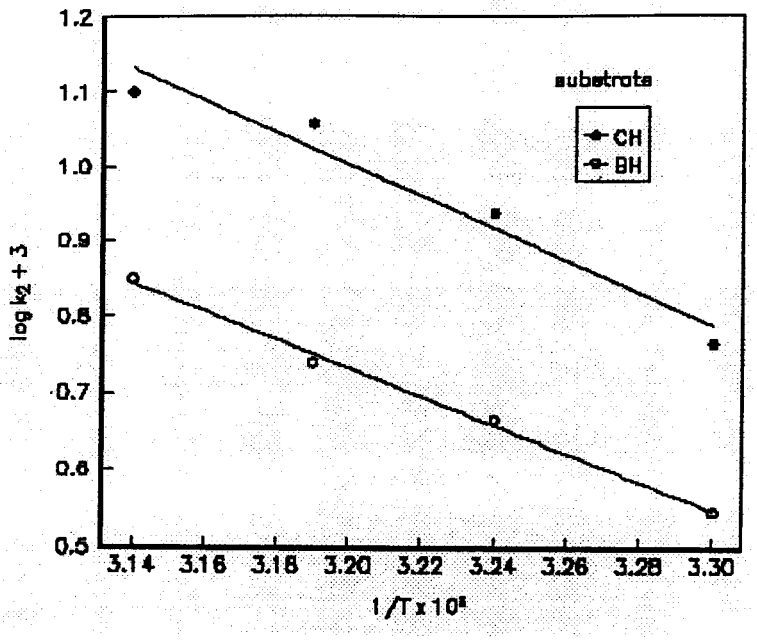


Fig. 4.3.20. log k_2 Vs. 1/T plot of CH and BH in aq. acetic acid

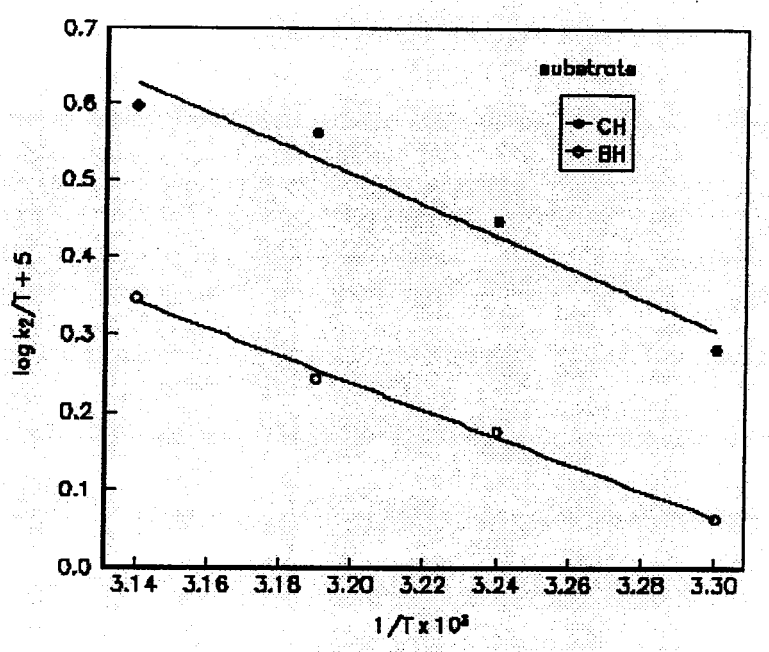


Fig. 4.3.21. log k_2/T Vs. 1/T plot of CH and BH in aq. acetic acid

DISCUSSION

The results obtained under the investigation on the oxidation of 1-phenyl ethanol in aqueous medium shows that more or less similar mechanism is operating as in the case of phase transfer catalysed oxidation in non polar medium.

Stoichiometric analysis shows a 3:2 ratio between [alcohol] : [oxidant]. Product of oxidation is identified as acetophenone and confirmed by 2,4-dinitrophenyl hydrazine test and yield was above 85%.

The oxidation was found to follow first order kinetics with respect to both oxidant and substrate concentrations.

The effect of added mineral acid shows that rate increases with increasing concentrations of H^+ ions. The plot of log k_{obs} Vs. log $[H^+]$ shows a positive slope. The increase in the rate of oxidation with acidity suggests the involvement of a protonated Cr(VI) species in the rate determining step.

The addition of varying concentrations of NaCl has not affected the rate constant values much. This ruled out the possibility of ion-ion interactions and suggests the possibility of ion-dipole or dipole-dipole interctions.

The effect of polarity of the medium on the reaction rate shows that the rate increases with decrease in the polarity of the medium. The plot of log k_2

Vs.1/D is linear with a positive slope. This suggests an interaction between a positive ion and a dipole. The increase in rate on increasing the percentage of acetic acid concentration, that is a decrease in polarity indicates the involvement of a protonated Cr(VI) species.

The reaction mixture failed to induce polymerisation of added acrylonitrile which rules out the involvement of free radical intermediate and suggests the interaction between ion and a dipole.

The substituent effect shows that the electron withdrawing groups present at the para position of the benzene ring retards the rate of oxidation whereas electron donating groups accelerate the rate of oxidation. The plot of log k_2 Vs. σ where σ is the substituent constant shows the correlation between structure and reactivity proposed by Hammet.

The rate of oxidation is found to increase with increasing the temperature under investigation. The activation parameters calculated from log k_2 Vs. 1/T and log k_2/T Vs. 1/T shows that enthalpy of activation and entropy of activation are linearly related. The isokinetic temperature calculated from ΔH Vs. ΔS plot is 782 K. This suggests similar mechanism for the oxidation of 1-phenyl ethanol and its para substituted derivatives under investigation.

Almost constant values are obtained for the free energy of activation of cyclohexanol and benzhydrol in aqueous acetic acid medium.

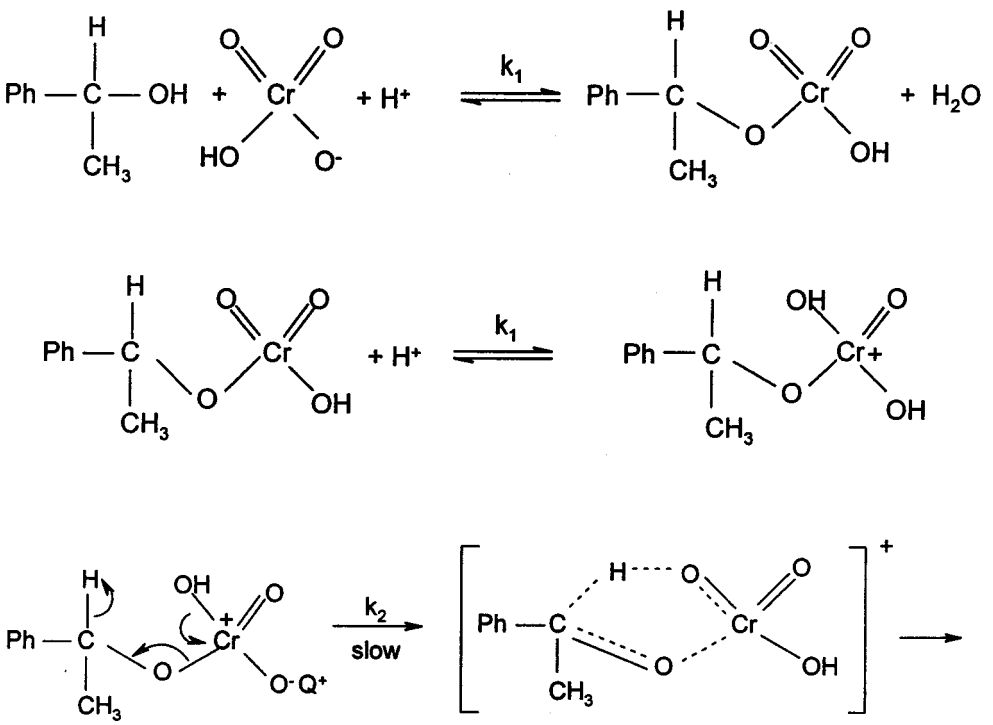
Mechanism

The active species which is responsible for the oxidation of primary and secondary alcohols using Cr(VI) compound is $HCrO_4^-$.[182,183] Failure of inducing polymerisation of acrylonitrile added ruled out the formation of free radical during the reaction. The reaction is found to obey first order kinetics with respect to both [oxidant] and [substrate]. Negative value of entropy of activation suggests the formation of an intermediate and subsequent disprotonation in the rate determining step. The αC–H bond cleavage is suggested from the reports of kinetic isotope effect exhibited during the oxidation of primary alcohols. The negative value of polar reaction constant and the chance of kinetic isotope effect in secondary alcohol indicate the formation of a carbocation in the transition state. Hence the transfer of hydride ion from alcohol to oxidant is suggested.

The increase in the rate of reaction with acidity suggests the involvement of a protonated Cr(VI) species in the rate determining step.

The negative values of entropy of activation are in agreement with the formation of a chromate ester as an intermediate. Litter[181] has shown that a cyclic hydride ion transfer in the oxidation of alcohols by Cr(VI) involves six

electrons and being a Huckel type system,. is an allowed process. The overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a disprotonation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme II). The observed increase in the rate of reaction with acidity and also increased rate in 10% aqueous acetic acid medium compared to organic medium can be explained by assuming a rapid reversible protonation of the chromate ester and the protonated chromate ester decomposing at a faster rate than the chromate ester.



$PhCOCH_3 + Cr(IV) + H_2O + H^+$

$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$

Scheme II

A suitable rate expression inconsistent with the above mechanism for the oxidation of secondary alcohols using potassium dichromate in aqueous acetic acid medium can be given as

$$\frac{-d[HCrO_4^-]}{dt} = k_2 \text{ (complex)}$$

$$= K k_2 [PhCHOHCH_3] [HCrO_4^-]$$

SUMMARY

The kinetic oxidation of 1-phenyl ethanol and some of its para substituted derivatives are carried out both in aqueous and organic medium. The temperature effect of cyclohexanol and benzhydrol were also studied.

In aqueous medium10% acetic acid was used as solvent and the effect of [oxidant], [substrate], $[H^+]$, ionic strength, temperature, dielectric constant of the medium and substituents on the rates of the reaction was carried out.

The rate of reaction is found to be first order with respect to both [oxidant] and [substrate]. In aqueous medium the rate is increased with increasing percentage of acetic acid and increasing the concentration of mineral acid. This may due to the case of formation of $HCrO_4^-$ in aqueous medium. Substituent effect shows acceleration of rate by electron donating groups and retardation of rate by electron withdrawing groups. Thermodynamic parameters calculated from temperature effect is in accordance with the mechanism proposed.

In organic medium the effect of [oxidant], [substrate], solvent polarity, temperature and substituent on the rate of oxidation was studied. The rate is found overall second order, i.e., first order with respect to both [substrate] and [oxidant]. The effect of polarity of the solvents showed that the increase in dielectric constant increases the rate. Electron withdrawing groups retard

whereas electron donating groups accelerate the rate of reaction according to substituent effects. Thermodynamic parameters are also calculated for reactions in organic medium.

The product analysis showed acetophenone as the product.

The following steps are suggested for the oxidation of 1-phenyl ethanol with $HCrO_4^-$ under phase transfer catalysis.

$$Q^+ + HCrO_4^- (aq) \longrightarrow Q^+ HCrO_4^- (aq)$$

$$Q^+HCrO_4^- (aq) \rightleftharpoons Q^+HCrO_4^- (org)$$

$$Q^+HCrO_4^- + C_6H_5CHOHCH_3 \longrightarrow C_6H_5COCH_3$$

CONCLUSION

The oxidation of 1-phenyl ethanol and some of its para substituted derivatives are carried out in aqueous as well as organic medium very smoothly and found to obey an overall second order kinetics. Out of the two phase transfer catalysts TBAB and TBPB, the rates are found to be somewhat higher for TBAB than TBPB in most cases. This may be due to the difference in the cation of PTC.

Even though the rates of reactions in aqueous phase is higher than that of organic medium in this particular reaction, this method has greater application synthetically and theoretically.

(1) The feasibility of the reaction between an inorganic ion and an organic substrate in organic medium is proved.

(2) Unwanted products can be avoided as the reaction is between anion of the oxidant and the substrate.

(3) Separation of the product is easier.

(4) Synthesis of so many organic compounds can be done in organic medium.

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Appendix – Kinetic data

1. Oxidation using phase transferred monochromate

TABLE 4.2.1

Effect of [oxidant] on the rate of oxidation of PE in organic medium

[Substrate] x 10^4 : 2 mol dm^{-3} Temp: 308 K

Solvent : benzene PTC : TBAB

[Oxidant] x 10^4 mol dm^{-3}	5	6.25	7.5	8.75
Time (min)	log (abs) at 364 nm			
0	0.1875	0.2638	0.3736	0.4275
10	0.1795	0.2553	0.3662	0.4189
20	0.171	0.246	0.3587	0.4105
30	0.1625	0.238	0.3495	0.402
40	0.1535	0.23	0.3416	0.3935
50	0.145	0.221	0.3328	0.385
k_{obs} x 10^5 S^{-1}	3.26	3.26	3.14	3.26
Corr. coeff.	0.9998	0.9997	0.9994	0.9999

TABLE 4.2.2

Effect of [oxidant] on the rate of oxidation of PE in organic medium

[Substrate] x 10^4 : 2 mol dm^{-3} Temp: 308 K

Solvent : benzene PTC : TBPB

[Oxidant] x 10^4 mol dm^{-3}	5	6.25	7.5	8.75
Time (min)	log (abs) at 364 nm			
0	0.184	0.2787	0.3765	0.4261
10	0.179	0.2723	0.3706	0.4202
20	0.174	0.2667	0.3655	0.415
30	0.168	0.2610	0.3602	0.4095
40	0.162	0.2552	0.3548	0.404
50	0.156	0.2494	0.3502	0.3974
k_{obs} x 10^5 S^{-1}	1.9575	2.226	2.03	2.14
Corr. coeff.	0.9994	0.9998	0.9945	0.9997

TABLE 4.2.3

Effect of [substrate] on the rate of oxidation of PE in organic medium

[Oxidant] x 10^4 : 5 mol dm^{-3} Temp: 308 K

Solvent : benzene PTC : TBAB

[Substrate] x 10 mol dm^{-3}	2	2.5	3	3.5
Time (min)	log (abs) at 364 nm			
0	0.1875	0.1761	0.1655	0.176
10	0.1795	0.1643	0.1511	0.1547
20	0.171	0.1547	0.1374	0.139
30	0.1625	0.1461	0.123	0.1205
40	0.1535	0.1348	0.1085	0.1006
50	0.145	0.1245	0.092	0.086
k_{obs} x 10^5 S^{-1}	3.260	3.876	5.6	6.9
Corr. coeff.	0.9998	0.9992	0.9995	0.9988

TABLE 4.2.4

Effect of [Substrate] on the rate of oxidation of PE in organic medium

[Oxidant] x 10^4 : 5 mol dm^{-3} Temp: 308 K

Solvent : benzene PTC : TBPB

[Substrate] x 10 mol dm^{-3}	2	2.5	3	3.5
Time (min)	log (abs) at 364 nm			
0	0.194	0.1810	0.1805	0.18
10	0.189	0.1735	0.1720	0.1710
20	0.184	0.1670	0.1645	0.1624
30	0.179	0.1612	0.1560	0.1532
40	0.174	0.1552	0.1475	0.1448
50	0.168	0.1488	0.1380	0.135
k_{obs} x 10^5 S^{-1}	1.9575	2.418	3.22	3.416
Corr. coeff.	0.9994	0.9991	0.9995	0.9998

TABLE 4.2.5

Effect of Solvent on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Temp: 308 K

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Solvent	Benzene	Toluene	Methylene chloride	Chloroform
Time (min)	log (abs) at 364 nm			
0	0.1875	0.1772	0.1583	0.1655
10	0.1784	0.1652	0.1285	0.1373
20	0.1749	0.1530	0.1049	0.1099
30	0.1702	0.1408	0.0718	0.0863
40	0.1643	0.1284	0.0429	0.0599
50	0.1607	0.1168	0.0086	0.0334
k_{obs} x 10^5 S^{-1}	3.26	4.644	11.39	10.05
Corr. coeff.	0.9998	0.9997	0.9988	0.9997

TABLE 4.2.6

Effect of Solvent on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Temp: 308 K

[Oxidant] x 10^4 : 5 mol dm^3 PTC : TBPB

Solvent	Benzene	Toluene	Methylene chloride	Chloroform
Time (min)	log (abs) at 364 nm			
0	0.194	0.1607	0.1623	0.1643
10	0.189	0.1510	0.1216	0.1360
20	0.184	0.1386	0.0812	0.0933
30	0.179	0.1309	0.0913	0.0607
40	0.174	0.1231	0.0040	0.0334
50	0.168	0.1179	0.0010	0.0032
k_{obs} x 10^5 S^{-1}	1.9575	3.33	13.16	12.55
Corr. coeff.	0.9994	0.9998	0.9835	0.9997

TABLE 4.2.7

Effect of Substituent on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Temp: 308 K

[Oxidant] x 10^4 : 5 mol dm^3 PTC : TBAB

Substrate	PE	PCPE	PMEPE	PMEOPE
Time (min)	log (abs) at 364 nm			
0	0.1875	0.1868	0.1908	0.1964
10	0.1795	0.1800	0.1760	0.1762
20	0.171	0.1734	0.1643	0.1592
30	0.1625	0.1672	0.1510	0.1422
40	0.1535	0.1610	0.1368	0.1354
50	0.145	0.1542	0.1233	0.1182
k_{obs} x 10^5 S^{-1}	3.26	2.494	5.143	5.834
Corr. coeff.	0.9998	0.9998	0.9996	0.9997

TABLE 4.2.8

Effect of Substituent on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Temp: 308 K

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Substrate	PE	PCPE	PMEPE	PMEOPE
Time (min)	log (abs) at 364 nm			
0	0.194	0.176	0.1990	0.189
10	0.189	0.1726	0.190	0.1795
20	0.184	0.1702	0.1812	0.1600
30	0.179	0.1667	0.1728	0.1512
40	0.174	0.1631	0.1634	0.1426
50	0.168	0.1619	0.154	0.1338
k_{obs} x 10^5 S^{-1}	1.9575	1.113	3.416	4.337
Corr. coeff.	0.9994	0.994	0.9998	0.9997

TABLE 4.2.9

Effect of Temperature on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1829	0.1875	0.1875	0.1818
10	0.1760	0.1795	0.1765	0.1726
20	0.1702	0.1710	0.1674	0.1619
30	0.1631	0.1625	0.1585	0.1498
40	0.1571	0.1535	0.1494	0.1398
50	0.1510	0.1450	0.1405	0.1258
k_{obs} x 10^5 S^{-1}	2.45	3.26	3.56	4.29
Corr. coeff.	0.9996	0.9998	0.9993	0.9998

TABLE 4.2.9

Effect of Temperature on the rate of oxidation of PE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1862	0.194	0.1842	0.1824
10	0.1820	0.189	0.1760	0.1720
20	0.1782	0.1840	0.1706	0.1648
30	0.1740	0.1790	0.1640	0.1480
40	0.1706	0.1740	0.1584	0.1382
50	0.1660	0.1680	0.1520	0.1260
k_{obs} x 10^5 S^{-1}	1.42	1.9575	2.68	4.145
Corr. coeff.	0.9989	0.9994	0.9992	0.998

TABLE 4.2.10

Effect of Temperature on the rate of oxidation of PCPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3}
[Oxidant] x 10^4 : 5 mol dm^{-3}

Solvent : Benzene
PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1875	0.1868	0.1860	0.1858
10	0.1820	0.1800	0.1780	0.1752
20	0.1768	0.1734	0.1708	0.1658
30	0.1718	0.1672	0.1616	0.1570
40	0.1660	0.610	0.1542	0.1488
50	0.1612	0.1542	0.1464	0.1400
k_{obs} x 10^5 S^{-1}	2.034	2.494	3.07	3.492
Corr. coeff.	0.9998	0.9998	0.9996	0.999

TABLE 4.2.10

Effect of Temperature on the rate of oxidation of PCPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3}
[Oxidant] x 10^4 : 5 mol dm^{-3}

Solvent : Benzene
PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1760	0.1760	0.1749	0.1749
10	0.1749	0.1726	0.1714	0.1690
20	0.1726	0.1702	0.1679	0.1643
30	0.169	0.1667	0.1643	0.1595
40	0.1669	0.1631	0.1595	0.1547
50	0.1643	0.1619	0.1559	0.1486
k_{obs} x 10^5 S^{-1}	0.959	1.113	1.458	1.957
Corr. coeff.	0.992	0.994	0.998	0.999

TABLE 4.2.11

Effect of Temperature on the rate of oxidation of PMPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1952	0.1908	0.1950	0.1950
10	0.1840	0.1760	0.1790	0.1760
20	0.1748	0.1642	0.1632	0.1572
30	0.1652	0.1510	0.1498	0.1384
40	0.1548	0.1368	0.1328	0.1196
50	0.1444	0.1234	0.1168	0.1008
k_{obs} x 10^5 S^{-1}	3.876	5.143	5.949	7.216
Corr. coeff.	0.9997	0.9996	0.9996	0.9992

TABLE 4.2.11

Effect of Temperature on the rate of oxidation of PMPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1994	0.1990	0.1982	0.1978
10	0.1920	0.1900	0.1880	0.1850
20	0.1850	0.1812	0.1778	0.1732
30	0.1778	0.1728	0.1672	0.1612
40	0.1708	0.1634	0.1568	0.1494
50	0.1630	0.1540	0.1464	0.1370
k_{obs} x 10^5 S^{-1}	2.763	3.416	3.991	4.644
Corr. coeff.	0.9998	0.9998	0.9994	0.9979

TABLE 4.2.12

Effect of Temperature on the rate of oxidation of PMEOPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1932	0.1964	0.1938	0.1938
10	0.1818	0.1762	0.1540	0.1540
20	0.1720	0.1592	0.1354	0.1154
30	0.1636	0.1422	0.1166	0.0846
40	0.1498	0.1354	0.0928	0.0528
50	0.1386	0.1182	0.0772	0.0322
k_{obs} x 10^5 S^{-1}	4.145	5.834	8.597	12.51
Corr. coeff.	0.9985	0.997	0.9988	0.998

TABLE 4.2.12

Effect of Temperature on the rate of oxidation of PMEOPE in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1886	0.189	0.1870	0.1860
10	0.1775	0.1795	0.1750	0.1725
20	0.1660	0.160	0.1625	0.16
30	0.1558	0.1512	0.1510	0.1465
40	0.1450	0.1426	0.1410	0.1330
50	0.1345	0.1338	0.129	0.1215
k_{obs} x 10^5 S^{-1}	4.145	4.337	4.452	4.9898
Corr. coeff.	0.9998	0.9997	0.9996	0.9997

TABLE 4.2.15

Effect of Temperature on the rate of oxidation of Benzhydrol in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1852	0.1848	0.1838	0.1830
10	0.1798	0.1776	0.1752	0.1720
20	0.1744	0.1702	0.1664	0.1608
30	0.1692	0.1678	0.1572	0.1480
40	0.1638	0.1552	0.1482	0.1358
50	0.1584	0.1478	0.1390	0.1242
k_{obs} x 10^5 S^{-1}	2.03	2.84	3.45	4.56
Corr. coeff.	0.9999	0.9999	0.9999	0.9997

TABLE 4.2.15

Effect of Temperature on the rate of oxidation of Benzhydrol in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1865	0.1852	0.1848	0.1842
10	0.1812	0.1784	0.1742	0.1712
20	0.1752	0.1702	0.1638	0.1584
30	0.1698	0.1618	0.1536	0.1448
40	0.1642	0.1538	0.1442	0.1312
50	0.1584	0.1442	0.1336	0.1184
k_{obs} x 10^5 S^{-1}	2.149	3.14	3.915	5.06
Corr. coeff.	0.9999	0.9998	0.9998	0.9999

TABLE 4.2.16

Effect of Temperature on the rate of oxidation of Cyclohexanol in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBAB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1838	0.1848	0.1838	0.1836
10	0.1752	0.1768	0.1698	0.1702
20	0.1664	0.1652	0.1548	0.1512
30	0.1572	0.1554	0.1402	0.1384
40	0.1482	0.1448	0.1360	0.1248
50	0.1390	0.1338	0.1228	0.1112
k_{obs} x 10^5 S^{-1}	3.45	3.95	4.606	5.6
Corr. coeff.	0.9999	0.9991	0.996	0.998

TABLE 4.2.16

Effect of Temperature on the rate of oxidation of Cyclohexanol in organic medium

[Substrate] x 10 : 2 mol dm^{-3} Solvent : Benzene

[Oxidant] x 10^4 : 5 mol dm^{-3} PTC : TBPB

Temp. K	303	308	313	318
Time (min)	log (abs) at 364 nm			
0	0.1852	0.1868	0.1838	0.1842
10	0.1788	0.1784	0.1752	0.1724
20	0.1722	0.1702	0.1664	0.1612
30	0.1654	0.1624	0.1572	0.1518
40	0.1592	0.1542	0.1482	0.1404
50	0.1524	0.1464	0.1390	0.1294
k_{obs} x 10^5 S^{-1}	2.303	3.1	3.45	4.14
Corr. coeff.	0.9999	0.9999	0.9999	0.9996

Oxidation using potassium dichromate in aqueous acetic acid medium

TABLE 4.3.1
Effect of [Oxidant] on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp.: 308 K
[HOAc] : 10% $[H_2SO_4]$ x 10: 5 mol dm^{-3}

[Oxidant] x 10^3 mol dm^{-3}	1	2	3	4
Time (min)	log (PDC) + 4			
0	0.9831	1.357	1.4779	1.6102
10	0.9131	1.28	1.4072	1.54
20	0.844	1.2193	1.3364	1.4708
30	0.772	1.1484	1.2615	1.4
40	0.704	1.0775	1.1904	1.3298
50	0.631	0.9966	1.1210	1.2568
k_{obs} x 10^4 S^{-1}	2.6983	2.682	2.752	2.706
Corr. coeff.	0.9999	0.9991	0.9999	0.9997

TABLE 4.3.2
Effect of [Substrate] on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Oxidant] x 10^2 : 1 mol dm^{-3} Temp.: 308 K
[HOAc] : 10% $[H_2SO_4]$ x 10: 5 mol dm^{-3}

[Substrate] x 10^2	2	3	4	5
Time (min)	log (PDC) + 4			
0	0.996	0.9985	0.9831	0.9764
10	0.9607	0.9478	0.9131	0.8941
20	0.924	0.8962	0.844	0.8098
30	0.891	0.8454	0.772	0.7244
40	0.855	0.7762	0.704	0.6458
50	0.828	0.7442	0.631	0.5592
k_{obs} x 10^4 S^{-1}	1.305	1.949	2.698	3.197
Corr. coeff.	0.9991	0.9999	0.9999	0.9999

TABLE 4.3.3

Effect of $[H_2SO_4]$ on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp : 308 K

[HOAc] : 10% [Oxidant] x 10^3 : 1 mol dm^{-3}

$[H_2SO_4]$	2.5	5	7.5	10
Time (min)	log (PDC) + 4			
0	0.9928	0.9831	0.9764	0.9643
10	0.9362	0.9131	0.894	0.854
20	0.8724	0.844	0.8096	0.7438
30	0.8124	0.772	0.7238	0.6328
40	0.7506	0.704	0.6448	0.522
50	0.6914	0.631	0.5624	0.4122
k_{obs} x 10^4 S^{-1}	2.322	2.698	3.18	4.414
Corr. coeff.	0.9999	0.9999	0.9994	0.9999

TABLE 4.3.4

Effect of [NaCl] on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp. : 308 K

[HOAc] : 10% $[H_2SO_4]$ x 10 : 5 mol dm^{-3}

[Oxidant] x 10^3 : 1 mol dm^{-3}

[NaCl] x 10^{-2} mol dm^{-3}	2	3	4	5
Time (min)	log (PDC) + 4			
0	0.9831	0.9842	0.9856	0.9842
10	0.9131	0.9148	0.9142	0.9138
20	0.844	0.8456	0.8468	0.844
30	0.772	0.768	0.778	0.78
40	0.704	0.712	0.714	0.714
50	0.631	0.664	0.649	0.642
k_{obs} x 10^4 S^{-1}	2.698	2.506	2.579	2.602
Corr. coeff.	0.9999	0.9971	0.9998	0.9998

TABLE 4.3.5

Effect of Solvent on the rate of oxidation of PE in aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} Temp.: 308 K

[Oxidant] x 10^2 : 1 mol dm^{-3} $[H_2SO_4]$ x 10: 5 mol dm^{-3}

HOAc %	10	20	30	40
Time (min)	log (PDC) + 4			
0	1.9831	1.9812	1.9887	1.9642
10	1.9131	1.846	1.708	1.492
20	1.844	1.7228	1.438	1.086
30	1.772	1.6018	1.164	0.727
40	1.704	1.4828	0.9248	0.359
50	1.631	1.364	0.7434	0.083
k_{obs} x 10^4 S^{-1}	2.698	4.713	9.707	14.43
Corr. coeff.	0.9997	0.9997	0.9976	0.9967

TABLE 4.3.6

Effect of temperature on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} $[H_2SO_4]$ x 10: 5 mol dm^{-3}

[Oxidant] x 10^3 : 1 mol dm^{-3} [HOAc] : 10%

Temp.	303	308	313	318
Time (min)	log (PDC) + 4			
0	0.9985	0.9831	0.9882	0.9812
10	0.9265	0.9131	0.8825	0.8456
20	0.8542	0.844	0.7664	0.6975
30	0.7858	0.772	0.6517	0.5348
40	0.7168	0.704	0.5446	0.3684
50	0.6542	0.631	0.4226	0.2135
k_{obs} x 10^4 S^{-1}	2.652	2.698	4.337	5.957
Corr. coeff.	0.9997	0.9999	0.9998	0.9994

TABLE 4.3.7

Effect of Substituents on the rate of oxidation of PE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3}
[Oxidant] x 10^3 : 1 mol dm^{-3}
Temp: 303 K
[H_2SO_4] x 10: 5 mol dm^{-3}
[HOAc] : 10%

Substrates	PE	PCPE	PNPE	PMEPE	PMEOPE
Time (min)	log (PDC) + 5				
0	1.9985	1.9998	1.9996	1.9997	1.9994
5					1.762
10	1.9265	1.9462	1.9848	1.854	1.595
15					1.419
20	1.8542	1.8841	1.9664	1.702	1.31
25					1.061
30	1.7858	1.8258	1.9472	1.544	
40	1.7168	1.7702	1.9298	1.394	
50	1.6542	1.7142	1.9084	1.225	
k_{obs} x 10^4 S^{-1}	2.652	2.23	0.725	5.944	13.65
Corre. coeff.	0.9997	0.9998	0.9997	0.9998	0.9998

TABLE 4.3.8

Effect of Temperature on the rate of oxidation of PCPE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3}
[Oxidant] x 10^3 : 1 mol dm^{-3}
[HOAc] : 10%
[H_2SO_4] x 10: 5 mol dm^{-3}

Temp. K	303	308	313	318
Time (min)	log (PDC) + 4			
0	0.9998	0.9996	0.9992	0.9992
10	0.9462	0.94	0.8994	0.8581
20	0.8846	0.8618	0.802	0.738
30	0.8258	0.7988	0.708	0.634
40	0.7702	0.7262	0.615	0.516
50	0.7142	0.6542	0.526	0.419
k_{obs} x 10^4 S^{-1}	2.23	2.68	3.65	4.421
Corr. coeff.	0.9998	0.9996	0.9996	0.9983

TABLE 4.3.8

Effect of Temperature on the rate of oxidation of PNPE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc] : 10%

[Oxidant] x 10^3 : 1 mol dm^{-3} [H_2SO_4] x 10: 5 mol dm^{-3}

Temp K	303	308	313	318
Time (min)	log (PDC) + 4			
0	0.9998	0.9996	0.9996	0.979
10	0.9848	0.9624	0.9434	0.8978
20	0.9664	0.9318	0.8828	0.8064
30	0.9472	0.9060	0.8218	0.7124
40	0.9298	0.8748	0.7642	0.6318
50	0.9084	0.8438	0.7022	0.5428
k_{obs} x 10^4 S^{-1}	0.725	1.19	2.3	3.37
Corr. coeff.	0.9997	0.9987	0.9999	0.9998

TABLE 4.3.8

Effect of Temperature on the rate of oxidation of PMEPE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc]: 10%

[Oxidant] x 10^3 : 1 mol [H_2SO_4] x 10: 5 mol dm^{-3}

Temp.	303	308	313	318
Time (min)	log (PDC) + 6			
0	2.9998	2.9996	2.982	2.98
10	2.854	2.797	2.669	2.486
20	2.702	2.58	2.325	2.164
30	2.544	2.37	1.997	1.8167
40	2.394	2.16	1.708	1.34
50	2.225	2.018	1.4645	0.8625
k_{obs} x 10^4 S^{-1}	5.946	7.741	11.82	15.76
Corr. coeff.	0.9998	0.9998	0.9985	0.9974

TABLE 4.3.9

Effect of Temperature on the rate of oxidation of PMEOPE in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc]: 10%

[Oxidant] x 10^3 : 1 mol dm^{-3} [H_2SO_4] x 10: 5 mol dm^{-3}

Temp.	303	308	313	318
Time (min)	log (PDC) + 5			
0	1.9994	1.9996	1.9831	1.987
5	1.762	1.749	1.6687	1.59
10	1.595	1.506	1.381	1.28
15	1.419	1.2604	1.0386	0.89
20	1.31	1.0386	0.796	0.54
25	1.067	0.7556	0.435	0.28
k_{obs} x 10^4 S^{-1}	13.65	19.67	23.47	25.29
Corr. coeff.	0.9968	0.9986	0.9995	0.997

TABLE 4.3.10

Effect of Temperature on the rate of oxidation of benzhydrol in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc]: 10%

[Oxidant] x 10^3 : 1 mol dm^{-3} [H_2SO_4] x 10: 5 mol dm^{-3}

Temp.	303	308	313	318
Time (min)	log (PDC) + 4			
0	0.9771	0.9996	0.99	0.9432
10	0.9439	0.9838	0.944	0.871
20	0.9177	0.9728	0.875	0.808
30	0.8826	0.9605	0.822	0.729
40	0.84	0.9495	0.768	0.66
50	0.803	0.9365	0.705	0.57
k_{obs} x 10^4 S^{-1}	1.4	1.85	2.19	2.82
Corr. coeff.	0.993	0.9987	0.9990	0.9987

TABLE 4.3.11

Effect of Temperature on the rate of oxidation of Cyclohexanol in 10% aqueous acetic acid medium

[Substrate] x 10^2 : 4 mol dm^{-3} [HOAc]: 10%

[Oxidant] x 10^3 : 1 mol dm^{-3} [H_2SO_4] x 10: 5 mol dm^{-3}

Temp.	303	308	313	318
Time (min)	log (PDC) + 4			
0	0.9895	0.9854	0.9764	0.9732
10	0.9298	0.8948	0.8658	0.8452
20	0.8684	0.8052	0.7432	0.7138
30	0.8078	0.7138	0.6242	0.5828
40	0.7472	0.6242	0.5082	0.4512
50	0.6868	0.5352	0.3798	0.3222
k_{obs} x 10^4 S^{-1}	2.32	3.45	4.57	5.03
Corr. coeff.	0.9998	0.9999	0.9998	0.9998

NB 5329