A KINETIC STUDY ON PHASE TRANSFER CATALYSED OXIDATION OF SECONDARY CARBINOLS USING ALKYLAMMONIUM COMPOUNDS

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

By

RAJENDRAN P

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

DECLARATION

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

P. Rajendran

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

Calicut University
Kerala - 673 635
22/04/2002

CERTIFICATE

The thesis presented herewith embodies the observation on **"A kinetic study on phase transfer catalysed oxidation of secondary carbinols using alkylammonium compounds"**. This is an authentic record of the research work carried out by P. Rajendran 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.

Dr. T.D. Radhakrishanan Nair

Supervising Teacher

ACKNOWLEDGEMENT

My guide, ***Dr. T.D. RADHAKRISHNAN NAIR,*** *Professor, Department of Chemistry, University of Calicut, put me on the right track and guided me to my destination diligently. But for him a novice like me in the field of research would still be groping in darkness. His able guidance, inspiring encouragement and solid support helped me a lot in giving a concrete form to my otherwise disordered ideas. My indebtedness to him is beyond the grasp of ordinary expression. I am happy to place on record his love and care that instilled confidence in me to take up and complete the project.*

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PREFACE

This thesis reports in four chapters the results of the kinetic investigation carried out by the author on the kinetic studies on phase transfer catalysed oxidation of secondary carbinols using alkyl ammonium compounds.

The first chapter gives a general introduction to the principles and theories of phase transfer catalysis. An exhaustive review of the kinetics of the oxidation of various carbinols; both in aqueous media and in organic solvents using phase transfer catalysts are included in chapter two.

Chapter three covers the experimental part of the entire work. It deals with the material and methods employed for the kinetic investigation.

The last chapter presents the results and discussion of the work done. Mechanism and rate law of the oxidation of secondary carbinols both by PTC method and conventional method have been discussed separately. Finally a conclusion of the work is given at the last of the chapter.

This is followed by the references and appendix of kinetic data.

LIST OF ABBREVIATIONS

Abbreviations

PTC	: Phase Transfer Catalysis
PT	: Phase Transfer
TCMAC	: Tricaprylmethyl ammonium chloride
TBAB	: Tetrabutyl ammonium bromide
TCMAP	: Tricaprylmethyl ammonium permanganate
TBAP	: Tetrabutyl ammonium permanganate
Q^+	: Quaternary ammonium cation
$PhCHOHCH_3$ or $ArCHOHCH_3$	: 1-phenylethanol
p-$MePhCHOHCH_3$	: p-methyl 1-phenylethanol
P-$OMePhCHOHCH_3$	: p-methoxy 1-phenylethanol
p-$NO_2pHCHOHCH_3$	: p-nitro 1-phenylethanol
p-Cl $PhCHOHCH_3$	: p-chloro 1-phenylethanol
aq. HOAC	: Aqueous acetic acid

CONTENTS

Page

CHAPTER I INTRODUCTION

CHAPTER II REVIEW AND SCOPE OF THE PRESENT WORK

CHAPTER III EXPERIMENTAL

CHAPTER IV RESULTS AND DISCUSSION

CHAPTER I

INTRODUCTION

INTRODUCTION

1.0 General

Oxidation of organic compounds are quite important from synthetic and technological viewpoints. Most of the oxidations in organic chemistry involve gain of oxygen or loss of hydrogen. However, we classify reactions as oxidation or reductions depending on whether the organic compound has lost or gained electrons from an electronic point of view. Many of the industrially important organic compounds like glycols, oximes, nitriles, azo compounds, aldehydes, ketones, carboxylic acids etc can be produced by the oxidation of related substrates by the use of suitable oxidising agents. The oxidants more commonly being used for organic oxidation include many inorganic oxidants such as permanganate[1], dichromate[2], hypochlorite[3] bromate[4] etc. Chemoselective oxidising agents like N-halo imides[5] and related compounds are also used. Certain metallic oxides like ruthenium tetroxide[6], osmium tetroxide[7], vanadium pentoxide etc. are quite common and play major role in these types of reactions.

In all these cases the use of inorganic oxidants in synthesis and kinetic studies are limited to those oxidation of organic substrates that are at least partially soluble in water. If the solubility of the substrate is too low there cannot be proper interaction between oxidant in the aqueous phase and the organic substrate in the organic medium. The classical way of overcoming the solubility problem has been by the use of a polar organic solvent system that will dissolve both the reactants and has not been successful always. The use of dipolar aprotic solvents like dimethyl foramide (DMF), dimethyl sulfoxide (DMSO), acetonitriles etc are also limited due to their high cost and toxic nature. Moreover the solubility problem also remains.

Much of these problems could be solved by the use of certain substances like crown ethers[8], quaternary onium salts[9] etc in catalytic quantities. These substances not only effect the mutual solubility of the inorganic oxidants and the organic substrates in the same phase (usually in the organic phase) but also increase the rate of oxidation. These materials, phase transfer the required reactants into the phase where the substrate is present and the technique has found extensive application under the heading phase transfer catalysis. This novel technique was introduced by M. Makosza and subsequently developed by Brandstrom and C.M. Stark to carry out reactions of organic substrates with reactant ions in non-polar media. It is a fact that the technique not only enables nucleophiles to react in non-polar medium but also with enhanced rate and hence catalysis. Now a day this technique has emerged as a versatile, convenient and cost effective synthetic method, which is commercially important. Certain reactions that are otherwise not possible by conventional method can be carried out smoothly under PTC condition. This technique simplifies and accelerates numerous reactions traditionally conducted in non-aqueous media and hence is indeed a tribute to chemists involved in research and development. Even though a large number of organic syntheses have been carried out by this technique, kinetic aspects of the subject remain without much investigation. Only a limited number of cases have been reported on the kinetics of reactions involving phase transferred inorganic reactants[10,11,12].

1.1 Ionic Reactions in non-polar Organic media – a retrospective

Reactions between substances located partly in an organic phase and partly in an aqueous phase that are mutually immiscible are frequently low and ineffective. This is due to the inability of the reactant and the substrate to mutually cross over the phase boundary to come together for effective interaction. The fundamental requirement for a bimolecular process to occur is that collisions or interaction of the reactants and the substrate species should happen.

Such heterogeneous problems in media have traditionally been solved by utilizing a co-solvent which exhibit both lipophilic and hydrophilic properties. For example methanol, ethanol, acetone, acetic acid and dioxane have all been used as co-solvents with water for reactions involving ionic salts and organic substrates. Even then reactions proceeds relatively slowly owing to the solvation of anions and solvolytic side reactions.

Under such situations use of dipolar aprotic solvents such as dimethyl sulfoxide (DMSO) dimethyl formamide (DMF), acetonitrile, hexamethyl phosphoramide (HMPA) etc. have been found more useful. These solvents while ensuring mutual miscibility and solubility of both ionic salts and organic substrates, often also helped reactions to occur with better speed. They solvate cationic part of the salt leaving the anion in a relatively "bare" or de-solvated situation. The de-solvated anions become very reactive. But there are difficulties with such solvents in that they are costly, difficult to purify and toxic in nature. Moreover it is very difficult to keep such solvents in anhydrous state and difficult to recover. In addition they also cause serious adverse environmental pollution. The situation become quite handy and free from many of the adverse effects with the use of phase transfer catalysts. The spectacular display of enhancement of reactivity of PT catalysts has been quite amazing.

1.2 Phase transfer catalysts in organic reactions

Small quantities of phase transfer catalysts transfer reactants in active form from its normal phase of existence into the normal phase of existence of the substrate so that reactions are effected with appreciable rate. The phase transferring reagent (that is the catalyst) is not consumed in the reaction and it performs the transport duty repeatedly and efficiently. The crown ethers [8, 13-15] are classic examples of PT catalysts. These are difficult to be prepared and commercially expensive. It has become evident during 1960's that quaternary ammonium or phosphonium salts[9, 16-18] (generally known as quaternary'onium salts') can be used as very effective PT catalysts. The PEO's or PEG's[19-22] otherwise known as poor chemists crown also come under this category even though these are less effective. In addition compounds like N‗alkyl phosphoramides (particularly n-dodecyl or n-hexadecyl), methylene bridged phosphorous and sulphur oxides, tris[(2-methoxy ethoxy)ethyl] amine (TDA-1)[23] are also being employed as phase transfer catalysts.

Thus the difficulties associated with the bringing together of reactants can be overcome with the aid of phase transfer catalysts. Many ionic reactants can be easily transferred into non- polar organic solvents where many organic syntheses can be carried out.

This novel technique is superior to the conventional methods in many aspects as can be seen from the following facts.

- Expensive anhydrous dipolar aprotic solvents are no longer required.
- High selectivity of reaction
- Synthetically easier to work up because lower reaction temperatures are often needed.
- Increased yield through suppression of side reactions.
- Moreover it is in fact possible for smooth and efficient conduct of reaction under milder conditions.

The simplicity of operation, the rapidity of reactions rates, the high yield of the product and the comparatively low cost of the process make the phase transfer catalysis (PTC) as a pervasive and widely accepted synthetic tool in industry. The PT method has been shown to be applicable to a wide variety of reactions like nucleophilic substitution[24-28], elimination[29-34] carbene reactions[35-40], alkylation[41-45], esterification[46-48], etherification[49-53], condensation[54-57], addition[58-60,] polymerisation[61-65] hydrolysis[66-70], isomerization[71-74], oxidation, reduction[75-80] reactions etc.

1.3 Principle of phase transfer catalysis

The foundations of this technique were laid by M. Makosza, C.M. Stark and A. Brandstrom in the late1960's. Mieczyslaw Makosza and co-workers of the Technical University in Warsaw began a systematic exploration of alkylation in two-phase systems containing mainly concentrated alkalimetal hydroxide. The term used by them were "catalytic two phase reactions" or "catalytic alkylation"[81-84].

Almost at the same time, Arne Brandstrom of AB Hassle, Sweden developed a process that he called "ion-pair extraction"[85-87] in preparative organic chemistry. His ion-pair extraction method logically led to the PTC technique. In this method anions from an aqueous phase were quantitatively extracted into chloroform or methylene chloride with the aid of quaternary ammonium salt. He showed that many anions could be extracted into organic phase as ion pairs with the quaternary ammonium ion as counterpart. The ion pairs have a tendency to associate in the organic phase and hence to overcome the unfavourable extraction barriers. Concentration of the organic phase furnishes the pure ammonium salt that is soluble in most organic solvents and can be subsequently used for reactions with organic substrate.

It was Charles M. Stark[16] who named the process as “phase transfer catalysis” and clearly outlined the scope of the method by extending it to various chemical processes. Furthermore a unifying mechanistic concept was proposed for all these types of reactions.

Phase transfer catalysis utilizing quaternary ‘onium’ salt as PT catalysts works in the following manner. The vessel contains two immiscible phases, usually an aqueous phase and an organic phase. The aqueous phase is a source of anion in the form of salt to function as the nucleophile. The organic phase contains the organic substrate. As the salt containing phase is insoluble in the substrate- containing phase, there will be no reaction in the absence of interfacial transport phenomena[88]. However if a small amount of quaternary ammonium or phosphonium halides having a lipophilic cation is added, than the reaction takes place rapidly. The lipophilic cation being soluble both in aqueous phase and organic phase, exchange its anions with the excess anion in the salt solution. The anion exchange is represented by the equilibrium as shown in equation 1.1

$$\overset{+}{Q}\overset{-}{X}_{(aq)} + \overset{+}{M}\overset{-}{Nu}_{(aq)} \rightleftharpoons \overset{+}{Q}\overset{-}{Nu}_{(aq)} + \overset{+}{M}\overset{-}{X}_{(aq)} \tag{1.1}$$

(The symbol Q^+ stands for quaternary cation)

The nucleophilic anion paired with Q^+ is transferred into the organic phase. A second equilibrium termed phase transfer equilibrium is therefore required for a PTC to be successful. This phase transfer equilibrium is shown in equation 1.2

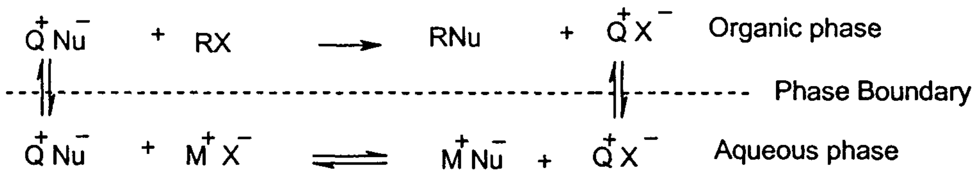
$$\overset{+}{Q}\overset{-}{Nu}_{(aq)} \rightleftharpoons \overset{+}{Q}\overset{-}{Nu}_{(org)} \tag{1.2}$$

The nucleophile in the non-polar organic medium undergoes actual reaction with the organic substrate present in that phase (Equation 1.3). In the case of nucleophilic substitution reaction, the Q^+ would ultimately be ion-paired with the nucleofuge; thus generating the Q^+X^-, which is subjected to further equilibrium as shown in equation 1.4

$$\overset{+}{Q}\overset{-}{Nu}_{(org)} + RX_{(org)} \longrightarrow RNu_{(org)} + \overset{+}{Q}\overset{-}{X}_{(org)} \tag{1.3}$$

$$\overset{+}{Q}\overset{-}{X}_{(org)} \rightleftharpoons \overset{+}{Q}\overset{-}{X}_{(aq)} \tag{1.4}$$

A classical diagram shown in the scheme 1.1 as proposed by Stark can represent this phase transfer catalytic cycle.



Scheme 1.1 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 lipophilic cation, Q^+ must be present in solution and whatever be the X^-, it must be exchangeable with Nu.

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 reactant; and second is that the transferred reagent in the new phase must be available in a highly active form.

For the fulfillment of the above requirements, at first, a PT catalyst must be cationic and must have enough organic structure so that the catalyst can be substantially partitioned into the organic phase with the desired anion. Second is that the effective cation anion binding must be "loose" enough to allow high anion reactivity.[89] In addition to the above essential requirements, additional parameters like stability of the catalyst under the reaction conditions, availability of the catalyst, cost, ease of removal or recovery and the selectivity in catalytic activity etc. are to be considered.

Though a variety of PT catalysts are available, two types are of general interest particularly in anion transfer system. They are

1. Quaternary salts
2. Macrocyclic ethers (Crown ethers)

1.4 Quaternary salts as phase transfer catalysts[90-92]

Numerous quaternary salts like quaternary ammonium, phosphonium[16-18], arsonium salts have been claimed as PT Catalysts. However in practice only a limited number of ammonium or phosphonium salts are widely being used as PT catalysts. This is based on some factors involved in their anion transfer ability, reactivity, stability etc. The simple notation $R_4\ N^+X^-$ and $R_4\ P^+X^-$ are used for ammonium and phosphonium salts respectively.

1.4.1 Factors affecting efficiency of quaternary salts as PT Catalysts

The following are the important factors affecting the efficiency of quaternary salts as PT catalysts.

- Various combination of R groups
- Different central onium atom
- Different anions in the given catalyst cation
- Polarity of the organic phase

Various combination of R groups

The primary requirement of the groups R is that they are sufficiently organic to transfer the desired anion into the organic phase. The required amount of the organic structure depends on the anion transferred, and the polarity of the organic phase. For most phase transfer catalysed reactions involving anion transfer from aqueous to organic phase it is better to select a catalyst that will be soluble in organic phase. Commonly used quaternary salts have a total of 10-30 carbon atoms.

According to A.W. Harriot and D.Picker[93], the larger R groups with almost symmetric structure are the most effective, both in anion transfer and in reactivity. Quaternary salt of the type $R\text{-}N^{+}(R^{1})_{3}\ X^{-}$ in which $R^{1} >> R$ are frequently used because of their ease of preparation or commercial availability and their efficiency in PT reactions. The striking effect of even small changes in carbon structure is illustrated from the increase in the distribution ratio

$$\alpha = \frac{[\text{QX in the organic phase}]}{[\text{QX in the aqueous phase}]}$$

The ratio increases by a factor of about 2 for each CH_2 group added in a given homologous series[94]. The organic structure of the catalyst cation not only affects its ability to transport an anion from the aqueous phase to the organic phase, but it also strongly affects the rate of the organic phase reactions. Catalyst with R^1 = butyl or larger appears to activate anions most strongly because they provide for 'near-maximum" cation-anion interionic distances. Ugalstad and co-workers[89] found that the high reactivity of the quaternary salts resulted from the greater distance of separation of the anion and cation which reduces the cation-anion interaction energy as compared to the potassium salt.

By simple application of Coloumb's law the cation-anion interaction energy E, for a univalent cation and anion may be calculated by the expression.

$$E = e^2N/\varepsilon r \quad = 33.18/\varepsilon r \quad \text{Kcal/mol}$$

where r is in A^{o} is the effective distance separating the centres of positive and negative charge, ε the dielectric constant of the medium employed,N the Avogardo's number e the charge of the electron. The expression shows that cation - anion interaction energy is inversely proportional to r and ε. For quaternary salts r is generally greater and hence cation – anion interaction energy is considerably reduced is a particular solvent, which will appear in the reduction of the free energy of activation for displacement reaction by that amount and hence a rate acceleration.

Quaternary salts with cationic part as tetrabutyl, trioctyl methyl, hexadecyl tributyl, tricaprylyl methyl are useful when the organic phase reaction is relatively slow. Aryl substituted quaternary salts are usually poor phase transfer catalyst for simple displacement reactions for reasons which are not clear. The salts having one long alkyl group and three methyl or ethyl groups or one pyridyl group at the quaternary centre, are rather good enusifying agents but often are poor phase transfer catalysts. This results from their tendency to form micelles and remain in the aqueous phase or if salted out of the aqueous phase, they may even form a third phase if the organic phase is relatively non- polar.

Different central 'onium' atom

Quaternary ammonium and phosphonium salts have been successfully employed as PT catalysts, phosphonium are somewhat more effective than ammonium bearing the same substituents[92]. They are also thermally stable than the corresponding ammonium salts. Phosphonium salts are thermally stable up to 150-170°C, where as ammonium salts lose their activity at temperature greater than 110°C. Phosponium ions are exceedingly sensitive to hydroxide ions and are irreversibly converted to R_3PO under alkali condition[95,96]. So R_4N^+ catalysts are preferred over R_4P^+ in strongly alkaline medium. Moreover ammonium salts are widely available in large variety of organic structures and are less expensive. Arsonium salts have been used on occasion as phase transfer catalysts, although they have not been extensively tested and compared with other onium salts. Trialkyl sulfonium salts $R_3S^+X^-$ have been found to be poor phase transfer catalysts.

Different anions with the given catalyst cation

The activity of a quaternary salt as a PT catalyst depends on the anion originally present. The quaternary salt is useful only if the anion accompanying the catalyst is distributed into the organic phase to a much smaller extent than the anions to be reacted (nucleophile).Generally the large lyophilic quaternary cations are soft acids in the HASB[97] concept, so that these cations tend to pair with the soft anion available in solution and transfer it into the organic phase. Therefore the catalyst in the iodide form perform less actively than those of in the chloride or bromide form in displacement reactions. The most commonly used catalysts have chloride, bromide or hydrogen sulphate as the anion moiety.

Considering the case of the quaternary salt Q^+X^- with X^- = Cl, Br or I; the I^- ion associates much strongly with the quaternary cation than the other anions. Hence the transfer of other 'active anions' from aqueous to organic phase using quaternary salt as PT catalyst is less effective.

$$R_4\overset{+}{N}\overset{-}{I}_{(org)} + OH^-_{(aq)} \rightleftharpoons R_4\overset{+}{N}OH^-_{(org)} + I^-_{(aq)} \tag{1.5}$$

The $[OH^-]/[I^-]$ exchange coefficient is low, only 0.002% of the catalyst will be in the active $R_4N^+OH^-$ form. But if $R_4N^+Cl^-$ is used as PT catalyst, about 50% of the catalyst will be in the active $R_4N^+OH^-$ form. That is the exchange coefficient of OH^-/Cl^- is high. The approximate exchange coefficient (α) of the various active anions associated with the catalyst cation ($Q = TBA^+$) is given below [93].

System	α
MnO_4^-/Cl^-	200
ClO^-/Cl^-	2.5
OH^-/I^-	.002
OH^-/Cl^-	5

Effect of polarity of organic phase

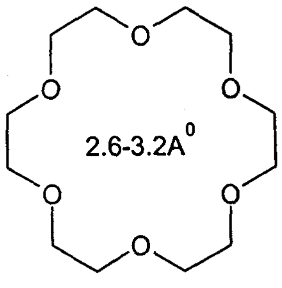
It is known that the solubility and partitioning behaviour of the quaternary salts are markedly affected by slight changes in the nature of the organic phase. Solubility and partitioning of quaternary salts are increased by increasing the polarity of the aprotic organic phase. Quaternary salts that are only slightly soluble is a given alkane may be highly soluble in an alkene having the same carbon skeleton. For example tetrabutyl phosphonium cyanide is predominantly (95%) partitioned into aqueous phase (aqueous sodium cyanide) when the organic phase is 1-bromooctane, but the salt is predominantly (90%) partitioned into the organic phase when it is 1-cyanoctane. Chloroform and methylene chloride are excellent solvents even for such smaller quaternary salts with tetraethyl and tetrapropyl ammonium as cation. By far the most commonly used solvent is methylene chloride, which is sufficiently polar to bring almost all tetrabutyl ammonium salts into its solution. Its low boiling points (40^0C) allows it to be easily removed after the reaction and is inert in most, but not all reactions.

PTC reactions are usually carried out in aprotic solvents of low polarity like, benzene, toluene, carbon tetrachloride, chloroform, methylene chloride etc.

1.5 Crown ethers as phase transfer catalysts

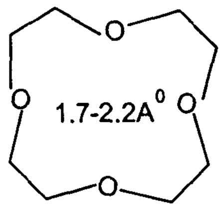
Crown ethers[8,13-15] are large heterocyclic ring compounds containing several oxygen atom usually in a regular pattern. These compounds have the property of forming complexes with cation. In most cases the ions are held tightly in the centre of the cavity. Each crown ether binds different ions depending on the size of the cavity.

The size of some simple crown eathers and the ionic diameters of some simple alkali metal ions are given below[92]



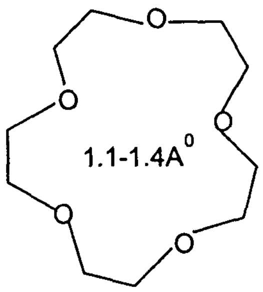
Ionic diameter: K$^+$=2.66

18 Crown 6



Na$^+$=1.94

15 Crown 5



Li$^+$=1.36

12 Crown 4

Using the simple 'lock and key' approach it is evident that 18 crown 6 has cavity dimensions of the same magnitude as that of K^+ ions, while the 15 crown 5 and the 12 crown 4 have cavity size suited for the ionic diameter of Na^+ and Li^+ respectively. Therefore in principle a particular crown should be more specific for a particular metal ion than the others.

"lock and key approach"

Thus with the advent of crown ethers simple and efficient means became available for solubilizing simple metal salts in non-polar and dipolar aprotic solvents where salvation of the anionic portion of the salt is minimum.

The dimension of 18 crown 6 is such that it can effectively co-ordinate with a potassium ion. Since the complex has a hydrophobic exterior part, it is readily solubilized by the non-polar or dipolar aprotic solvent. In order to preserve electrical neutrality, the anion must accompany the potassium crown complex into the solution.

Crown ethers are recovered by repeatedly washing the reaction mixture with an acidified saturated KCl solution. This solution is evaporated and the solid residue extracted with methylene chloride dried with anhydrous $MgSO_4$; filtered and evaporated. The resulting solid is recrystallised from acetonitrile to remove the KCl .

Because of their open structure crown ethers are even able to abstract cation from a crystalline solid. Hence these are used to carry out reactions with solid salts also.

1.5.1 General comparison of quaternary salts and Macrocyclic Ethers as phase transfer catalysts[92]

Factor	Quaternary salt	Macrocyclic ether complexes
Activity	Generally high; depends on the structure of catalyst	Generally high; depends on structure
Stability	Generally stable to ~150^{0}C	Stable
Ease of preparation or availability	Wide variety of quaternary ammonium salts available or easily prepared; other functional groups are easily introduced	Certain macrocyclic ethers are easily prepared and commercially available
Recovery	Lower salts are easily recovered; higher ones may be difficult	Easily recovered
Cost	Relatively low	Relatively high
Water use for dissolution of the inorganic reagent	Addition of some water is usually but not always required	Addition of water is not required some times added water inhibits reaction
Other features	Some quaternary salts tend to form emulsions	No emulsions

1.6 Phase transfer catalysis as applied to organic oxidation

It has been reported that many inorganic oxidant such as hypochlorite, chromic acid, chromates, dichromate, H_2O_2, permanganate, bromate, iodate etc. can be transferred into suitable organic phase using PT catalysts. Oxidation reaction can be then carried out smoothly in the organic phase by the phase-transferred oxidant. Oxidation of large number of olefins, oxoacids, unsaturated esters, aliphatic and aromatic carbinol and carbonyl compounds are possible with phase transferred permanganate.

1.7 Phase transfer assisted permanganate oxidation

Permanganate is probably one of the most powerful and useful oxidant in the laboratory. The great reactivity of permanganate as an oxidant is reflected in its ability to use different reaction paths, depending on the structure of the organic substrate, counter ions present, and on the nature of the reaction medium. The oxidizing ability and its selectivity seems to depend on the nature of the counter ions. Anionic reagents in organic reactions can be greatly activated by the modification of the counter ions. The use of permanganate ions as a selective oxidant for a variety of organic reactions have been reviewed by Stewart[1], Arndt[98], D.G. Lee[99], Freeman[100], Littler[101] and Waters[102].

Different ways of solubilizing $KMnO_4$ in low polarity organic solvents have been reported[103]. Among them the use of phase transfer agents in particular (1) crown ethers and (2) quaternary ammonium or phosphonium salts are notable. Gibson and Hosking[104] were the first to report on phase transfer assisted permanganate oxidation of organic compounds. Permanganate anion was extracted from aqueous potassium permanganate by the exchange of the chloride ion of methyl triphenyl arsonium chloride. The methyl triphenyl arsonium permanganate thus prepared in chloroform was found to oxidize water-insoluble substrates like olefin, alcohols etc.

Sam and Simmons[14] extracted upto 0.06M $KMnO_4$ in benzene using crown ethers. The resulting 'purple benzene' could be effectively used for the oxidation of wide variety of organic compounds. Later Harriot and Picker[77] reported that 'purple benzene' could be more readily obtained using quaternary ammonium salt by a simple liquid to liquid exchange. Such solutions were found to be very effective for the oxidation of olefins, amines and aryl carbinols. They observed that the extraction of permanganate from aqueous to organic phase was quantitative at low concentration of quaternary ammonium salts. With the use of excess quaternary ammonium salts (almost twice the concentration of aqueous

$KMnO_4$), the permanganate ions could almost fully transferred into the benzene medium. They found that the efficiency of extraction slightly varied with the structure of the quaternary cation salt and the nature of the organic solvent employed for extractions. This solution was rather stable and the permanganate titre value had decreased only 17% after 45 hrs. This benzene solution can be separated, dried and used for oxidation under anhydrous condition.

Dimethyl polyethylene glycol can solubilize potassium permanganate in benzene or methylene chloride and the resulting solution could be used for the oxidation of hydrocarbon as reported by D.G. Lee and V.S. Chang[19]. In the case of crown ether and polyethylene glycol a solid to liquid transfer is preferred than liquid to liquid. That is PEG and crown ethers efficiently solubilize solid $KMnO_4$ in benzene and methylene chloride.

The salts such as tetrabutylammonium permanganate[105], benzyltriethylammonium permanganate,[106] cetyltrimethylammonium permanganate[107-109]etc. in suitable organic solvents or even directly can be treated for oxidation with substrates. The salts because of the organophilicity of the quaternary cations are soluble in non- polar solvents. The salts can be prepared by adding solid quaternary ammonium halides to a concentrated aqueous solution of potassium permanganate. The precipitated quaternary ammonium permanganate is washed with distilled water, dried and kept in a refrigerator. The principal difficulties in handling such salts are their tendency for decomposition at room temperatures in the presence of sunlight.

The effectiveness of various phase transfer agents to transfer permanganate ion into the organic media were studied by Brandstrom[26], Stark and owen[24], Harriort & Picker[77], Cram and co-workers, Landini & Montanari[110], with special interest to quaternary salts as PT catalysts. They all found that quaternary ammonium permanganate practically exists as ion pairs in organic solvents of low dielectric constants.

The fact that the point at which ion-pair formation occurs is inversely dependent on the dielectric constant of the solvent means that ion- pairing is much more likely to occur in non-polar solvents with low dielectric constants. The value of ‘r’ for the permanganate ion is substantially less than $e^2/2DkT$ in solvents with low dielectric constants, accepting the value of about 2.5 A for the ionic radius of permanganate ion and about 6 A for tetraoctyl ammonium ion[111]. The $e^2/2DkT$ value of the quaternary permanganate ion in benzene is approximately 123 while ‘r’ is ~8.5A^0. Consequently, it can be assumed that quaternary ammonium permanganate exists predominantly as ion pairs in a non polar organic solvents[112,113].

The experimental studies so far reported revealed that the rate of phase transfer catalysed reactions have been directly proportional to the concentration of the catalyst cation in the organic phase[92]. These results are in agreement with the observation that the ion-pairs can react with substrate with high reaction rate. In the resulting ion-pair the anion are highly reactive. Ugelstad and co-workers[89] concluded that the high reactivity of the quaternary ion-pairs resulted from their greater distance separating the anion and the cation and therefore the reduced the cation-anion interaction energy.

It can be concluded that the concentration of quaternary ammonium permanganate ion-pair that can be obtained in non- polar solvents depends on three factors.

1. The structure of the lyophilic cation of the quaternary salt.
2. Polarity of the organic phase
3. The nature of the anion associated with the quaternary salt.

CHAPTER II

REVIEW AND SCOPE OF THE PRESENT WORK

REVIEW AND SCOPE OF THE PRESENT WORK

2.1 Review of the present work

2.1.1 Kinetics of the oxidation of alcohols

There have been studies on the rate of oxidation of various alcohols and ethers using different reagents like bromine, permanganate and mercury (II) etc. in aqueous acetic medium in the presence and the absence of mineral acids[101]. The oxidation of alcohols involved hydride ion transfer from α carbon of the substrate to the oxidant The results on the effect of alkyl substituents on the rates and kinetic isotopic effect favour this mechanistic mode.

Lee D.G. & Vanden Engh. M[114] reported that oxidant such as ruthenium tetroxide which reacts with alcohols and ethers at comparable rates are assumed to proceed by the initial cleavage of α C-H bond without prior involvement of the hydroxyl group. Since α-hydrogen in alcohols and ethers are electronically similar, it is expected that they would react at similar rate with the oxidant whose mode of action involves cleavage of α C-H bond.

The kinetics and mechanism of the oxidation of benzyl alcohol to benzaldehyde by bromine were studied[115] in aqueous acetic acid medium in the presence of added buffer salt. The observation was that the rate of oxidation is influenced by polarity of the substituents and the reaction constant ρ = -2.29 is reported. Activation enthalpies and entropies for 11 benzyl alcohols are linerly related. Benzyl Alchahol is oxidized by bromine at a rate four times faster than α,α dideuterio benzyl alchahol at 25^0 C. A mechanism involving hydride transfer from alcohol to oxidant is suggested.

The kinetics of the oxidation of benzyl alcohols to benzaldehyde by acid permanganate in the presence of fluoride ion have been studied by Banerji, K.K[116]. The reaction constant, ρ for the oxidation of benzyl alcohol and nine substituted benzyl alcohols has a value of -1.76 at 30°C. The activation enthalpies and entropies for the ten compounds are linearly related. The oxidation of α-α^- dideuteriobenzyl alcohol indicated a kinetic isotopic effect k_H/k_D = 2.70 at 30°C. The negative value of ρ points to and electron-defsicient carbon centre in the transition state. The reaction does not show any solvent isotopic effect. A mechanism involving transfer of a hydride ion from the alcohol carbon to the oxidant is suggested.

Sreenivasan N.S. & Venkatasubramanian N.[117] made kinetic studies on the oxidation of alcohols by N- chlorosuccinimide. The findings were, independence of the rate on the salt concentration, on structure of alcohols, the fractional order dependence on the concentration of added H^+ and Cl^-. This has been interpreted by assuming that the reaction proceeds through the formation of Cl_2 generated in a steady concentration in a slow rate determining step followed by a rapid uptake of the alcohol. A rate expression for the observed kinetics has been suggested accordingly.

Kinetics of the oxidation of primary aliphatic alcohols by acid permanganate was reported[118]. Based on labeled studies the conclusion is that the rate determining step involves a C-H bond rupture from the carbinol carbon as evidenced from substantial kinetic isotopic effect.

Kinetics and mechanism of the oxidation of primary alcohols by Chloramine T in acid medium has been studied.[119] The reaction is first order each with respect to the alcohols and to the oxidant. The rate is reported to be proportional to the square of the acidity. The kinetic isotopic effect $k_H/k_D = 4.31$ at 30°C. Application of the Hammett equation shows that the reaction constant $\rho = -1.60$. The activation of enthalpies and entropies are linearly related. A mechanism involving a hydride transfer from alcohol to oxidant has been suggested.

Stevan RV, Chapman KT & Weller HN[120] reported a convenient and inexpensive procedure for the oxidation of secondary alcohols to ketones with sodium hypochlorite in acetic acid in the absence of catalyst. Inexpensive concentrated solution of sodium hypochlorite sold commercially as "swimming pool chlorine". The ketones are isolated in excellent yield (85-95%). Methyl ketones are formed without the involvement of subsequent haloform reaction. Primary showed alcohols showed sluggish reactivity and formed dimeric esters via hemiacetals intermediates.

The kinetics and mechanism of the oxidation of ten ortho substituted benzyl alcohols by acid permanganate have been studied by Mathur etal[121]. The reaction was first order each with respect to the [alcohol], the [permanganate] and the [H^+]. The correlation of the rate of oxidation with Chartons extended Hammett equation, involving inductive, resonance, and steric parameters gave excellent results. The polar reaction is subjected to steric acceleration by the ortho substituents.

Kinetics of the oxidation of substituted benzyl alcohols by quinolinium dichromate in dimethyl formamide (DMF) in the presence of added acid were reported[122]. The reaction has unit dependence on each of the alcohol, QDC and acid concentration. Electron releasing substituents accelerate the reaction where as electron withdrawing group retard the reaction and the rate data obeyed Hammett's relationship. The kinetic isotopic effect k_H/k_D= 5.89 at 313K was obtained. A hydride transfer mechanism from alcohol to oxidant has been reported.

Kinetics and mechanism of the oxidation of primary aliphatic alcohols by bis (2,2-bipyridyl) copper (II) permanganate was reported[123]. The oxidation leads to the formation of corresponding aldehydes. The reaction is first order with respect to BBCP, Michaelis-Menton type kinetics was observed with respect to the alcohols. The formation constant for the alcohol–BBCP complex and the rates of decomposition have been evaluated. The reaction rate increases with increase in the concentration of hydrogen ion. With an increase in the amount of acetic acid in the solvent mixture of acetic and water, the rate increases. The oxidation of 1,1 dideuterio ethanol exhibited a substantial kinetic isotopic effect.

The oxidation of benzyl alcohol its methoxy, chloro and nitro substituted derivatives by permanganate have been studied in aqueous acetic acid medium in the presence of perchloric acid[124]. The reaction is first order in $[MnO_4^-]$ and $[XC_6H_4CH_2OH]$, but the order is complex with respect to $[H^+]$. The reaction involves protonation of the alcohol in a fast pre-equilibrium step, followed by a rate-determining oxidation step. A two electron- transfer oxidation step has been suggested for benzyl alcohol, chloro and nitro substituted alcohols while the oxidation of the methoxy compounds involves a one-electron transfer via free radical mechanism.

Kinetics and mechanism of secondary alcohols by bis,(2,2^1–bipyridyl) copper(II) permanganate in aqueous acetic acid medium was reported by Anjali *et al* [125]. The oxidation leads to the formation of corresponding ketones. The reaction is first order with respect to BBCP and the alcohols. The reaction rate increases with increase in the concentration of H^+ ions. The oxidation of benzhydrol α-d exhibited substantial kinetic isotopic effect ($k_H/k_D = 5.34$). With increase in the amount of acetic acid in the solvent mixture of acetic acid and water, the rate increases. Suitable mechanism has been proposed.

The oxidation of substituted benzyl alcohol by bis,(2,2 bipyridyl) copper (II), permanganate (BBCP)[126] leading to the corresponding benzaldehydes is first order with respect to BBCP. Michaelis–Menten type kinetics were observed with respect to the alcohols. The oxidation of α-α^- dideuteriobenzyl alcohol indicated the presence of a substantial kinetic isotopic effect. The rates of oxidation of meta and para-substituted benzyl alcohols were correlated in terms of Charton's triparametric LDR equation where as ortho substituted benzyl alcohols were correlated with a four parametric LDR equations. The results of correlation analysis point to an electron deficient reaction centre in the transition state.

Oxidation of benzyl and some ortho, meta and para monosubstituted benzyl alcohols by benzyltrimethyl ammonium chlorobromate (BTMACB) in aqueous acetic acid were studied[127]. The corresponding benzaldehydes were formed as product. The reaction is first order each in BTMACB and alcohol concentration. The reaction rate increases with increase in polarity of the medium. Suitable mechanism has been proposed.

Kinetics and Mechanism of the oxidation of primary aliphatic alcohols by tetrabutyl ammonium tribromide in aqueous acetic acid were investigated[128]. The corresponding aldehydes are produced. The reaction is first order with respect to TBATB. Mechaelis Menten type kinetic is observed with respect to alcohols. The reactive oxidizing species is tribromide ion. The reaction is susceptible to both polar and steric effect. A mechanism involving transfer of hydride ion in the rate determining step has been proposed.

2.1.2 Phase Transfer catalysis as applied to oxidation

It has been reported that many inorganic oxidants can be transferred into the organic phase using PT catalysts [16,17,18]. For example oxidants like hypochlorite, dichromates, chromates, hydrogen peroxide, permanganate etc. can be transferred into the organic phase using quaternary ammonium salt as PT catalyst. These phase transferred oxidant can be used for effecting the oxidation of various organic substrates in organic media..

A PTC Oxidation using hypochlorite

Tabushi and Koga[129] 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 of benzyl alcohol with sodium hypochlorite was very slow, but accelerated by electron transfer or phase transfer catalyst. In the presence of such catalysts the oxidation was very fast.

Ishii and Kishi[130] studied the oxidation of alkyl and aryl-substituted hydroquinone with aqueous sodium hypochlorite in various organic solvents in the presence of catalytic amount of tetrabutyl ammonium hydrogen sulphate. For the oxidation of mono-substituted hydroquinones, dichloromethane and chloroform were found to be suitable solvents compared to ethyl acetate and benzene. Hydroquinones are oxidized to benzoquinones.

A new triphasic solid-solid-liquid catalytic system for the inexpensive and selective oxidation of secondary alcohols by calcium hypochlorite is reported.[131] In contrast with the result under homogenous phase, steric and geometric factors were found to affect rate constants. The catalyst is recovered without any regeneration process and it could be used several times with no loss of activity.

Lee and Freeman[132] reported the use of catalytic amount of lypophilic quaternary ammonium salts for the transfer of hypochlorite ion from aqueous to organic media where by it is extremely effective and convenient for the oxidation of many alcohols and amines. An interesting and unexpected solvent effect in accelerating the rate has also been discovered with the use of ethyl acetate which greatly expands the synthetic utility of the method.

Benzyl alcohol was oxidized by aqueous sodium hypochlorite in a phase transfer catalysis condition catalysed by quaternary ammonium salts[133]. Two products were obtained, benzaldehyde and benzyl benzoate. The concentration of organic phase and the pH of the aqueous phase affected the product distribution, a dilute organic phase and low pH favoured benzaldehyde as the product, where as a concentrated organic phase and a high pH favoured benzyl benzoate as a product.

Aromatic aldehydes were oxidized to carboxylic acids in high yeids using sodium hypochrite as oxidant in a PTC system[134]. The reaction 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 into the organic phase, the former significantly increasing the reaction rate.

The oxidation of benzyl alcohol was conducted using hypochlorite with benzyl triethyl ammonium chloride as PT catalyst in two phase system[135.] There is an evidence for the initial chlorination at the benzyl carbon. Since no reaction takes place in the absence of a PT catalyst, the involvements of an ionic species in the organic phase is clearly indicated.

The anodic oxidation of benzyl alcohol has been studied in the two phase system containing both the redox mediator ClO^-/Cl^- and a phase transfer catalyst[136]. The reaction mechanism and the factors which affect the current efficiency for benzaldehyde production were explored. The result showed that benzyl alcohol was mainly oxidized in the organic phase by the shuttling of the ClO^-/Cl^- mediator.

Chou T.S. and Do. J.S.[10] systematically investigated the extraction of hypochlorite ion from aqueous to organic phase and the oxidation of benzyl alcohol in the organic phase using tetrabutyl ammonium bromide as PT catalyst. The result reveal that the rate of oxidation of benzyl alcohol in two immiscible aqueous/dichloromethane system was controlled and occurred in the organic phase when the stirring rate was larger than 500 rpm. The reaction order was found to be unity with respect to tetrabutyl ammonium hypochlorite concentration and with respect to benzyl alcohol concentration respectively in the organic phase.

A procedure for the oxidation of benzhydrol to benzophenone using bleach as oxidant in ethyl acetate solvent by tetrabutyl ammonium hydrogen sulfate as PT catalyst was reported[137]. The oxidation was essentially complete in 30 minutes and the yield range from 70 to 85%.

Heterogeneous oxidation of benzyl alcohol using hypochlorite ion with phase transfer catalyst has been carried out in an agitated vessel with a flat interface[138]. The observed reaction rates are proportional to the interfacial concentration of cetyltrimethyl ammonium hypochlorite in the organic phase, which is formed by the ion exchange between bromide and hypochlorite ions. Cetyl trimethyl ammonium bromide and toluene were chosen as the best catalyst and the solvent respectively.

B. PTC oxidation using dichromate

A fascile solubilization of potassium dichromate was effected in several organic solvents using a 2:1 ratio of adogen 464 to dichromate[139]. The resulting orange solution is fairly stable at ambient temperature for effecting oxidation of alcohols under neutral condition.

Pletcher and Tait[140] have investigated the oxidation of alcohols with stoichiometric quantity of dichromate in 3M sulphuric acid using tetrabutyl ammonium bisulphate as PT catalyst. They have suggested that the reaction is assumed to be proceeded by the disproportionation of chromate ester catalysed by proton.The Cr (VI) in aqueous solution exists as a pH dependent mixture of several species.

The kinetics of the oxidation of benzyl alcohol by chromic acid was determined in two phase system[141]. The result showed an order one both with respect to [alcohol] and [dichromate] and a partial order with respect to acid concentration. The use of two- phase system allowed to obtain clean kinetic results by preventing further oxidation of benzaldehyde to carboxylic acid.

The use of onium salt as PT catalysts to get complex chromate salts that were soluble in aprotic solvents has been reported by Gelbard *et al*[1142]. This complex chromate was used for the oxidation of several alcohols.

Dodwad and Archana[143] reported the oxidation of alcohols to corresponding carbonyl compound in excellent yield under mild condition using tricaprylmethylammonium chloride as PT catalyst in dichloromethane.

The kinetics and mechanism of liquid-liquid phase transfer catalysed oxidation of benzyl chloride with chromate salts under PTC condition were investigated in great deal in a systematic way[11]. This system presents a complex case of consecutive and parallel reactions in which benzyl alcohol formed as an intermediate is further oxidized to benzaldehyde. The fact that the rate of reaction depends on the pH of the aqueous phase revealed that chromium exists as dichromates, chromates or perchromate depending on the pH. It was observed that $Q^+HCrO^-_4$ was the active species for oxidation. The results are not novel and the experimental data fit the theoretical model very well.

C PTC oxidation using Hydrogen peroxide

Quaternary ammonium salts assist the extraction of both hydrogen peroxide and metal salts like ruthenium or $PdCl_2$ from aqueous to organic phase of a heterogeneous system[144]. This system has been used for the oxidation of styrene to benzaldehyde. Dichloromethane was used as the organic phase.

Ballislreri *et al*[145] have reported a phase transfer procedure for the oxidation of terminal alkynes under PTC condition. The catalytic system involves dilute H_2O_2 solution Na_2MO_4 (M = Mo, W) and Hg $(OAC)_2$. In the absence of mercuric acetate no oxidation take place. By changing the pH of the aqueous phase and the nature of the PT agent as well as metal (Mo or W), carboxylic acid or keto aldehydes may be selectively obtained in fairly good yields.

The selective oxidation of primary aliphatic 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 duel role of extraction of $RuCl_3$ and H_2O_2 into the organic phase and also to protect the metallic catalyst against reduction.

D PTC oxidation using Permanganate

Starks[16] has reported that terminal olefins can be oxidized to carboxylic acid by $KMnO_4$ using quaternary ammonium salt as PT catalyst. Thus when 1-octene is added to a mixture of aqueous potassium permanganate and 5% solution of quaternary salt in benzene, an essentially quantitative yield of hexanoic acid was obtained. Benzene and toluene are not rapidly attacked by quaternary ammonium permanganate below 60^0C.

Sam and Simmons[14] found that dicyclohexyl-18 crown–6 ether complex of $KMnO_4$ in benzene (purple benzene) is effective in quantitative oxidation of olefin to diacids.

A controlled oxidation of olifins to cis glycols in moderate yield by $KMnO_4$ in dichloromethane using benzyl triethyl ammonium chloride as PT catalyst was reported.[147]

Harriot and Picker[77] have studied the extraction of permanganate ions from aqueous to benzene medium using various quaternary ammonium salts as PT catalysts. They found that permanganate ions can be almost fully extracted from aqueous to benzene medium by using excess of TBAB or TCMAC as PT catalyst. The resulting solution called purple benzene is relatively stable and could be conveniently used for the oxidation of various organic compounds like benzyl alcohol olefin etc. in anhydrous condition in benzene medium.

A kinetic study of the oxidation of methyl-(E)-cinnamate with quaternary ammonium permanganate in methylene chloride has been reported[148]. The rate of the reaction is fastest for those ions which permit the interionic distance in the quaternary ammonium ion to be minimized. An attempt has been made to visualize a mechanism in which the reaction can proceed through similar intermediate but via either an electron rich or an electron deficient transition state depending on the demands of the substituents.

Rathore[108] et al have reported a convenient method for the selective oxidative cleavage of aryl-substituted olefins to carbonyl compounds in excellent yields with cetyl trimethyl ammounim permanganate (CTAP) at room temperature.

Kinetics and mechanism of the oxidation of unsaturated carboxylic acid by methyl tributyl ammonium permanganate in methylene chloride solution has been investigated[149]. The involvement of a free-radical process is indicated by the formation of a polymer during the oxidation of acrylic acid and methacrylic acid. The reaction is believed to be initiated by the formation of an organometallic complex. Rearrangement of the complex result in the formation of a reactive manganese (V)cyclic diester, which undergoes a rapid (free-radical) reduction to Mn (III).

The use of cetyltrimethyl ammonium permanganate (CTAP) for the oxidation of cycloalkenes in dichloromethane has been investigated by Freeman & Kappos[150]. The relative rates of oxidation versus vertical ionization potential and strain energies are discussed. A comparison of the relative rates of permanganate ions oxidation with the relative rates of addition of other reagents to carbon double bonds suggests that it may act as a 1,3 dipole. The order of reaction with respect to permanganate ion concentration is unity and is also first order in cycloalkene concentration. The kinetic data were consistent with initial interaction between cycloalkene and permanganate ion (charge- transfer complex) with [2+2] cycloadditon leading to an intermediate. A very fast reaction of the intermediate affords 1,2-diol and manganese dioxide.

The formation of a cyclic manganate (V) diester intermediate was reported during the oxidation of endo-dicyclopentadiene by permanganate ion in dichloromethane in the presence of a quaternary salt[151]. The reaction is first order both with respect to permanganate ion and alkene concentration. Spectrophotometric behaviour and the kinetic results of the intermediate formation are strikingly similar to those of manganese species reported before as soluble (colloidal) manganese dioxide. The manganese (V) ester intermediate is formed in first order dependence on the concentration of alkene at a rate faster than of its decomposition into colloidal manganese dioxide which is also first-order dependent on alkene concentration.

Oxidation of benzaldehyde, nitro, chloro and methyl substituted benzaldehydes and benzyl cyanide by potassium permanganate under

PTC condition using different catalysts and solvents were reported[152]. A correlation of structure and activity of the catalyst was made. Tetrabutyl ammonium bromide and tricaprylmethyl ammonium chloride functioned as better catalysts and benzene as the best solvents.

Holba[153] *et al* have investigated the oxidation of higher aliphatic alcohols like hexan-1-ol, hexan-2-ol, hexan-3-ol, heptan-1-ol, heptan-2-ol, octan-1-ol and octan-2-ol with tetrabutylammonium permanganate dissolved in the same alcohols. The oxidation proceeds partly autocatalytically. The rate constant of both catalytic and non catalytic reactions have been evaluated.

Kinetics of the oxidation of aliphatic aldehydes by quaternary-ammonium permanganate in dichloromethane was reported with special regard to colloidal manganese (IV) intermediate[154].

A spectrophotometric method for the kinetic study of the oxidation of cyclohexene with $KMnO_4$ in biphase system is reported[155]. Kinetic parameters in the presence of PT catalyst have been determined.

Permanganate solubilized in methylene chloride with the aid of TDA-1 as phase transfer agent, oxidizes benzyl alcohol to benzaldehyde and benzyl ethers to benzoate esters[156]. Although the rate of oxidation of ether is about an order of magnitude slower than alcohol oxidation, both respond in an identical way to the unique effects caused by the introduction of substituents in the benzene ring. Because of these similarities, similar mechanisms are proposed for the oxidation of benzyl alcohols and benzyl ethers.

Sheeba and Radhakrishnan Nair[12] have made kinetic studies on the permanganate oxidation of acetophenones and some of its substituents in organic media using the phase transfer technique. Tricaprylmethyl ammonium chloride and tetrabutyl ammonium bromide have been used as the phase transfer catalysts. The reaction showed first order dependence each on [ketones] and the [permanganate ions]. The rate coefficients fit well with the Hammett equation. The reactivities of different substituted acetophenones are reported to be in the order

p-No_2 > m-NO_2 > p-Cl > - H > p- CH_3 > p-OCH_3

2.2 Scope and objectives of the present investigation

In spite of the fact that potassium permanganate is a powerful and useful oxidant, the studies on permanganate oxidation were limited to only water-soluble compounds. Only a few oxidation studies of organic substrates have been reported so far in non- polar organic solvent. With the assistance of phase transfer catalysts (PT catalyst) it is now possible to study the kinetics and mechanism of permanganate oxidation of various organic compounds in non- polar organic solvents. Moreover, it is possible to modify the activity and selectivity of the permanganate ions. Quaternary ammonium salts are phase transfer catalysts whose lipophilic cation can solubilize permanganate ions in many of the aprotic organic solvents with considerable modification in activity. The present investigation is on the oxidation of secondary aromatic carbinols using phase transferred permanganate ions. The oxidation of secondary alcohols to ketones is important synthetically and has theoretical significance also. The kinetic and mechanistic studies of secondary alcohols are scanty and hence the present work.

The oxidation of 1-phenyl ethanol and some of its para-substituted derivatives using phase transferred permanganate in benzene medium have been carried out. Tetrabutylammonium bromide (TBAB) and tricaprylmethylammonium chloride (TCMAC) were used as phase transfer catalyst. In addition to benzene various other solvents such as carbon tetra chloride, toluene, chloroform, methylene chloride and chlorobenzene were also used.

The objectives of the present work are

1. To study the rate of oxidation of 1-phenyl ethanol and its para-substituted derivatives in benzene medium using phase transferred permanganate to evaluate the kinetic parameters such as order of the reaction and rate coefficients.
2. To study the chemical nature of the product and to find the stoichiometry of the reaction.
3. To find the temperature coefficient of the reaction rates for evaluating the various related thermodynamic parameters.
4. To study the effect of dielectric constant of medium on the rates of oxidation.
5. To compare the rates of oxidation of 1-phenyl ethanol using TBAB and TCMAC in benzene.
6. To study the effect of substituents at the para postion of the aryl ring on the rate of oxidation of the 1-phenyl ethanol

7. To study the added effect of TBAB on the rate of oxidation in benzene medium.
8. To study the temperature coefficients of the reaction rates for evaluating related thermodynamic parameters for the oxidation of cyclohexanol and benzhydrol in benzene.
9. To formulate the mechanism in consistent with the observation made.

An attempt has also been made to study the stoichiometry and the kinetics of permanganate oxidation of 1-phenyl ethanol and its para-substituted derivatives in aqueous acetic acid medium in order to compare the results with the results of PTC method.

Prior to the kinetic investigation of the oxidation of carbinols in organic solvents, the permanganate ions were first extracted from aqueous to the organic phase. The efficiency of the extraction and the stability of the resulting organic permanganate solution (purple benzene) were determined with respect to the

1. concentration of quaternary ammonium salts
2. Nature (structure) of quaternary salts
3. nature of the organic solvents

CHAPTER III

EXPERIMENTAL

EXPERIMENTAL

3.0 This chapter deals with the materials and methods employed for the kinetic investigation. Tetrabutylammonium bromide (TBAB) and tricaprylmethylammonium chloride (TCMAC) or 'Aliquat' 336 were used as phase transfer catalysts (PT Catalysts). The oxidation of various secondary alcohols like 1-phenyl ethanol, p-Me, p-OMe, p-Cl and p-NO_2 , benzhydrol, and alicyclic alcohol like cyclohexanol were studied in benzene medium at 303K and at different temperatures. The usual kinetic parameters viz enthalpy of activation, entropy of activation, free energy of activation were determined by standard procedure. The oxidation rates of 1-phenyl ethanol were analysed in different organic solvents like toluene, carbon tetrachloride, chloroform, methylene chloride and chlorobenzene in order to investigate the solvent dielectric effect on PT catalysed oxidation. The effect of adding TBAB into the reaction system was also studied to investigate the salt effect due to it.

Prior to the kinetic study the extraction of permanganate ions from aqueous to organic medium with the assistance of PT catalysts were investigated. The extraction was studied with respect to

1. Concentration of $KMnO_4$
2. Concentration of PT catalysts
3. Structure of the catalyst
4. Various solvents
5. Concentration of added salts

Stability of the extracted permanganate ions in various organic solvents were analysed spectrophotometrically by measuring the absorption of MnO^-_4 ion at $\lambda_{max} = 528$ nm.

3.1 Materials

Analar grade potassium permanganate was used for the preparation of $KMnO_4$ solution in double distilled water. Benzene (E Merck) and other solvents like toluene, chloroform, carbon tetrachloride, chlorobenzene and methylene chloride were purified according to standard procedure[157,158]. All the purified solvents (except toluene) were refluxed for 1-2 hrs with a mixture of quaternary salt and $KMnO_4$ and then distilled.

1-phenyl ethanol used was of E Merck German quality. The para-substituted derivatives of the alcohols like p-Cl, p-CH_3, p-OCH_3 and p-NO_2 carbinols were prepared by reduction of the corresponding acetophenones with sodium borohydride[157-159]. The p-Cl and p-CH_3 1-phenyl ethanols were purified by vacuum distillation, p-NO_2 and p-MeO 1-phenyl ethanols were purified by converting them into their corresponding pthalate esters followed by hydrolysis[160]. The purity of the compounds were checked by I.R. (Figs 3.1 to 3.4). Benzhydrol was prepared by the reduction of benzophenone according to standard procedure[157] and was purified by recrystallisation. Purity of the compound was checked by m.p determination (65^{0}C) and by I.R. (Fig 3.5). Tetrabutylmmonium bromide (TBAB) and tricapryl methylammonium chloride (TCMAC) or 'Aliquat' 336 used as PT catalysts were of SISCO quality and were used as such.

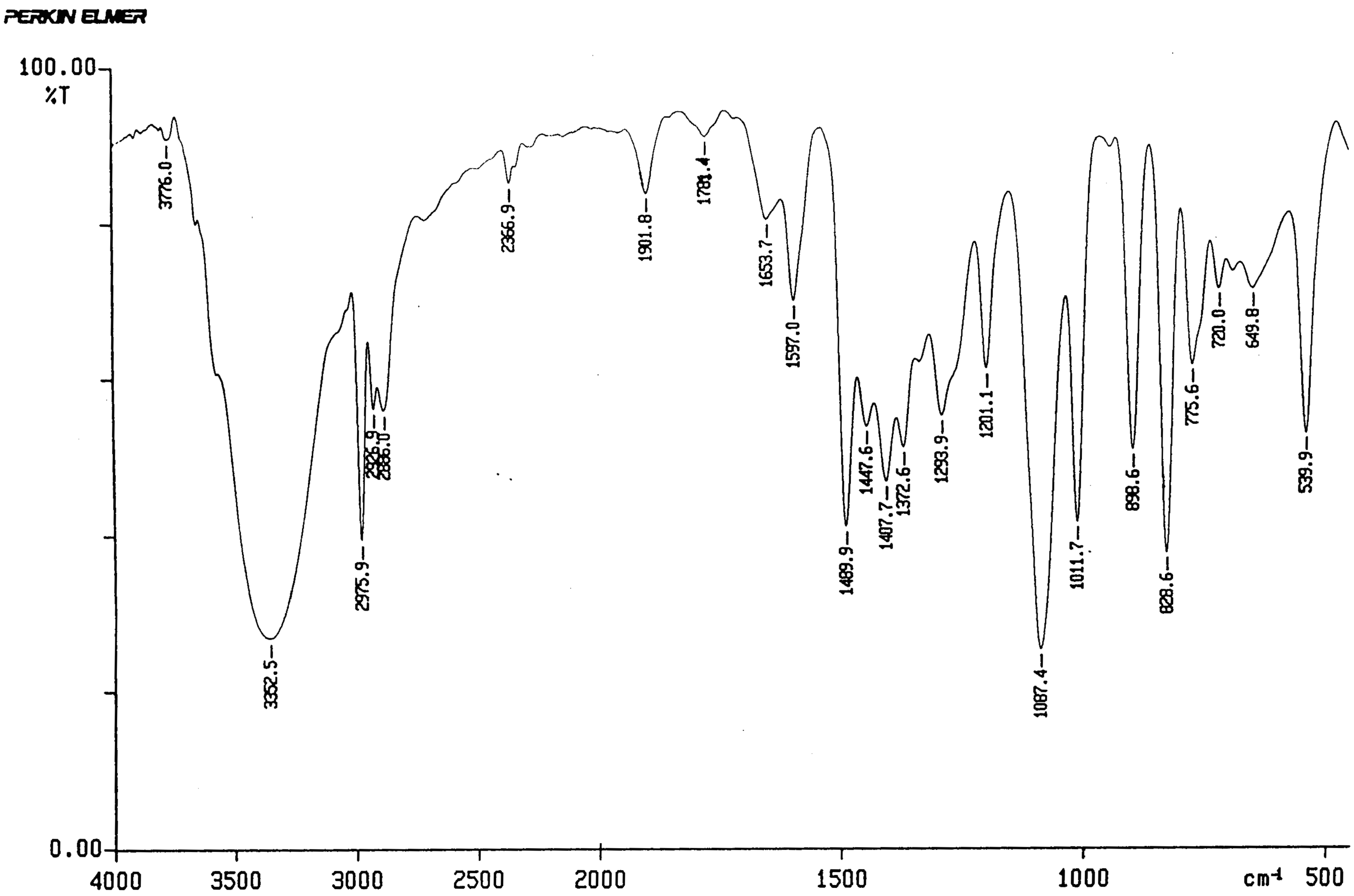


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Fig 3.1 I.R Spectrum of p-Cl 1-phenyl ethanol

X: 4 scans, 4.0cm-1, flat, smooth, apex

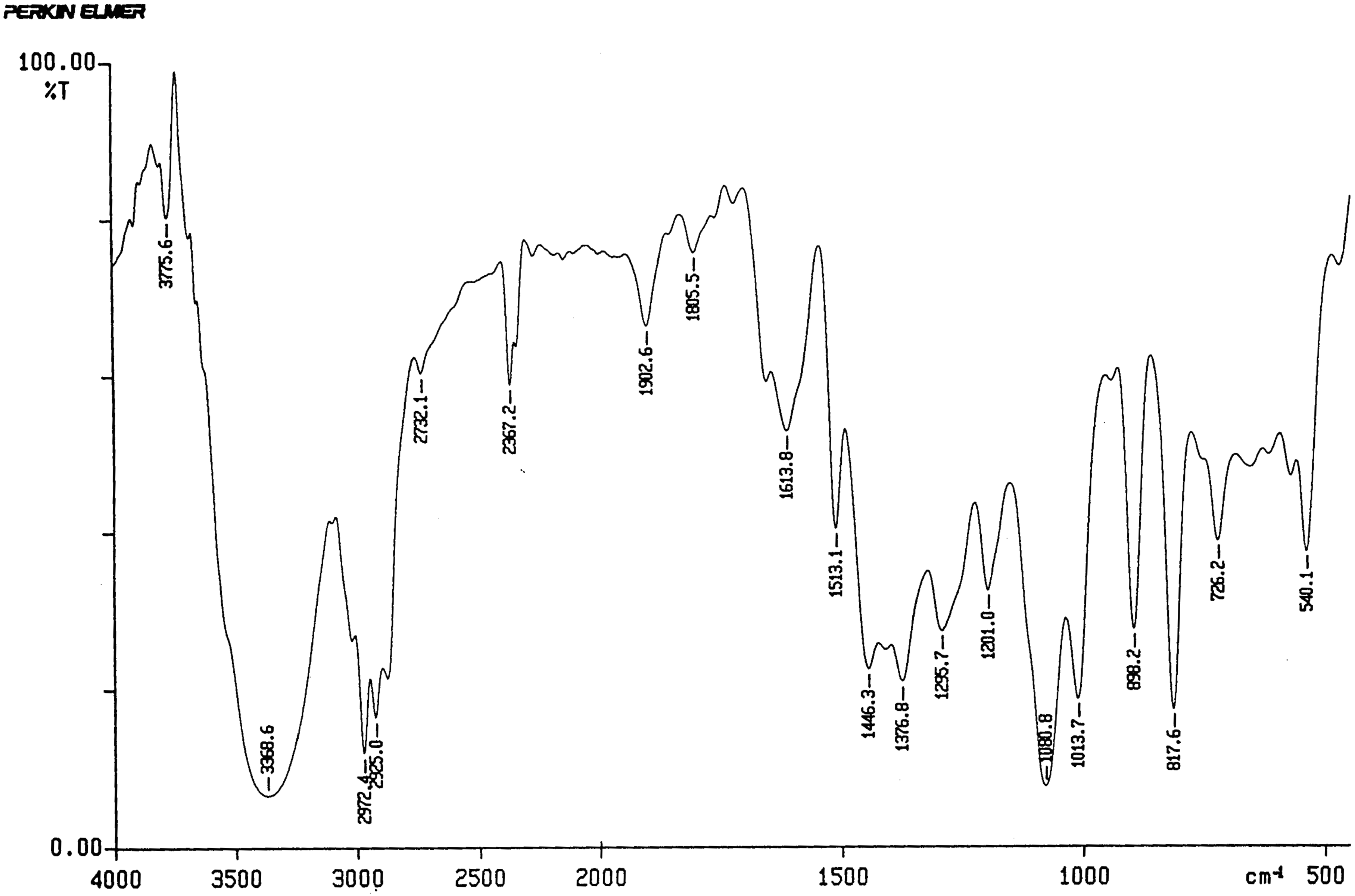

Fig 3.2 I.R Spectrum of p-CH_3 1-phenyl ethanol

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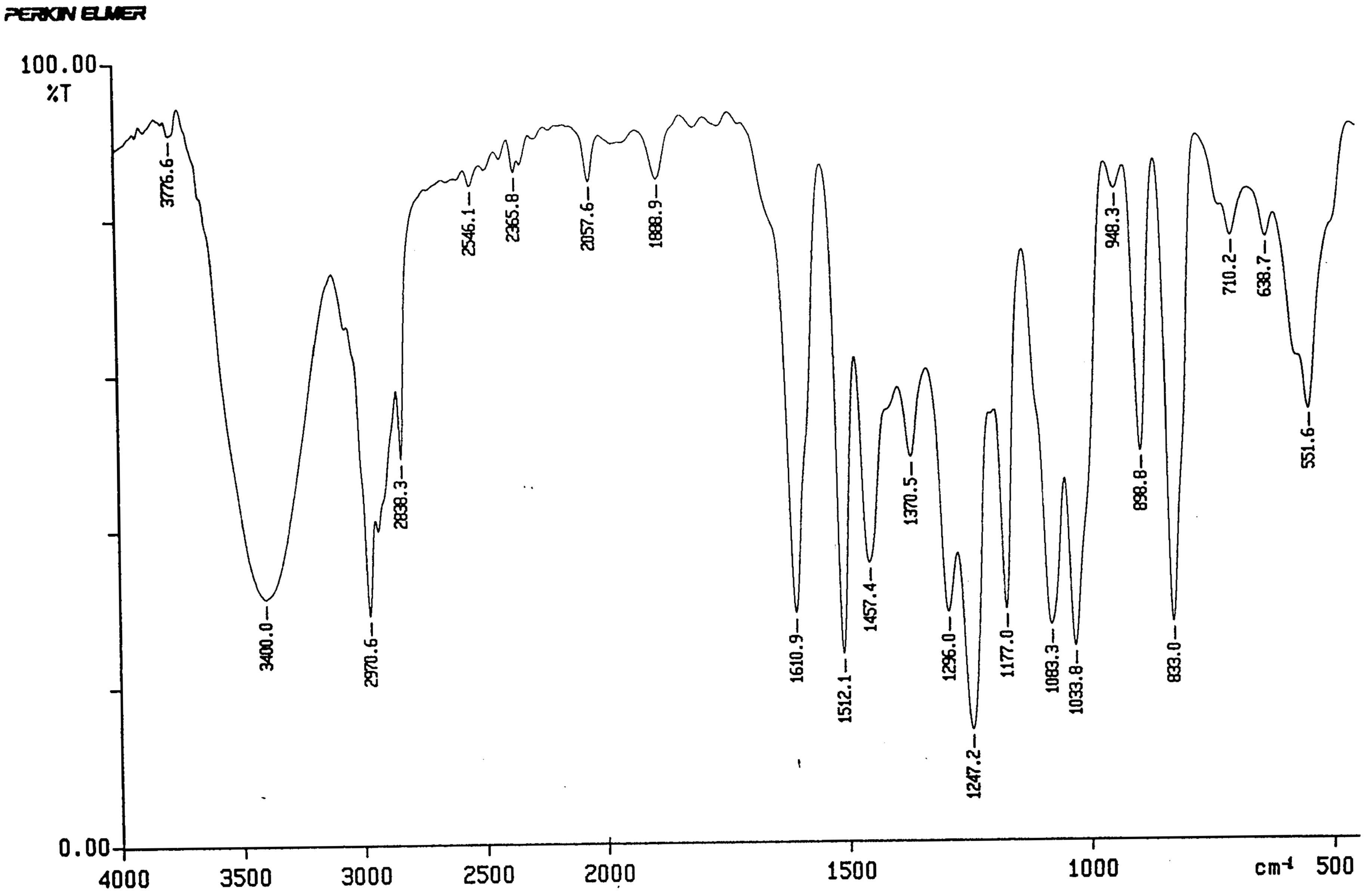
X: 4 scans, 4.0cm-1, flat, smooth, abex



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X: 4 scans, 4.0cm-1, flat, smooth, abex

Fig 3.3 I.R Spectrum of p-OCH_3 1-phenyl ethanol

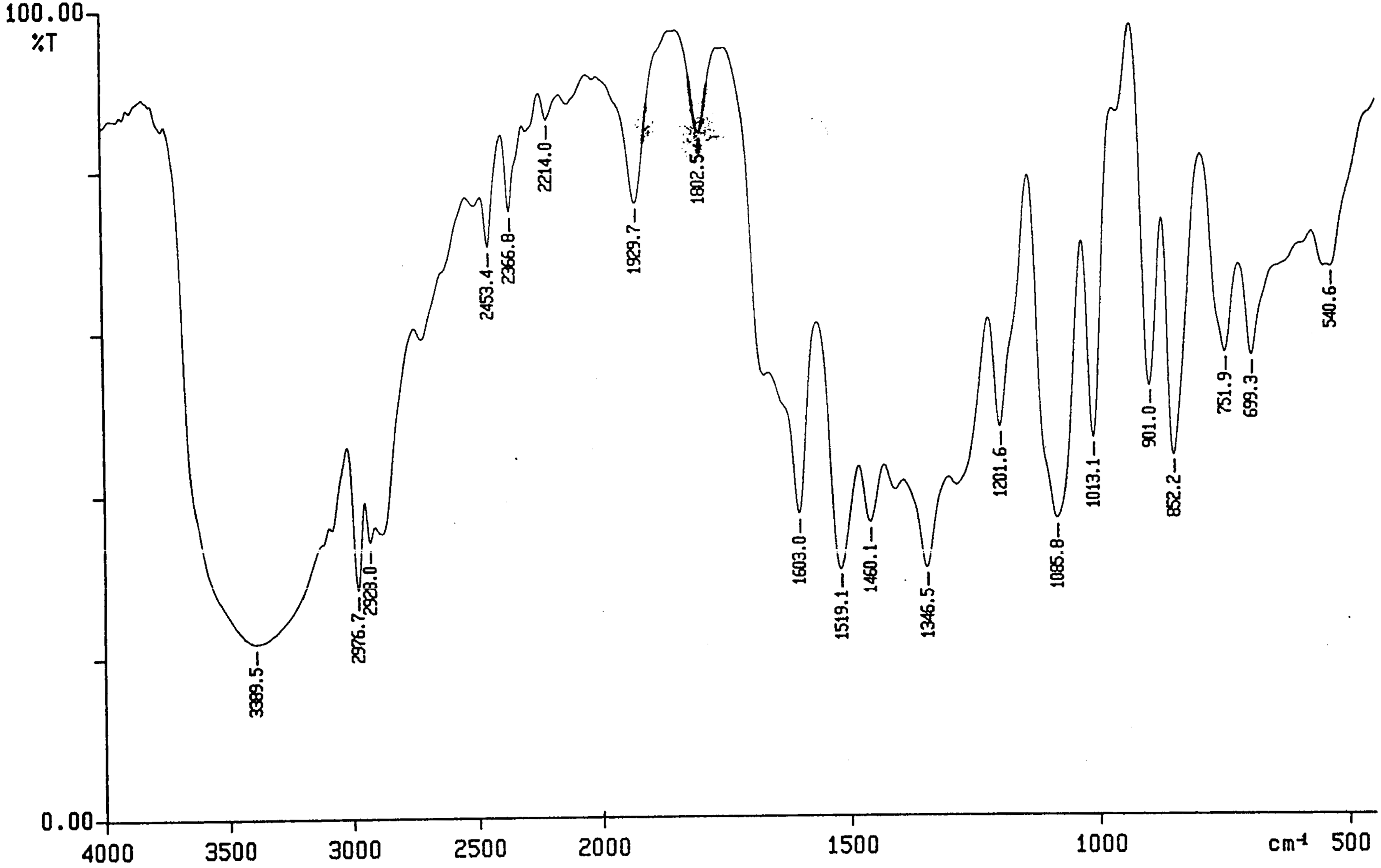


Fig 3.4 I.R Spectrum of p-NO_2 1-phenyl ethanol

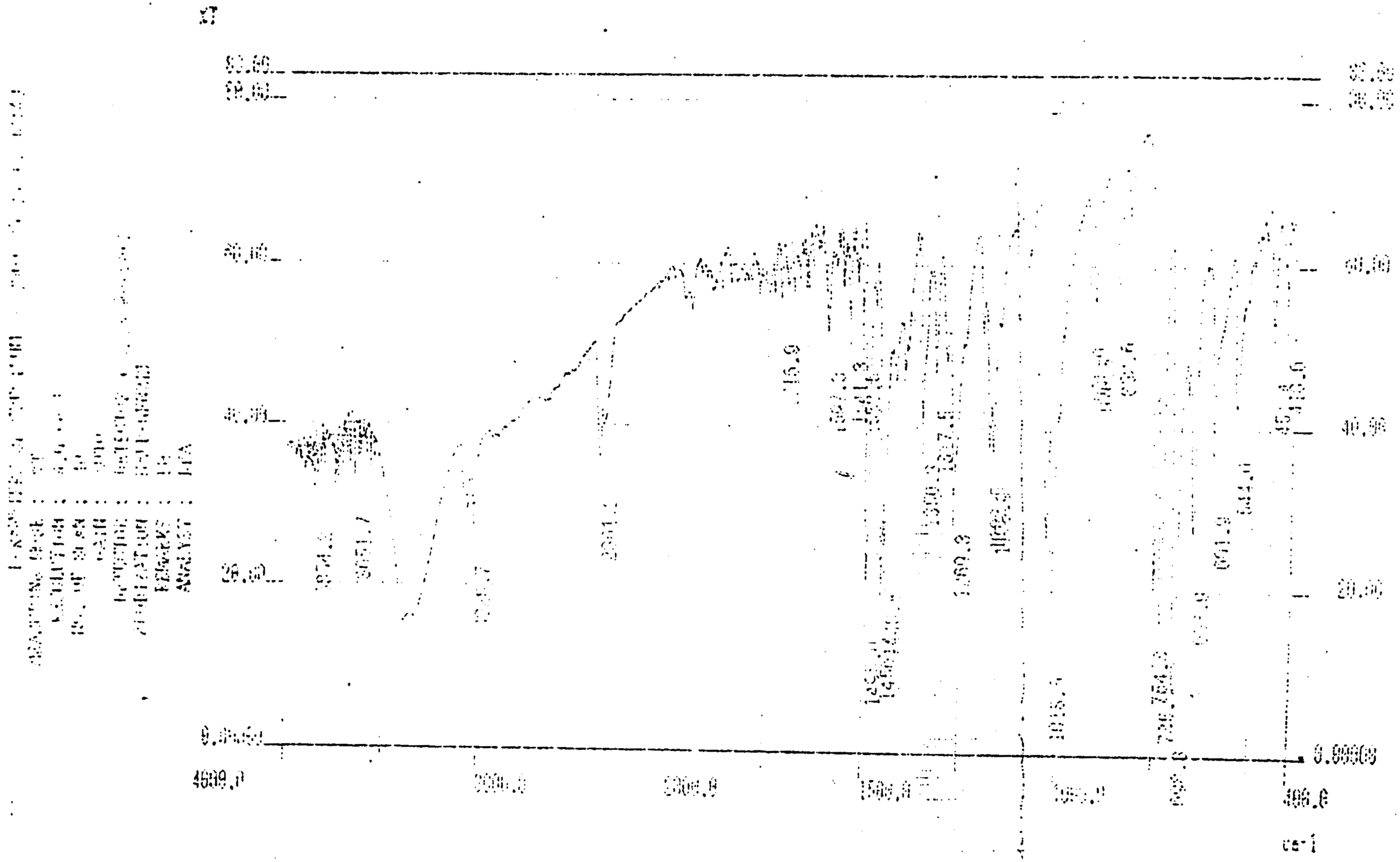


Fig 3.5 I.R Spectrum of benzhydrol

3.2 Kinetic Investigations

The kinetic experiments were carried out at various desired temperatures in suitable thermostats fitted with thermoregulators to maintain the accuracy of the temperature of the system within a variation of $\pm 0.1^0$C.The thermostat was set to the desired temperature. A known volume of 0.005M aqueous $KMnO_4$ is equilibrated with equal volume of benzene containing 0.02M PT catalyst. The $QMnO_4$ formed in benzene was separated and made anhydrous by adding little anhydrous Na_2SO_4. A known volume of $QMnO_4$ was mixed with a known volume of benzene and the mixture was thermostated for 20 minutes at the desired temperature. To the reaction mixture a required volume of previously thermostated alcohol (prepared in benzene) solution was added by means of calibrated pipette. The reaction mixture was shaken well and kept undisturbed in the thermostat. Aliquots were withdrawn at regular time intervals (5 or 10 minutes) from the reaction mixture and the progress of the reaction was monitored spectrophotometrically in a Shimadzu 1601 u.v spectrophotometer by measuring the absorption of MnO^-_4 ions at λ_{max} of 528 nm upto 80% completion of the reaction. Pseudo first order condition was maintained by keeping [Carbinol] >> [$QMnO_4$].

The experiments were carried out at varying concentration of oxidant, varying concentration of carbinol, at various desired temperatures and in various organic solvents. The influence of the catalyst structure on the rate of oxidation of carbinols was studied with respect to two different PT catalysts, TBAB and TCMAC

The experiments were conducted at various desired temperatures with different para substituted 1-phenyl ethanols, benzhydrol and cyclohexanol. In all the cases pseudo first order conditions are maintained by keeping [carbinol] >> [$QMnO_4$].

The kinetics of the oxidation of 1-phenyl ethanol and its para substituted derivatives were studied in aqueous acetic acid (40% v/v). The effect of temperatures, the effect of varying the percentage of acetic acid(polarity of the medium), the effect of addition of mineral acids, and the effect of added salt etc on the rate of oxidation were investigated. Various activation parameters were computed. Kinetics were studied under the condition [carbinol] >> [MnO_4^-] and the concentration of unreacted permanganate ions were determined iodometrically at regular intervals of time. Stoichiometry of the reaction was determined under the condition [MnO_4] > [carbinol], and the product formation is ascertained.

Acetic acid used was of E Merck quality and was purified by distillation by the standard procedure.[157-8]

3.2.1 Computation of Kinetic data and Evaluation of rate constants[103,161-163]

The pseudo-first order rate constants were determined from the plots of log absorbance of $QMnO_4$ versus time. The slopes of these plots were calculated by linear regression analysis (by the method of least squares). From the slopes the rate constants were calculated. All the rate constants are the average of two to three kinetic runs.

3.2.2 Thermodynamic Parameters[163-165]

The thermodynamic parameters such as the energy of activation Ea, enthalpy of activation $\Delta H^{\neq}$, entropy of activation $\Delta S^{\neq}$ and the free energy of activation $\Delta G^{\neq}$ were calculated using standard equation.

Energy of activation Ea

Energy of activation Ea was calculated using Arrhenius equation.

$$k = A.e^{-Ea/RT}$$

Where A = frequency factors

R = universal gas constant

T = absolute temperature

A plot of logk vs I/T gave a linear relationship with slope equal to -Ea/2.303R and the values of Ea were calculated from the slope values.

Enthalpy of Activation $\Delta H^{\neq}$ and Entropy of activation $\Delta S^{\neq}$.

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

$$k = \frac{k_bT}{h} \exp \frac{T\Delta S^{\neq} - \Delta H^{\neq}}{RT}$$

$$\text{or} \quad \log \frac{k}{T} = \log\frac{k_b}{h} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT}.$$

Where $k_b \rightarrow$ Boltzmann constant

h – Plancks constant

A plot of log k/T vs I/T should therefore be linear with a slope equal to $-\Delta H^{\neq}/2.303R$, from which $\Delta H^{\neq}$ can be determined. Substituting the values of k_b, h, R and $\Delta H^{\neq}$ into the above equation, $\Delta S^{\neq}$ values would be evaluated for a given temperature.

Free energy of activation $\Delta G^{\neq}$

The free energy of activation was computed from the equation

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

3.3 Extraction of Permanganate ions from aqueous to organic media with the aid of PT catalysts.

For the kinetic studies of oxidation of carbinols in organic medium, the permanganate ions from aqueous media should first be extracted into organic medium with the assistance of phase transfer catalysts (Liquid – Liquid phase transfer). The extractions were studied with respect to

1. The initial concentration of $KMnO_4$.
2. Concentration of PT catalysts
3. Structure of the catalysts
4. Nature of the solvents
5. Addition of salt to the aqueous phase.

The effectiveness of a PT catalyst depends on its ability to transfer anions from aqueous to organic phase.

The extraction was studied by equilibrating a definite volume of known concentration of aqueous potassium permanganate with equal volume of organic solvents containing a definite concentration of PT catalyst followed by stirring for 30 minutes. The extraction was almost steady after 30 minutes. The percentage of extraction of permanganate ion from aqueous to organic phase is calculated by the equation.

$$\% \text{ of } MnO^-_4 \text{ ion extracted into the organic phase} = \frac{[QMnO_4]_{org}}{[MnO^-_4]_{aqueous}} \times 100$$

3.3.1 Effect of catalytic structure and its concentration

The amount of extraction of permanganate ion from aqueous to organic phase in a given solvent increased with the increase in the concentration of PT catalysts. The extraction became almost complete and attained a steady state with the catalytic concentration twice that of the aqueous permanganate concentration. Further it was found that in a given solvent the extractive power of the TCMAC is greater than TBAB.

The results are represented as shown in Table 3.1 and fig 3.6

Table 3.1

Effect of catalytic concentration and structure on the extraction of MnO^-_4 ions

Time – 30 minutes

$[MnO_4^-] = 0.01$ mol dm^{-3}

Solvent = Benzene

Temp =303K

[PT catalyst] (mol dm^{-3})	% of MnO^-_4 extracted into organic phase	
	TBAB	TCMAC
0.0025	24	30
0.005	52	60
0.01	76	89
0.015	88	93
0.02	94	98
0.025	94	98

The TCMAC catalyst was found to extract MnO_4^- ions more effectively than TBAB catalyst. The greater effeciency of TCMAC as compared to TBAB is probably due to the high organophilicity imparted by the three large alkyl groups combined with a small methyl group, which would allow the MnO_4^- ions to be more closely associated with the positive nitrogen[111]. Thus there is a relation between the cation size and extraction efficiency. The extractive power of the catalyst is the most important factor in the permanganate oxidation. It is found that with the use of moderate excess of lipophilic quarternary salt it is possible to extract MnO_4^- almost quantitatively in to the organic phase.[12,77]

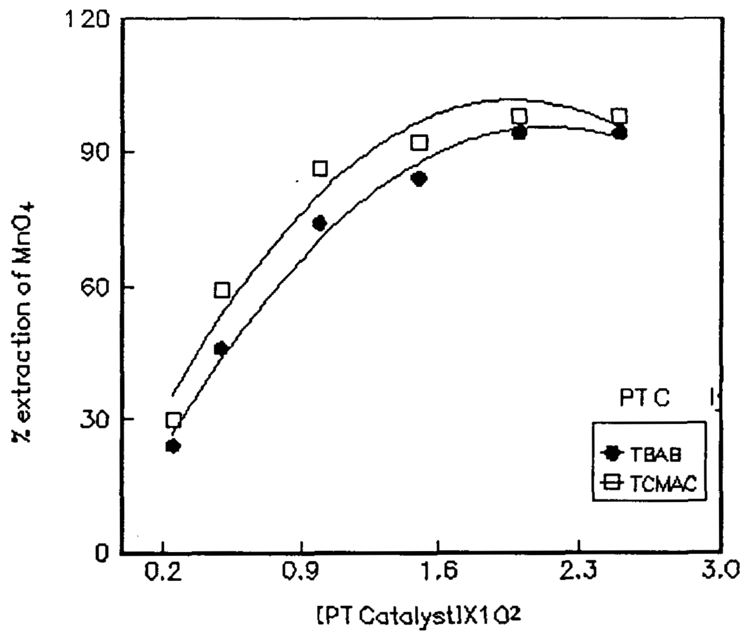


Fig 3.6 Effect of catalytic concentration and structure on the extraction of MnO_4^- ions from aqueous to benzene

3.3.2 Effect of Solvent Polarity

The effects of solvent polarity on the extraction of permanganate ions from aqueous phase to organic phase were investigated with respect to various organic solvents like benzene, toluene, carbon tetrachloride, chloroform, methylene chloride and chlorobenzene. Results are represented in Table 3.2.

Table 3.2

Effect of solvent polarity on the extraction of MnO^-_4 ions

[PT catalyst] = 0.01 mol dm^{-3} [MnO_4^-] = 0.01 mol dm^{-3}

Time = 30 minutes Temp=303K

Organic solvents		C_6H_6	$C_6H_5CH_3$	CCl_4	$CHCl_3$	CH_2Cl_2	C_6H_5Cl
Dielectric constants		2.27	2.40	2.22	4.70	9.08	5.62
% Extraction of MnO^-_4	TBAB	76	74	72	88	90	78
	TCMAC	89	82	78	90	98	86

The effect of the solvent on the extraction was found to be quite small (Table 3.2). A very little correlation was found between the extracting ability and the dielectric constant of the solvent. For TBAB, methylene chloride and chloroform were found to be the best solvents. For TCMAC all the solvents were found to be equally good but with better extraction in chloroform and methylene chloride. Thus chloroform and methylene chloride are the best solvents for the extraction of MnO_4^- ions using quaternary salts as PT catalyst as already been reported by various workers[18, 86, 113, 164].

3.3.3 Effect of initial concentration of $KMnO_4$

Increase in the concentration of MnO_4^- in the aqueous phase increased the amount of extraction. However there should be an optimum amount of catalytic concentration in the organic phase. The results are represented in Table 3.3

Table 3.3

The effect of initial concentration of MnO_4^-

Time = 30 minutes [PT catalyst] = 0.01 mol dm^{-3}.

Solvent = Benzene Temp =303K

$[MnO_4^-]$ mol dm^{-3}	% Extraction of MnO_4^- into organic phase	
	TBAB	TCMAC
0.005	52	60
0.01	76	89
0.015	84	92
0.02	88	98
0.025	90	98

The increase in the amount of extraction with increase in the initial concentration of the anions may be due to facts that the increasing concentration of inorganic anions, tie up additional water of hydration, reducing the amount of water available for anions hydration, providing easier transfer of the anions in to the organic phase[92,111].

3.3.4 Effect of added salt in the aqueous phase

Increasing the concentration of inorganic salt in the aqueous phase tend to salt out more amount of MnO_4^- ions into the organic phase in the form of $Q^+MnO_4^-$ Table 3.4 represents the result.

Table 3.4

Effect of added NaCl

Time =30 minutes [PT catalyst] = 0.01 mol dm^{-3}

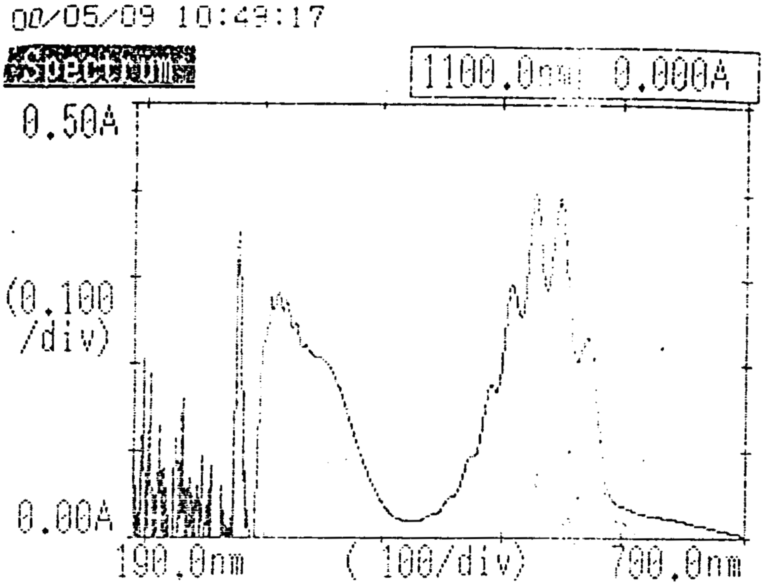
solvent – Benzene $[MnO_4^-]$ = 0.01 mol dm^{-3}

[NaCl] mol dm^{-3}	% of MnO^-_4 extracted into organic phase	
	TBAB	TCMAC
0	76	82
.005	82	89
.01	86	92
.02	89	96

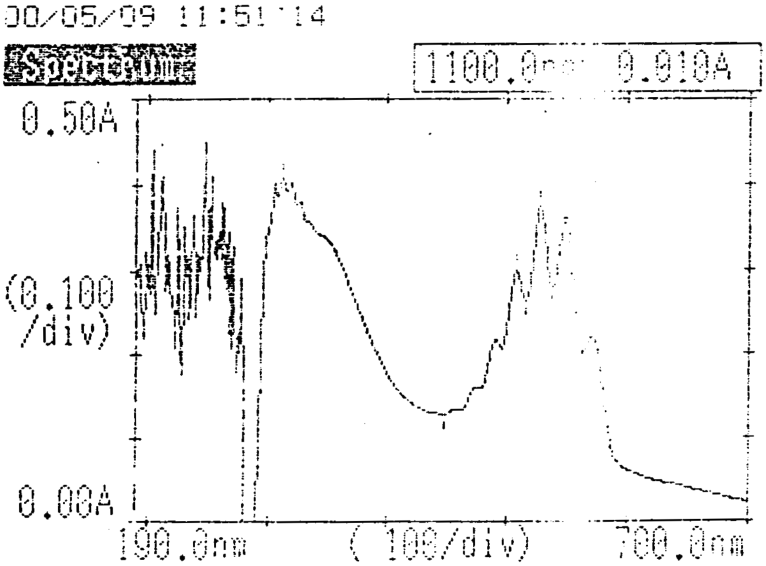
The addition of foreign salt like NaCl, may cause salting out effect. Increasing the concentration of inorganic salt (NaCl) in aqueous phase tends to salt out organic salt pushing them in to the organic phase[92, 111].

3.3.5 Stability of Permanganate ion in the organic medium

The stability of MnO_4^- extracted into various organic solvents was studied by measuring its absorbance at λ_{max} of 528nm for a period of one to two hours. It was found that the absorption remained almost unchanged for about one hour and decreased slightly by 3 to 4% within a time of one and half hours. (Fig 3.7) The tetrabutyl ammonium permanganate was found to be slightly more stable than tricapryl methyl ammonium permanganate in a given organic solvent. Thus the quaternary ammonium permanganate in organic solvents obtained with the assistance of PT catalysts were suitable for studying the kinetics of oxidation of organic substrates in organic media.



(a) Initial Absorption Spectrum



(b) Absorption Spectrum after 1 hour

Fig 3.7(a & b) UV/Visible Spectrum of $QMnO_4$ ($Q = TBA^+$) in benzene

3.4 Oxidation of 1-phenyl ethanol by phase transferred permanganate in benzene-tetrabutylammonium bromide as PT catalyst

10 ml of 0.005M aqueous $KMnO_4$ was equilibrated with 10ml of benzene containing 0.02M TBAB. The tetrabutylammonium permanganate (TBAP) obtained in benzene was made anhydrous and its concentration was determined spectrophotometrically.

3.4.1 Stoichiometry of reaction

A reaction mixture containing known concentration of 1-phenyl ethanol and $QMnO_4$ in benzene was kept for nearly 4 to 5 hours in a thermostat at 35^0C until the reaction was completed under the condition $[QMnO_4] > [\text{Carbinol}]$. The concentration of unreacted MnO_4^- ions was determined spectrophotometrically by measuring its absorbance at λ_{max} of 528nm. (Corresponding to the stage when MnO_4^- absorbance became almost constant). By computing the concentration of Mno_4^- ions reacted with the known concentration of carbinol, the stoichiometry of the reaction was calculated.

3.4.2 Product analysis

A reaction mixture containing excess of $QMnO_4$ over 1-phenyl ethanol in benzene was allowed to react completely by keeping it at 40^0C for 4 hrs. The unreacted permanganate ions were destroyed by the addition of sodium sulphite and H_2SO_4. The resulting solution was extracted with ether for three times and the ether layers were combined. The ether layer was then extracted repeatedly with 5% sodium carbonate and the sodium carbonate layers were combined which on acidification gave no precipitate ruled out the formation of benzoic acid. The ether layer was washed with distilled water, made anhydrous and the ether evaporated off. The resulting solution was treated with excess 2,4 dinitrophenyl hydrazone in methanol. The precipitated 2,4 dinitrophenyl hydrazone is filtered, dried and weight is determined (Yield 85%).

The product was ascertained to be acetophenone by spectral method also. UV spectrum characteristics of acetophenone with λ_{max} 319.5 was obtained (Fig. 3.8).

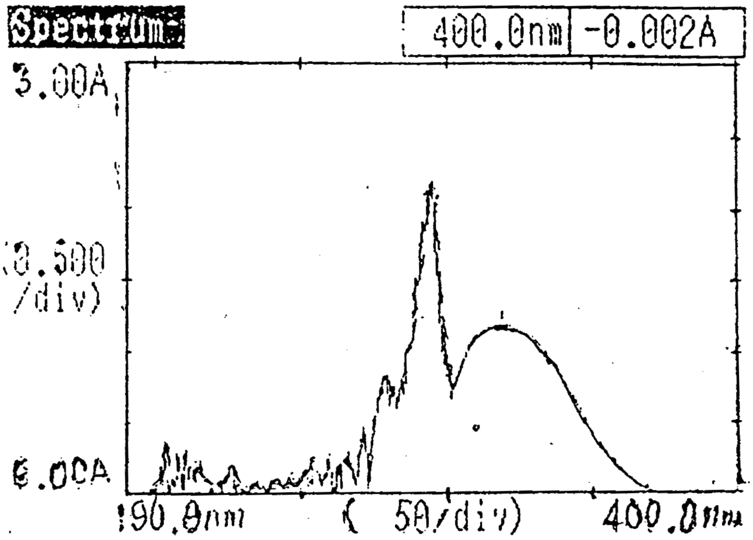


Fig 3.8 U.V. Spectrum of the product of oxidation of 1-phenyl ethanol in benzene medium

3.5 Kinetic Studies

The oxidation of 1-phenyl ethanol by phase transferred permanganate was studied at different conditions such as varying oxidant concentration, varying substrate concentration, at different temperatures, in varying solvents etc under the condition [carbinol] >> [$QMnO_4$].

3.5.1 Effect of oxidant (TBAP) concentration on the rate of oxidation of 1-phenyl ethanol

The kinetics of the oxidation of 1-phenylethanol with phase transferred MnO_4^- (TBAP) obtained with the assistance of TBAB in benzene were studied by taking fixed concentration of substrate (1.245 x 10^{-2}M of 1-phenyl ethanol) and varying concentration of oxidant (TBAP). The concentration of substrate in all cases was kept greater at least by a factor of 10 ensuring pseudo first order condition with respect to oxidants. The progress of the reaction was followed upto 80% competition spectrophotometrically by measuring the absorbance of MnO_4^- ions at λ_{max} of 528nm. The pseudo-order rate constants, k_{obs} were computed from the linear least square plot of log (absorbance) of $QMnO_4$ versus time (Fig 3.9). Duplicate kinetic runs showed that the rate constants were reproducable within ±5 %. The pseudo first order rate constants, k_{obs} as determined by the method of least square is represented in table 3.5

Table 3.5

Effect of oxidant concentration, [TBAP] on the rate of oxidation of 1-phenyl ethanol

[$PhCHOHCH_3$] = 1.245 x 10^{-3} mol dm^{-3} PT catalyst – TBAB

Solvent = Benzene T = 303 K

10^4 x [TBAP] (mol dm^{-3})	10^2 x [carbinol] (mol dm^{-3})	10^5 x k_{obs} (s^{-1})	K_2 x 10^3 = k_{ob}/[substrate] (dm^{3}ml^{-1}s^{-1})	Correlation
2.43	1.245	4.22	3.38	0.9993
5.12	1.245	3.92	3.14	0.9991
7.60	1.245	4.15	3.33	0.9990
12.20	1.245	4.10	3.29	0.9988

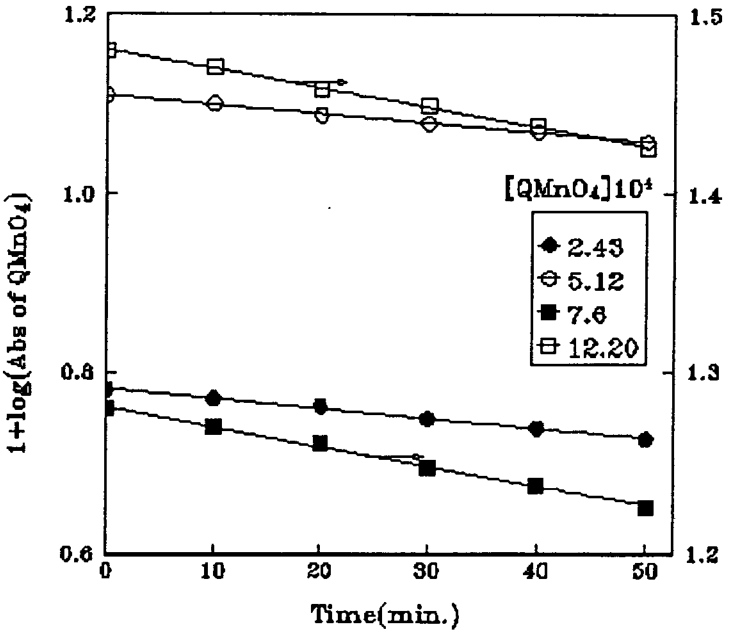


Fig 3.9 Effect of oxidant concentration, [TBAP] on the rate of oxidation of 1-phenyl ethanol

3.5.2 Effect of varying the concentration of substrate on the rate of oxidation of 1-phenyl ethanol

The effect of varying the concentration of 1-phenyl ethanol on the rate of oxidation was studied for a concentration range of carbinol from 1.245 x 10^{-2}M to 4.38 x 1^{-2} M keeping the kinetic condition the same. In all the cases the concentration of carbinol was kept large excess to that of $QMnO_4$ concentration which was kept constant at 5.12 x 10^{-4}M. Hence the order would be that with respect to $QMnO_4$. From the observed pseudo first order rate constant, (Fig 3.10) the order with respect to carbinol is obtained by dividing the k_{ob} with carbinol concentration when constancy in the rate was observed. (Table 3.6)

Table 3.6

Effect of substrate concentration on the rate of oxidation.

Medium – Benzene T = 303K

10^4 x [TBAP] (mol dm^{-3})	10^2 x [carbinol] (mol dm^{-3})	10^5 x k_{ob} (s^{-1})	k_2 x 10^3 k_{ob}/[carbinol]	Correlation
5.12	1.245	3.92	3.14	0.9991
5.12	2.49	8.10	3.25	0.9995
5.12	3.75	11.48	3.06	0.9998
5.12	4.98	15.58	3.13	0.9996

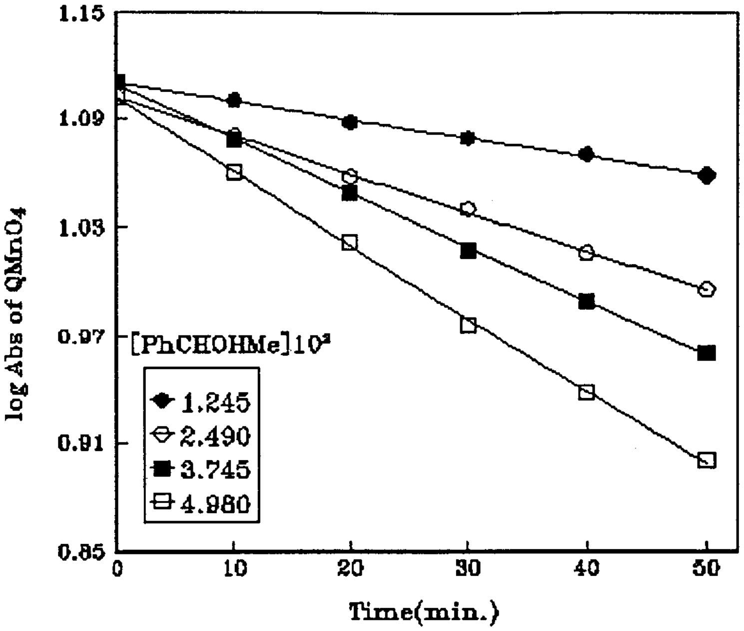


Fig 3.10 Effect of substrate concentration on the rate of oxidation using TBAP

3.5.3 Effect of adding TBAB into the reaction system – ionic strength

TBAB of varying concentrations were added to the reaction system under similar kinetic condition.with a view to see any salt effect in the organic medium. To study the influence of TBAB on the rate of oxidation its concentration was varied from 1.0 x 10^{-2} t0 4.0 x 10^{-2} mol dm^{-3}, while keeping all other conditions the same. The k_2 values are given in Table 3.7.

Table 3.7

Effect of addition of TBAB on the rate of oxidation

$[PhCHOHCH_3] = 1.245 \times 10^{-2}$ mol dm^{-3} Solvent = Benzene
$[TBAP] = 5.12 \times 10^{-4}$M Temp = 303K

[TBAB] x 10^{-2} (mol dm^{-3})	$k_{ob} \times 10^5$ (s^{-1})	$k_2 \times 10^3 = k_{ob}$ / [Carbinol] (dm^3 mol^{-1} s^{-1})
0	3.92	3.14
0.01	4.22	3.39
0.02	3.88	3.11
0.03	4.30	3.45
0.04	3.92	3.14

3.5.4 Effect of the Polarity of the medium on the rate of oxidation

The reaction was carried out in various organic solvents at 303K by keeping all the kinetic conditions the same. The reactions were carried out with a view to get the type of interaction in the rate determining slow step of the reaction. The non polar organic solvents chosen were benzene, toluene, carbon tetrachloride, chloroform, methylene chloride and chlorobenzene. The results are presented in Table 3.8 & Fig 3.11.

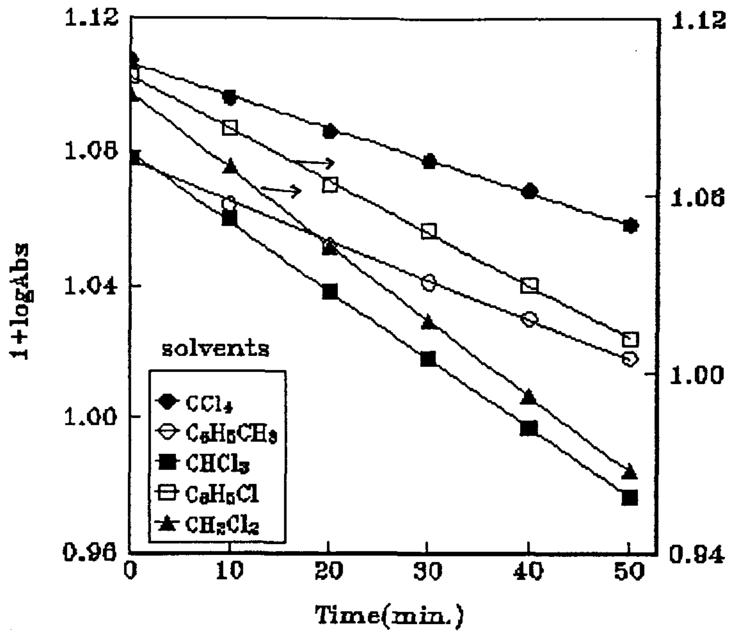


Fig 3.11 Effect of the Polarity of the medium on the rate of oxidation using TBAP

Table 3.8
Effect of solvent polarity on the rate of oxidation

[PhCHOH CH_3] = 1.245 x 10^{-2} mol dm^{-3} Temp = 303K

[TBAP] = 5.12 x 10^{-4} mol dm^{-3}

Solvent	Dielectric constant	k_2 x 10^3 (dm^3 mol^{-1} s^{-1})
Carbon tetrachloride	2.22	2.99
Benzene	2.27	3.14
Toluene	2.40	3.64
Chloroform	4.70	6.32
Chlorobenzene	5.62	5.42
Methylene chloride	9.08	7.86

3.5.5 Effect of the addition of acrylonitrile

To the reaction mixture containing 1.245 x 10^{-2} mol dm^{-3} carbinol and 5.12 x 10^{-4} mol dm^{-3} TBAP 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.

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

The influence of temperature on the rate of oxidation was studied at a temperature range of 303K to 318K under identical condition. The results are shown in Tables 3.9 and Fig 3.12 From the kinetic data the various thermodynamic parameters, namely, the energy of activation Ea, the entropy of activation $\Delta S^{\neq}$, the enthalpy of activation $\Delta H^{\neq}$, and the free energy of activation $\Delta G^{\neq}$ were evaluated.

Table 3.9

Effect of temperature on the rate of oxidation of 1-phenyl ethanol using TBAP (Tetrabutyl ammonium permanganate)

[TBAP] = 5.12 x 10^{-4} mol dm^{-3} [PhCHOH CH_3] = 1.245 x 10^{-2} mol dm^{-3}

Solvent - Benzene

Temp K	303	308	313	318
k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	3.14	5.55	9.56	13.31

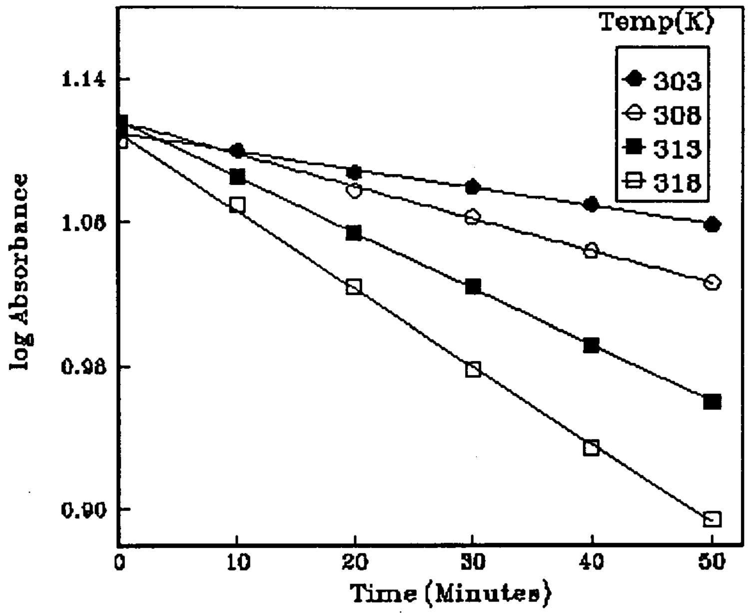


Fig 3.12 Effect of temperature on the rate of oxidation of 1-phenyl ethanol using TBAP (Tetrabutyl ammonium permanganate)

3.6 Effect of substituents on the rate of oxidation of 1-phenyl ethanol using TBAP

The effects of substituents on the benzene ring of phenyl methyl carbinol were studied using p-nitro, p-chloro, p-methyl and p-methoxy 1-phenylethanols (Fig 3.13). The kinetics were carried out with respect to all substituted derivative under the identical conditions and the values of rate constants, k_2 are presented in tables 3.10

Table 3.10

Substituent effect on the rate of oxidation of 1-phenyl ethanol using TBAP

[Substrate] =1.245 x 10^{-2} mol dm^{-3} T = 303K

[TBAP] = 5.12 x 10^{-4} mol dm^{-3} Solvent – Benzene

Substrate	10^3 x k_2 (dm^3 $mol^{-1}s^{-1}$)	Correlation coeff.
1-phenyl ethanol	3.14	0.9991
p-CH_3 1-phenyl ethanol	4.41	0.9975
p-Cl 1-phenyl ethanol	6.47	0.9998
p-OCH_3 1-phenyl ethanol	16.60	0.9997
p-NO_2 1-phenyl ethanol	29.25	0.9994

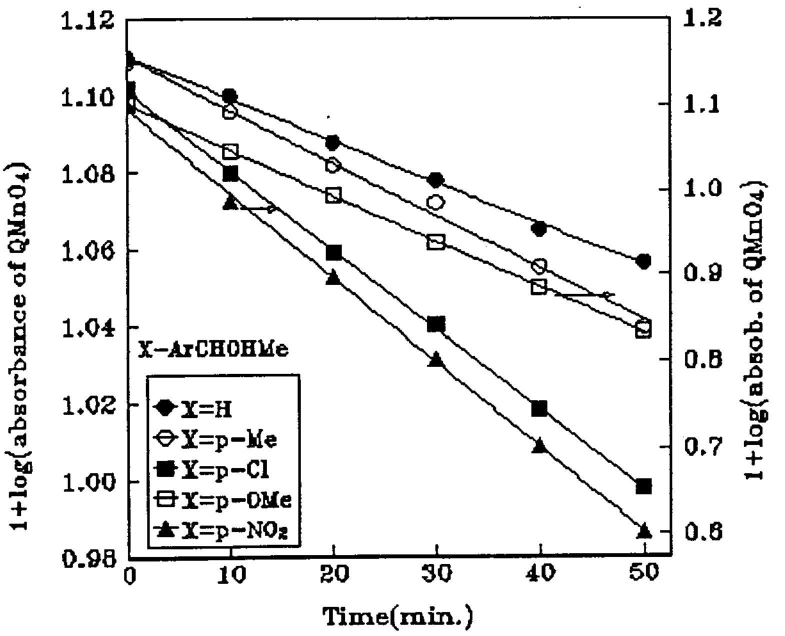


Fig 3.13 Substituent effect on the rate of oxidation of 1-phenyl ethanol using TBAP

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

The effect of temperature on the rate of oxidation of the substituted 1-phenyl ethanol viz p-NO_2, p-Cl, p-CH_3, p-OCH_3 were studied at a temperature range of 303K -318K (Fig 3.14 to 3.17). The k_2 values are presented in tables 3.11(a) to 3.11(d)

Table 3.11(a)

Effect of temperature on the rate of oxidation of p-NO_2 1-phenyl ethanol using TBAP

[p-NO_2 1-phenyl ethanol] = 1.245×10^{-2} mol dm^{-3}

[TBAP] = 5.12×10^{-4} mol dm^{-3} Solvent = Benzene

Temperature(K)	303	308	313	318
$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	29.25	42.40	60.80	86.32
Correlation coeff.	0.9994	0.9996	0.9998	0.9993

Table 3.11(b)

Effect of temperature on the rate of oxidation of p-Cl 1-phenyl ethanol using TBAP

[p-Cl $PhCHOHCH_3$] = 1.245×10^{-2} mol dm^{-3}

TBAP = 5.12×10^{-4} mol dm^{-3} Solvent = Benzene

Temperature(K)	303	308	313	318
$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	6.47	10.14	15.30	23.90
Correlation Coefft.	0.9938	0.9919	0.9998	0.9995

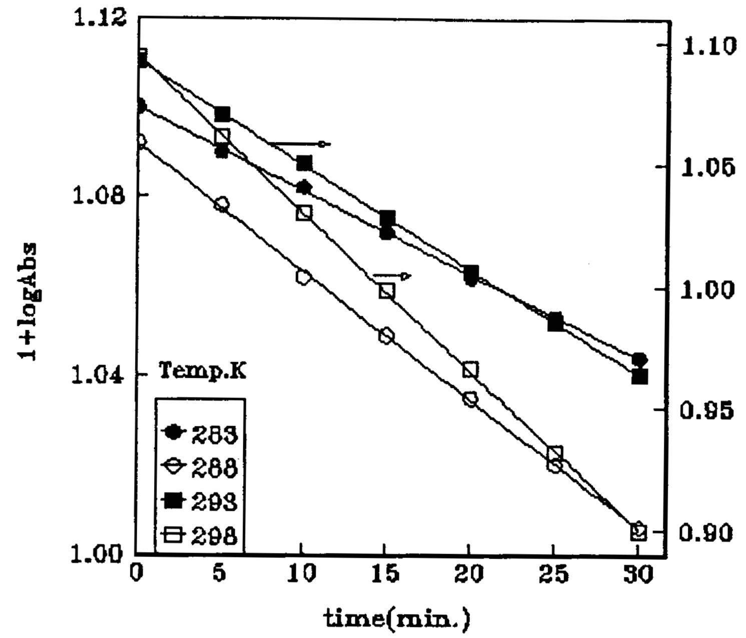


Fig 3.14 Effect of temperature on the rate of oxidation of p-NO_2 1-phenyl ethanol using TBAP

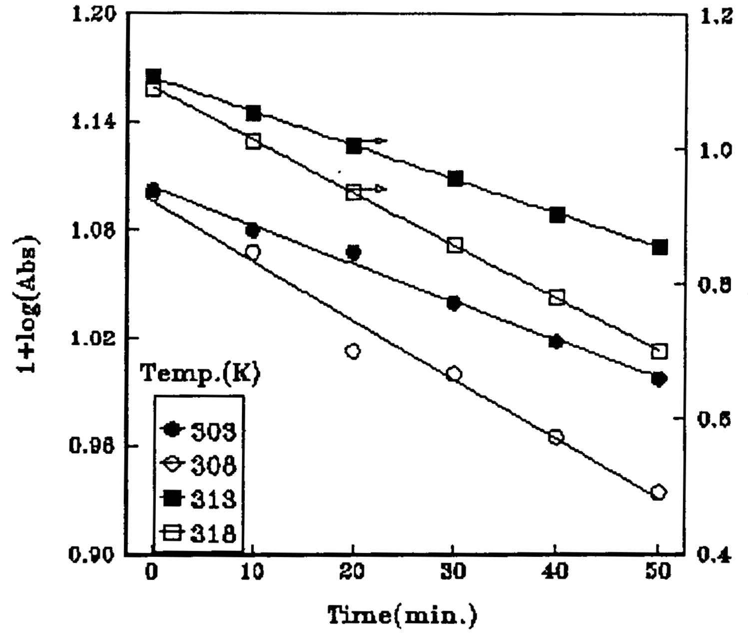


Fig 3.15 Effect of temperature on the rate of oxidation of p-Cl 1-phenyl ethanol using TBAP

Table 3.11(c)

Effect of temperature on the rate of oxidation of p-CH_3 1-phenyl ethanol using TBAP

[p-CH_3 $PhCHOHCH_3$] = 1.245 x 10^{-2} mol dm^{-3},

[TBAP] = 5.12 x 10^{-4} mol dm^{-3} Solvent = Benzene

Temperature(K)	303	308	313	318
Rate constant k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	4.41	7.37	11.53	16.65
Correlation Coefft.	0.9974	0.9995	0.9997	0.9995

Table 3.11 (d)

Effect of temperature on the rate of oxidation of p-OCH_3 1-phenyl ethanol using TBAP

[p-OCH_3 $PhCHOHCH_3$] = 1.245 x 10^{-2} mol dm^{-3},

[TBAP] = 5.12 x 10^{-4} mol dm^{-3} Solvent = Benzene

Temperature(K)	303	308	313	318
k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	16.60	25.7	37.70	55.20
Correlation Coefft.	0.9977	0.9984	0.9997	0.9998

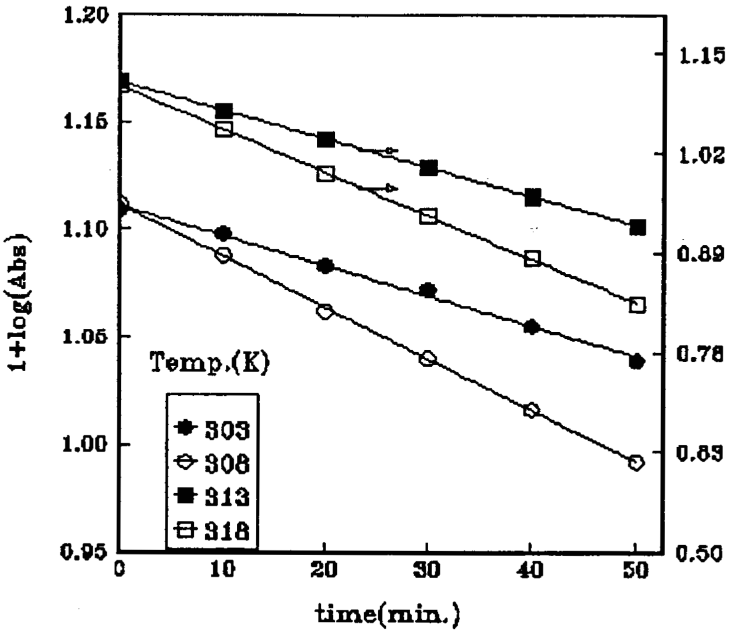


Fig 3.16 Effect of temperature on the rate of oxidation of p-CH_3 1-phenyl ethanol using TBAP

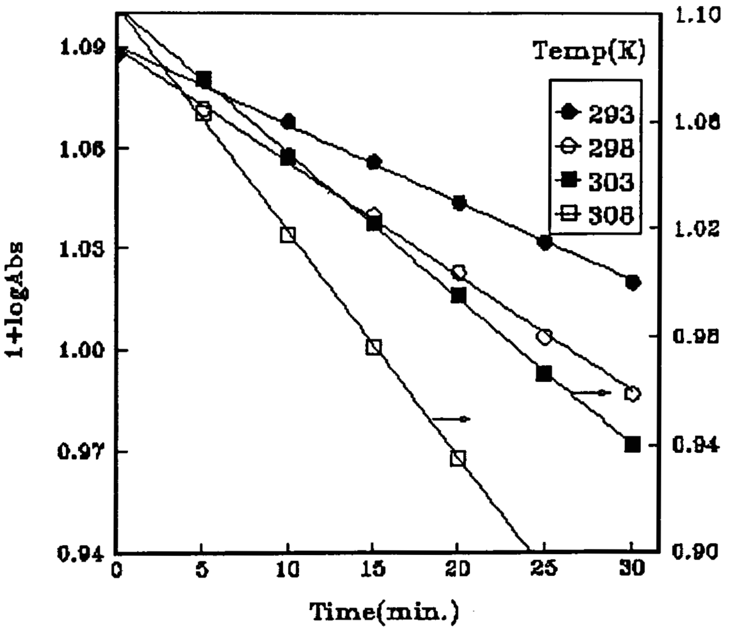


Fig 3.17 Effect of temperature on the rate of oxidation of p-OCH_3 1-phenyl ethanol using TBAP

3.7 Effect of temperature on the rate of oxidation of benzhydrol using TBAP

The rate of oxidation of a secondary alcohol, benzhydrol by MnO_4^- using TBAB as PTC was studied at a temperature range from 303K to 318K in benzene under identical kinetic conditions. The results representing kinetic data are given in table 3.12 & Fig 3.18

Table 3.12

Temperature effect on the rate of oxidation of benzhydrol using TBAP

[PhCHOHPh] = 1.245×10^{-2} mol dm^{-3} Solvent = Benzene

[TBAP] = 5.12×10^{-4} mol dm^{-3}

Temperature	303	308	313	318
$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	7.92	12.39	16.24	24.7
Correlation coefft.	0.9993	0.9995	0.9998	0.9948

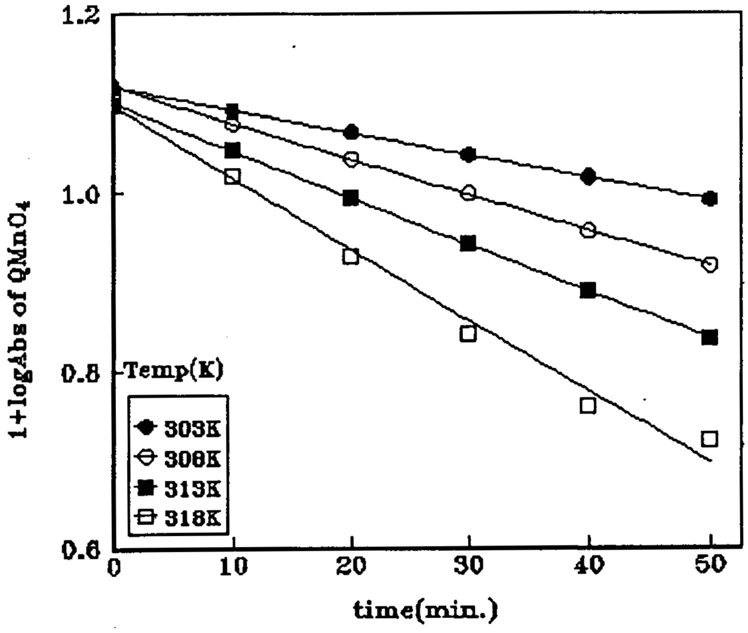


Fig 3.18 Temperature effect on the rate of oxidation of benzhydrol using TBAP

3.8 Effect of temperature on the rate of oxidation cyclohexanol using TBAP

The effect of temperature on the rate of oxidation of alicyclic secondary alcohol, cyclohexanol was investigated at a temperature range from 303K to 318K under identical kinetic condition in benzene. (Fig 3.19) The rate constants are given in table 3.13

Table 3.13

Effect of temperatures on the rate of oxidation of cyclohexanol using TBAP

[Cyclohexanol] = 1.245 x 10^{-2} mol dm^{-3} Solvent = Benzene

[TBAP] = 5.12 x 10^{-4} mol dm^{-3}

Temperature (K)	303	308	313	318
k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	2.86	5.36	7.39	12.64
Correlation coefft.	0.9996	0.9996	0.9990	0.9995

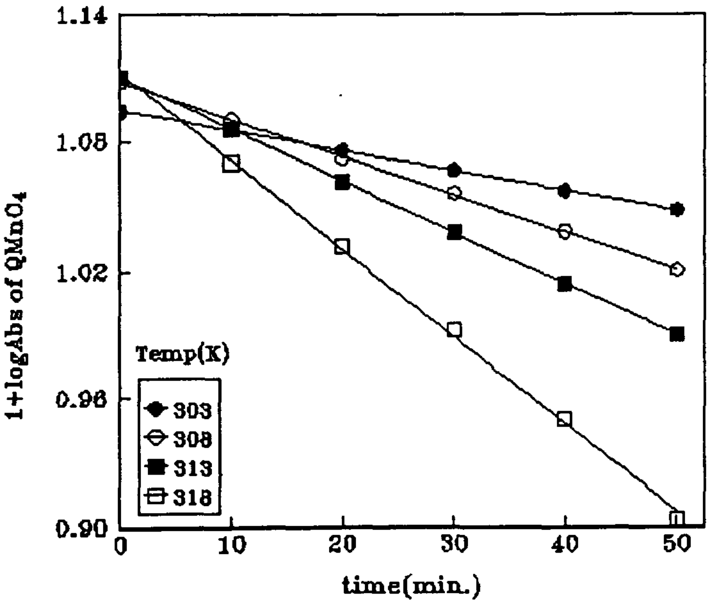


Fig 3.19 Effect of temperatures on the rate of oxidation of cyclohexanol using TBAP

3.9 Oxidation of 1-phenyl ethanol using by phase transferred permanganate ion in benzene - tricapryl methyl ammonium chloride (TCMAC) as PT catalyst

A solution of tricaprylmethyl ammonium permanganate (TCMAP) in benzene is prepared by equilibrating 0.005 M aqueous $KMnO_4$ with equal volume of benzene containing 0.02 M TCMAC. The solution was made anhydrous by adding anhydrous sodium sulphate and its concentration was determined spectrophotometrically.

3.9.1 Stoichiometry and product analysis

The stoichiometry for the oxidation of 1-phenyl ethanol in benzene using TCMAP as oxidant was determined as mentioned in section 3.4.1. It was found that the ratio of [carbinol] : [TCMAP] = 3:2

The product analysis was also done in a similar manner as section 3.4.2

3.10 Kinetic studies

The kinetics of the oxidation of 1-phenyl ethanol in benzene using tricapryl methyl ammonium permanganate (TCMAP) were carried out at different conditions such as varying oxidant concentration, varying substrate concentration, at different temperatures etc.

3.10.1 Effect of varying the concentration of the oxidant (TCMAP) on the rate of oxidation 1-phenyl ethanol

The kinetics were studied by keeping the concentration of carbinol in excess to that of TCMAP to maintain pseudo-first order condition. The decrease in the concentration of $QMnO_4$ was determined by measuring its optical density at 528 nm spectrophotometrically. The pseudo-first order rate constant were computed by the method of least squares (Table 3.14). A plot of log absorbance of $QMnO_4$ versus time is linear showing first order dependence on oxidant concentration. (Fig.3.20).

Table 3.14

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

Solvent - Benzene T= 303 K

[Carbinol]10^2 (mol dm^{-3})	[TCMAP] 10^4 (mol dm^{-3})	k_{obs} 10^5 (s^{-1})	k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	Corr. Coeff
1.245	2.50	5.83	4.68	0.9983
1.245	5.12	5.89	4.72	0.9996
1.245	7.50	6.06	4.86	0.9993
1.245	12.5	5.98	4.80	0.9997

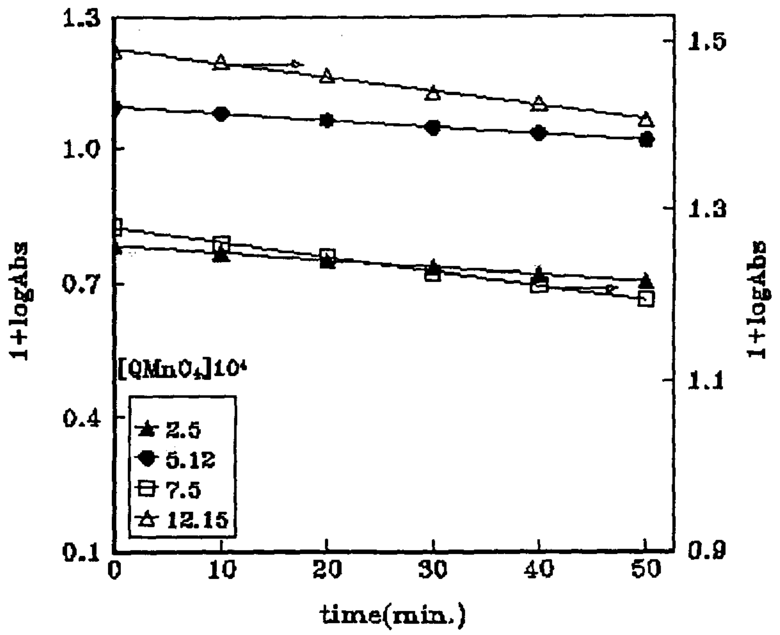


Fig 3.20 Effect of varying the concentration of the oxidant (TCMAP) on the rate of oxidation 1-phenyl ethanol

3.10.2 Effect of varying the concentration of substrate on the rate of oxidation of 1-phenyl ethanol

The concentration of carbinol was varied from 1.245x 10^{-2} to 4.78 x 10^{-2} mol dm^{-3}, keeping all other conditions the same. The observed pseudo-first order rate constants determined were divided by the respective carbinol concentration to get the second order rate constant which are almost constant. The results are presented in table 3.15 and in the fig 3.21.

Table 3.15

Effect of varying the concentration of the substrate on the rate of oxidation of 1-phenyl ethanol

Solvent - Benzene T= 303 K

[Carbinol]10^2 (mol dm^{-3})	[TCMAP] 10^4 (mol dm^{-3})	k_{obs} 10^5 (s^{-1})	k_2 x 10^3 (dm^3 mol^{-1}s^{-1})	Corr. Coeff
1.245	5.12	5.87	4.72	0.9996
2.490	5.12	11.55	4.63	0.9997
3.740	5.12	18.03	4.90	0.9998
4.980	5.12	23.37	4.59	0.9996

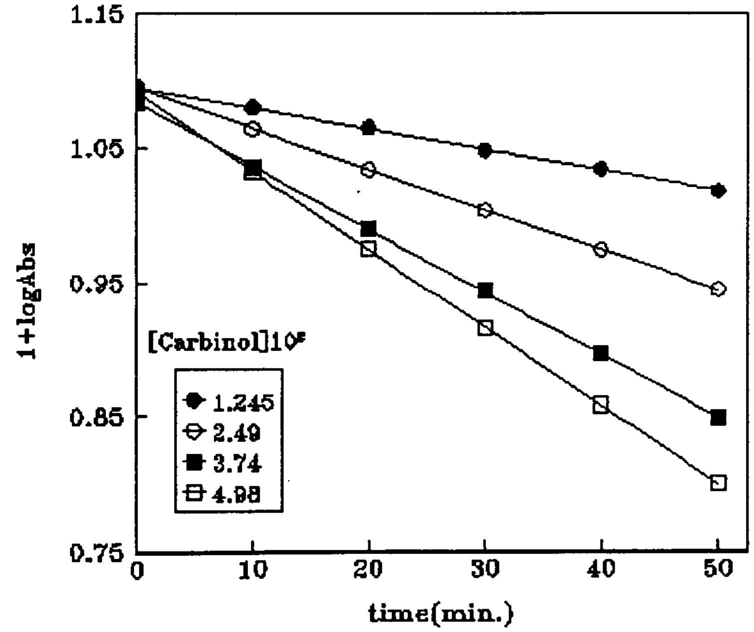


Fig 3.21 Effect of varying the concentration of the substrate on the rate of oxidation of 1-phenyl ethanol using TCMAP

3.10.3 Effect of adding TBAB into the reaction system

Varying concentrations of TBAB were added to the reaction system under similar kinetic conditions to see any salt effect in the organic medium. TBAB concentrations were varied from 1.0 x10^{-2} to 4.0 x 10^{-2} mol dm^{-3}. The results are represented in table 3.16.

Table 3.16

Effect of adding TBAB on the rate of oxidation of 1-phenyl ethanol.

[TCMAP] = 5.12 x 10^{-4} mol dm^{-3} Solvent – benzene

[$PhCHOHCH_3$] = 1.245 x 10^{-2} mol dm^{-3} T= 303K

[TBAB] x 10^2 (mol dm^{-3})	k_{obs} x 10^5 (s^{-1})	k_2x 10^3 (dm^3 $mol^{-1}s^{-1}$)
0	5.87	4.72
1	5.71	4.59
2	5.95	4.78
3	6.06	4.87
4	5.75	4.52

3.10.4 Effect of solvents on the rate of oxidation of 1-phenyl ethanol using TCMAP

The oxidation was studied in various organic solvents at 303 K by keeping all the kinetic conditions the same. The organic solvents employed were toluene, carbon tetrachloride, chloroform, methylene chloride and chlorobenzene in addition to benzene. The results are presented in table 3.17 and in figure 3.22.

Table 3.17

Effect of solvents on the rate of oxidation of 1-phenyl ethanol using TCMAP

$[TCMAP] = 5.12 \times 10^{-4}$ mol dm^{-3}

$[PhCHOHCH_3] = 1.245 \times 10^{-2}$ mol dm^{-3} T= 303K

Solvents	Dielectric constant	$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	Corr. Coeff
CCl_4	2.22	3.79	0.9995
C_6H_6	2.27	4.72	0.9996
$C_6H_5CH_3$	2.40	5.02	0.9990
$CHCl_3$	4.70	7.40	0.9997
C_6H_5Cl	5.62	6.07	0.9959
CH_2Cl_2	9.08	10.60	0.9994

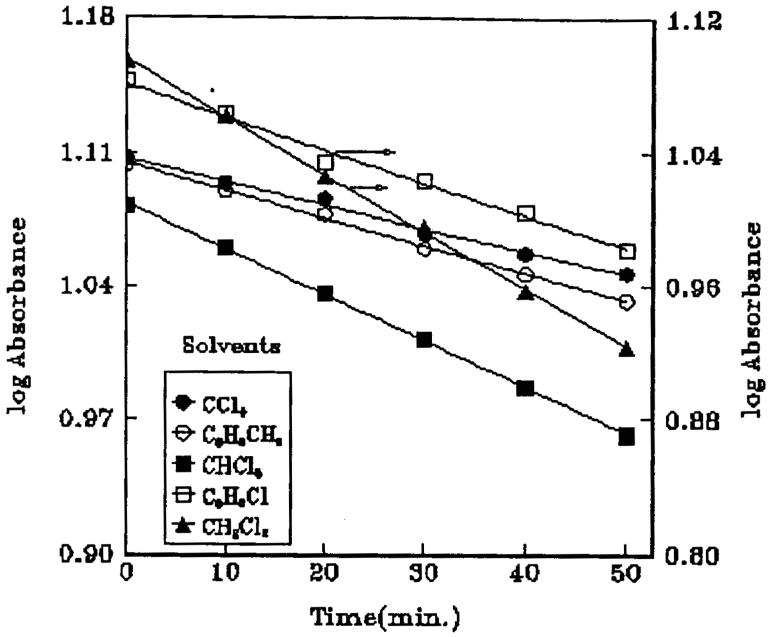


Fig 3.22 Effect of solvents on the rate of oxidation of 1-phenyl ethanol using TCMAP

3.10. 5 Effect of acrylonitrile

To the reaction mixture containing 1.245 x 10^{-2} mol dm^{-3} carbinol and 5.12x10^{-4} mol dm^{-3} TCMAP in benzene 5 ml of acrylonitrile was added and kept for 5 hours. No polymerization was observed indicating the absence of free radical during the course of oxidation.

3.10.6 Effect of temperature on the rate of oxidation of 1-phenyl ethanol using TCMAP

The influence of temperature on the rate of oxidation of 1-phenyl ethanol using TCMAP was studied by over a temperature range of 303K to 318K under pseudo- first condition. The results are shown in table 3.18 and in the figure 3.23

Table 3.18

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

[TCMAP] = 5.12×10^{-4} mol dm^{-3}

[$PhCHOHCH_3$] = 1.245×10^{-2} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	4.72	7.49	12.27	17.82
Corr.coeff.	0.9996	0.9998	0.9996	0.9997

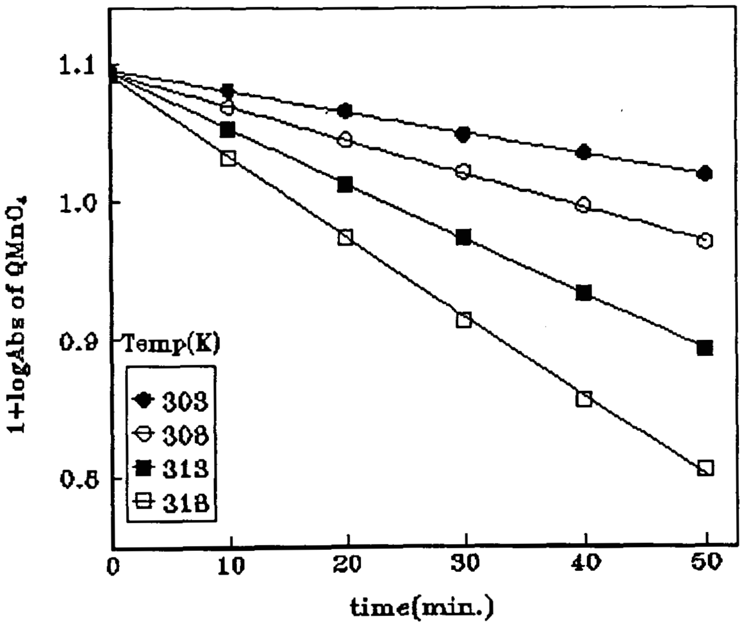


Fig 3.23 Effect of temperature on the rate of oxidation of 1-phenyl ethanol using TCMAP

3.11 Effect of substituents on the rate of oxidation of 1-phenyl ethanol using TCMAP

The effect of substituents on the benzene ring of 1-phenyl ethanol was studied using p-Me, p-Cl, p-OMe, p-NO_2 phenyl ethanols at 303K keeping all the kinetic conditions the same. (Fig.3.24)

The results are presented in table 3.19

Table 3.19

Effect of substituents on the rate of oxidation of 1-phenyl ethanol using TCMAP

[Carbinol] = 1.245×10^{-2} mol dm^{-3} T = 303K
[TCMAP] = 5.12×10^{-4} mol dm^{-3} Solvent- benzene

Carbinols	$k_2 \times 10^3$ ($dm^3 mol^{-1}s^{-1}$)	Corr. Coeff
$PhCHOHCH_3$	4.72	0.9996
p-Me $PhCHOH CH_3$	5.73	0.9997
p-Cl $PhCHOH CH_3$	8.42	0.9995
p-$OMePhCHOH CH_3$	22.59	0.9996
p-NO_2 $PhCHOH CH_3$	32.57	0.9992

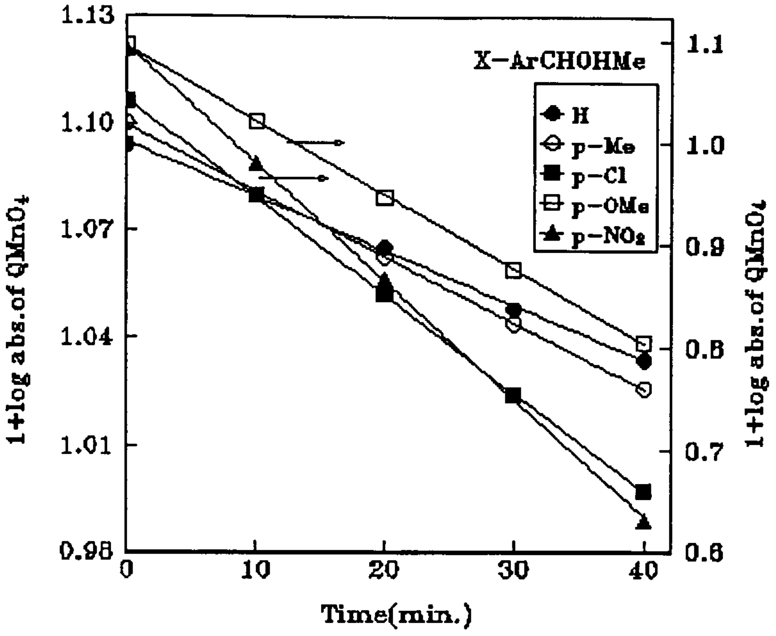


Fig. 3.24 Effect of substituents on the rate of oxidation of 1-phenyl ethanol using TCMAP

3.11.1 Effect of temperature on the rate of oxidation of substituted 1-phenyl ethanol using TCMAP

The effect of temperature on the rate of oxidation of the various substituted 1-phenyl ethanol was studied over a temperature range of 303K to 318K under pseudo-first order condition (fig. 3.25 to 3.28). The k_2 values are presented in tables 3.20 (a) to 3.20 (d).

Table 3.20 (a)

Effect of temperature on the rate of oxidation of p-Me 1-phenyl ethanol using TCMAP

[p-MePhCHOHCH$_3$] = 1.245 x 10^{-2} mol dm^{-3}

[TCMAP] = 5.12X10^{-4} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
k_2 x 10^3 (dm^3 mol^{-1}s^{-1})	5.73	9.17	13.66	21.01
Corr. coeff.	0.9998	0.9989	0.9990	0.9996

Table 3.20 (b)

Effect of temperature on the rate of oxidation of p-Cl 1-phenyl ethanol using TCMAP

[p-ClPhCHOHCH$_3$] = 1.245 x 10^{-2} mol dm^{-3}

[TCMAP] = 5.12X10^{-4} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
k_2 x 10^3 (dm^3 mol^{-1}s^{-1})	8.42	13.38	20.59	30.12
Corr.coeff.	0.9995	0.9998	0.9997	0.9995

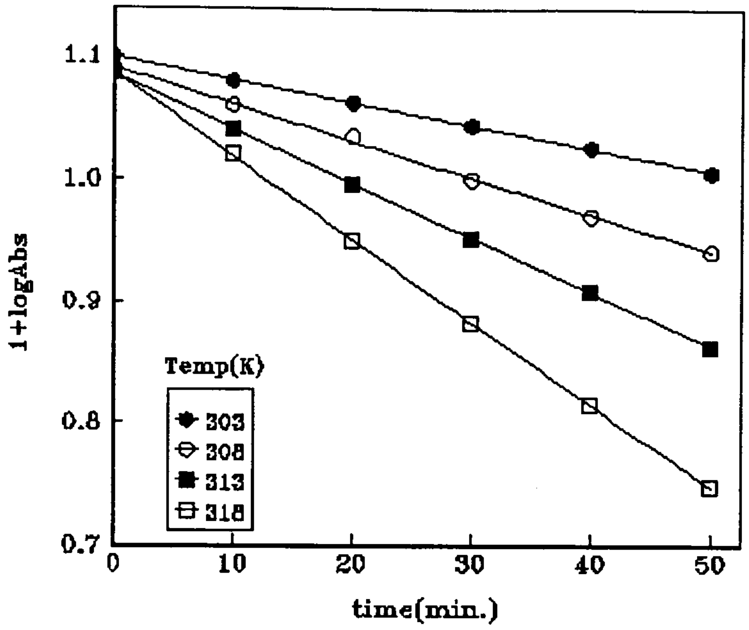


Fig 3.25 Effect of temperature on the rate of oxidation of p-Me 1-phenyl ethanol using TCMAP

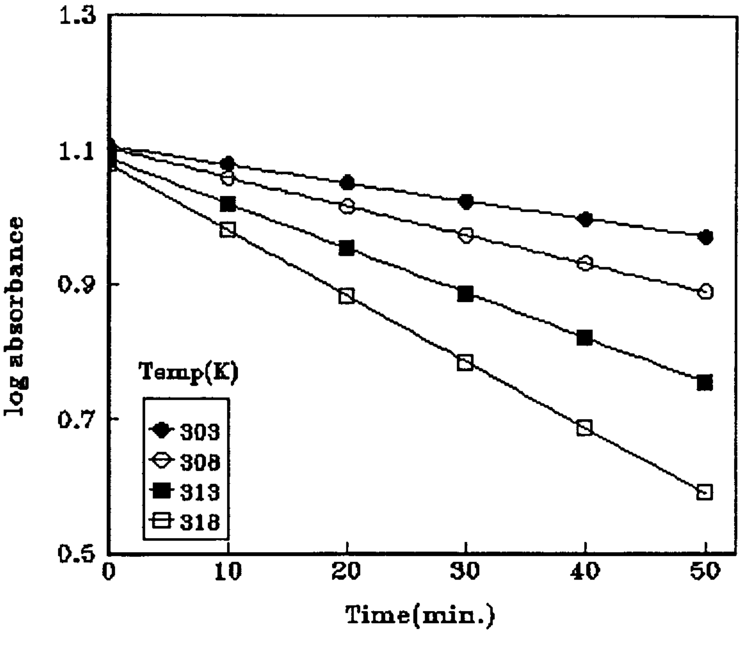


Fig 3.26 Effect of temperature on the rate of oxidation of p-Cl 1-phenyl ethanol using TCMAP

Table 3.20 (c)

Effect of temperature on the rate of oxidation of p-OMe 1-phenyl ethanol using TCMAP

[p-OMePhCHOHCH$_3$] = 1.245 x 10^{-2} mol dm^{-3}

[TCMAP] = 5.12X10^{-4} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
k$_2$ x 10^3 (dm^3 mol^{-1}s^{-1})	22.59	33.20	49.87	72.71
Corr.coeff.	0.9996	0.9982	0.9996	0.9990

Table 3.20 (d)

Effect of temperature on the rate of oxidation of p-NO$_2$-phenyl ethanol using TCMAP

[p-NO$_2$PhCHOHCH$_3$] = 1.245 x 10^{-2} mol dm^{-3}

[TCMAP] = 5.12X10^{-4} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
k$_2$ x 10^3 (dm^3 mol^{-1}s^{-1})	32.57	46.32	64.85	90.01
Corr.coeff.	0.9990	0.9998	0.9997	0.9995

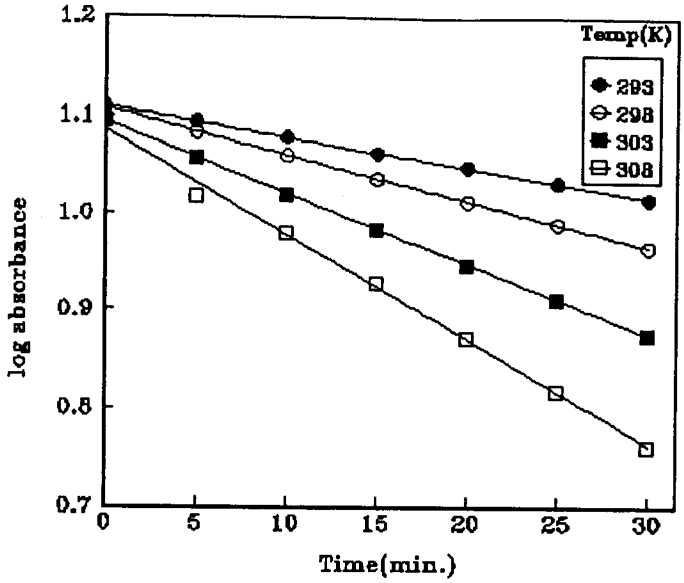


Fig 3.27 Effect of temperature on the rate of oxidation of p-OMe 1-phenyl ethanol using TCMAP

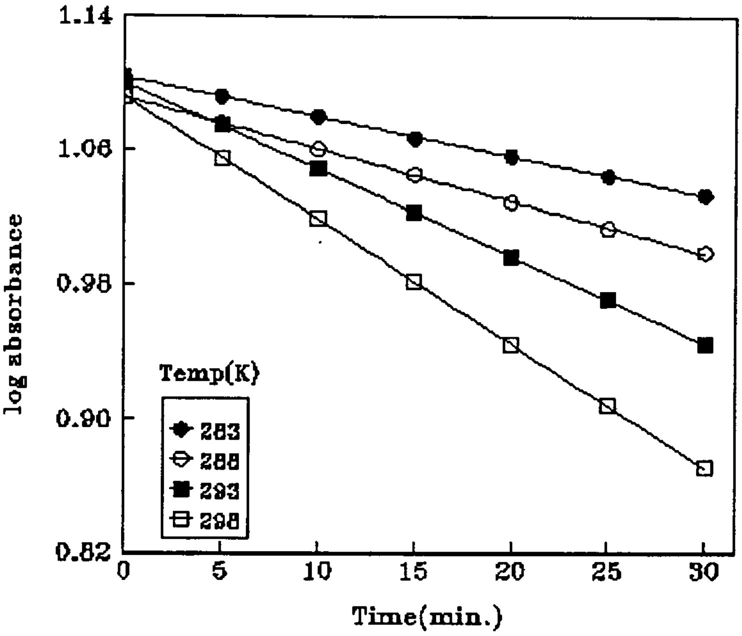


Fig 3.28 Effect of temperature on the rate of oxidation of $p\text{-}NO_2$-phenyl ethanol using TCMAP

3.12 Effect of temperature on the rate of oxidation of benzhydrol using TCMAP

The effect of temperature on the rate of oxidation of benzhydrol was studied at a temperature range of 303K to 318 K in benzene under pseudo-first order condition. (Fig.3.29). The k_2 values are presented in table 3.21.

Table 3.21

Effect of temperature on the rate of oxidation of benzhydrol using TCMAP

[PhCHOHPh] = 1.245 x 10^{-2} mol dm^{-3}

[TCMAP] = 5.12X10^{-4} mol dm^{-3} Solvent- benzene

Temp(K)	303	308	313	318
k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	10.79	15.19	22.54	29.40
Corr.coeff.	0.9997	0.9998	0.9995	0.9988

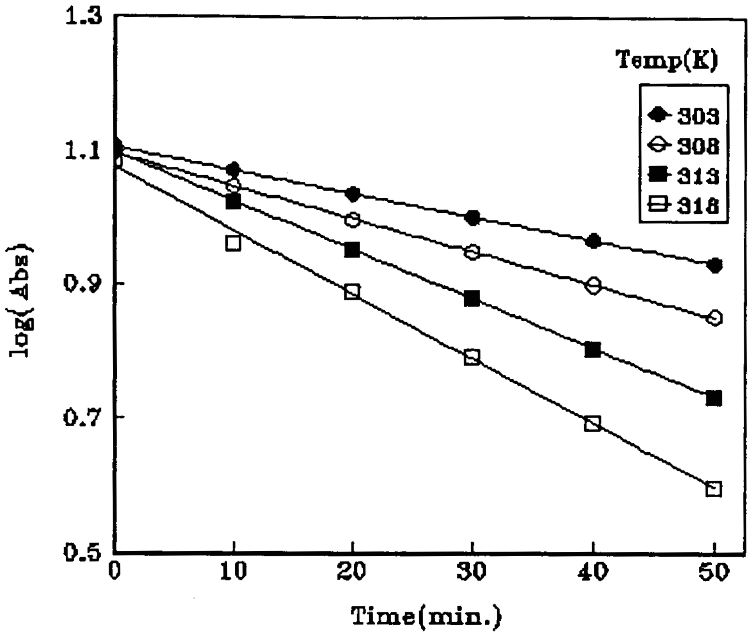


Fig 3.29 Effect of temperature on the rate of oxidation of benzhydrol using TCMAP

3.13. Effect of temperature on the rate of oxidation of cyclohexanol using TCMAP

The effect of temperature on the rate of oxidation of cyclohexanol was studied at temperature range of 303K to 318K in benzene under pseudo-first order condition using TCMAP as oxidant. The results are represented in table 3.22 and in the figure 3.30.

Table 3.22

Effect of temperature on the rate of oxidation of cyclohexanol using TCMAP

[Cyclohexanol] = 1.245×10^{-2} mol dm^{-3}

[TCMAP] = 5.12×10^{-4} mol dm^{-3} Solvent-benzene

Temp(K)	303	308	313	318
$k_2 \times 10^3$ (dm^3 mol^{-1}s^{-1})	3.92	6.53	10.12	15.69
Corr.coeff.	0.9998	0.9995	0.9994	0.9992

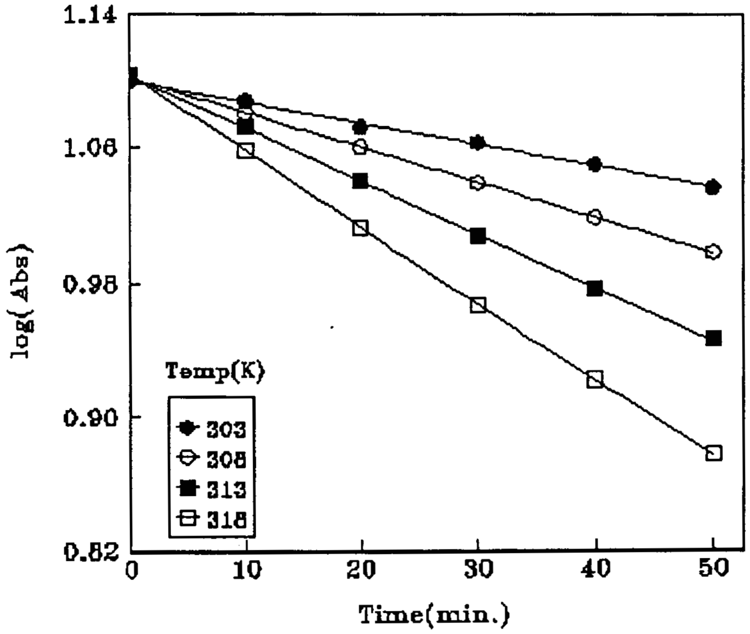


Fig 3.30 Effect of temperature on the rate of oxidation of cyclohexanol using TCMAP

3.14. Oxidation of 1-phenyl ethanol by $KMnO_4$ in aqueous acetic acid medium

The kinetics of the oxidation of 1-phenyl ethanol and some of its para-substituted derivatives like p-Me, p-Cl, p-OMe, and p-NO_2 carbinols were studied in 40% aqueous acetic acid medium with a view to compare the investigation with that of the PTC oxidation in benzene.

3.14.1 Stoichiometry of the reaction

A reaction mixture containing a known concentration of 1-phenyl ethanol and known concentration of $KMnO_4$ in 40% aqueous acetic acid was kept at room temperature for 5 hours (for the completion of reaction). 2ml aliquot of the reaction mixture was pipetted out and the concentration of unreacted MnO_4^- ions were estimated iodometricaly. The estimation were repeated at regular interval of time to get concordant thiosulphate titre value corresponding a constant concentration of $KMnO_4$. From the concentration of unreacted $KMnO_4$, the stoichiometry of the reaction was determined.

3.14.2 Isolation of product of the oxidation

A reaction mixture containing excess of $KMnO_4$ over 1-phenyl ethanol in 40% aqueous acetic acid was kept for 5 hours for the completion of reaction. Unreacted $KMnO_4$ is decolourised by the addition of sodiumbisulphite and suspended manganese dioxide particles were removed by filtration. The solution was extracted with ether three times and ether extract was collected. After evaporating off the ether the product was treated with methanolic 2,4 dinitrophenylhydrazine when orange yellow crystals of 2,4 dinitrophenylhydrozone (DNP) of acetophenone was produced. The aqueous layer on acidification did not give any precipitate ruled out the formation of benzoic acid.

3.15 Kinetic Studies

The kinetics of the oxidation of 1-phenyl ethanol by $KMnO_4$ in 40% aqueous acetic acid were studied at different conditions of oxidant concentration, susbstrate concentration, and at different temperatures. The effects addition of salts, mineral acid and change of polarity of the medium on the rate of oxidation were also analysed. The influence of various substituents at the para position of the aryl ring of 1-phenyl ethanol on the rate was also studied.

3.15.1 Effect of oxidant concentration on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid

The kinetics of the oxidation of 1-phenyl ethanol using $KMnO_4$ in 40% aqueous acetic acid were followed by taking fixed amount of substrate and varying amount of oxidant ($KMnO_4$). The pseudo-first order condition was maintained by keeping [carbinol] > [$KMnO_4$]. The concentration unreacted $KMnO_4$ was determined idometricaly at regular interval of time. The pseudo-first order rate constant were computed by the method of least square from the linear plot of log [$KMnO_4$] versus time . (Fig. 3.31) The results are tabulated in table 3.23.

Table 3.23

Effect of oxidant concentration on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid

Medium - 40% aq HOAc (v/v) T = 303 K

10^3 [$KMnO_4$] (mol dm^{-3})	10^2[carbinol] (mol dm^{-3})	10^5 k_{obs} (s^{-1})	$10^3 k_2$ ($dm^3 mol^{-1} s^{-1}$)	Correlation
0.50	1.00	15.62	15.62	0.9980
0.75	1.00	15.49	15.49	0.9978
1.00	1.00	15.23	15.23	0.9990
1.25	1.00	15.54	15.54	0.9959

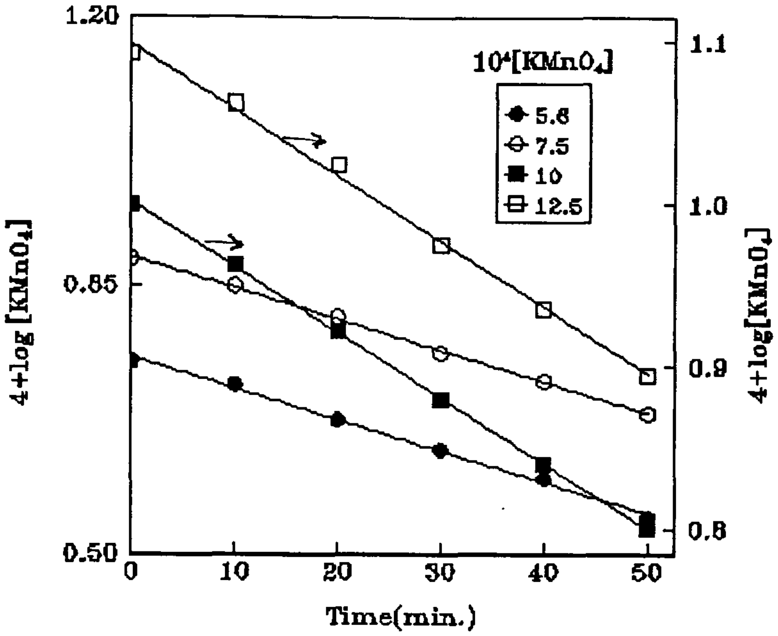


Fig. 3.31 Effect of oxidant concentration on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid

3.15.2 Effect of varying the concentration of substrate on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid

The effect of varying the concentration 1-phenyl ethanol on the rate of oxidation was studied at a concentration range of 1.0 x 10^{-2} mol dm^{-3} to 3.0 x 10^{-2} mol dm^{-3} of the carbinol by keeping all other kinetic conditions the same. (Fig.3.32) From the observed pseudo-first order constant, the second order rate constant was calculated by dividing it by [carbinol]. The results are presented in table 3.24.

Table 3.24

Effect of varying the concentration of substrate on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid

Medium - 40% aq HOAc (v/v) T = 303 K

10^3 [$KMnO_4$l] (mol dm^{-3})	10^2 [carbinol] (mol dm^{-3})	10^5 k_{obs} (s^{-1}) (mol dm^{-3})	10^3k_2 = k_{obs}/[carbinol] ($dm^3ml^{-1}s^{-1}$)	Correlation
1.00	1.00	15.23	15.23	0.9990
1.00	1.50	22.12	15.15	0.9989
1.00	2.00	31.47	15.73	0.9965
1.00	2.50	39.15	15.66	0.9978
1.00	3.00	45.06	15.35	0.9992

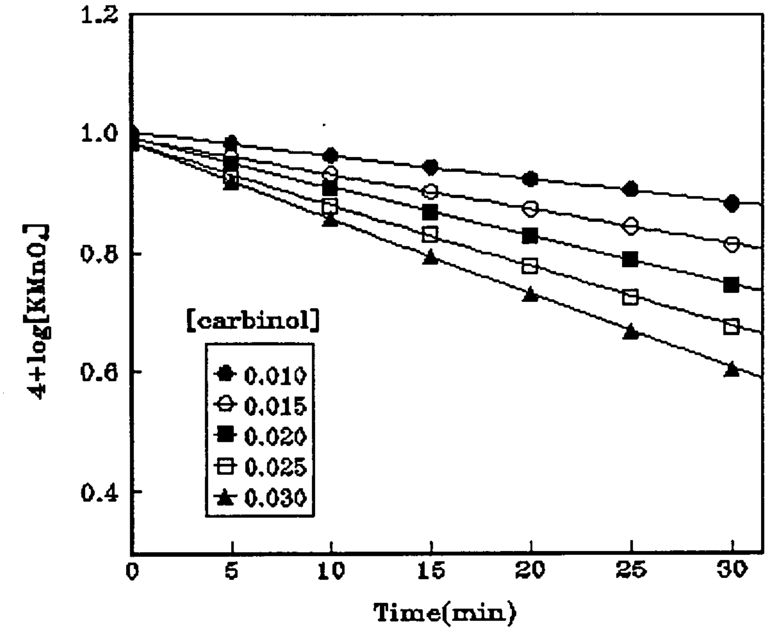


Fig 3.32 Effect of varying the concentration of substrate on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid

3.15.3 Influence of added salt on the rate of oxidation 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

The effect of ionic strength was studied using NaCl in 40% aqueous acetic medium under the pseudo-first condition. The concentration the salt was varied from 1.0×10^{-2} mol dm^{-3} to 4.0×10^{-2} mol dm^{-3}. The results are given in table 3.25.

Table 3.25

Influence of added salt on rate of oxidation 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [1-phenyl ethanol] $= 1.0 \times 10^{-2}$ mol dm^{-3}

Medium - 40% aq HOAc (v/v) T = 303 K

10^2 [NaCl] (mol dm^{-3})	10^5 k_{obs} (s^{-1})	10^3 k_2 (dm^{3}mol^{-1}s^{-1})	Correlation
0.00	15.23	15.23	0.9990
1.00	15.39	15.39	0.9978
2.00	15.43	15.43	0.9985
3.00	15.54	15.54	0.9989
4.00	15.62	15.62	0.9975

3.15.4 Effect of added mineral acid (effect of H^+ ion) on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

The effect of H^+ ions on the rate of oxidation of 1-phenyl ethanol was studied by varying the concentration of H_2SO_4 from 1.0 x 10^{-2} mol dm^{-3} to 15 x 10^{-2} mol dm^{-3} under pseudo-first order condition. (Fig.3.33). The observed rate constants are tabulated in table 3.26

Table 3.26

Effect of added mineral acid (effect of H^+ion) on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4]$ = 1.0 x 10^{-3} mol dm^{-3} [1-phenyl ethanol] = 1.0 x 10^{-2} mol dm^{-3}
Medium - 40% aq HOAc (v/v) T = 303 K

10^2 $[H_2SO_4]$ (mol dm^{-3})	10^5 k_{obs} (s^{-1})	10^3 k_2 ($dm^3mol^{-1}s^{-1}$)	Correlation
0.00	15.23	15.23	0.9990
2.27	17.29	17.29	0.9981
6.80	20.84	20.84	0.9995
11.36	27.15	27.15	0.9968
15.90	32.97	32.97	0.9968

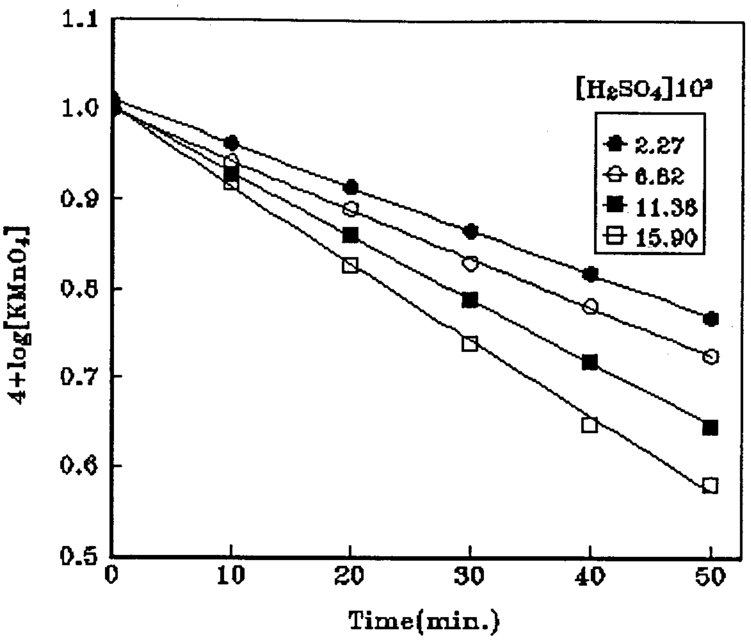


Fig 3.33 Effect of added mineral acid (effect of H$^+$ion) on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

3.15.5 Effect of polarity of the medium on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

The reaction was carried at different percentage of acetic acid composition in water (from 10-80%) at 303K under pseudo-order condition. The study was to get the information about the type of interaction in the rate-determining step of the reaction. The results are presented in table 3.27 and figure 3.34.

Table 3.27

Effect of polarity of the medium on the rate of oxidation of 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [1-phenyl ethanol] = 1.0×10^{-2} mol dm^{-3}

Medium - aq HOAc (v/v) T = 303 K

% of acetic acid (v/v)	10	20	30	40	50	60	70	80
Dielectric constant	67.5	61	53	47	39.8	32	24.5	17.5
$10^3 k_2$ (dm^{3}mol^{-1}s^{-1})	25.03	21.76	18.61	15.23	11.94	15.08	17.57	21.80
Correlation coefficient	0.9993	0.9997	0.9994	0.9996	0.9958	0.9990	0.9980	0.9986

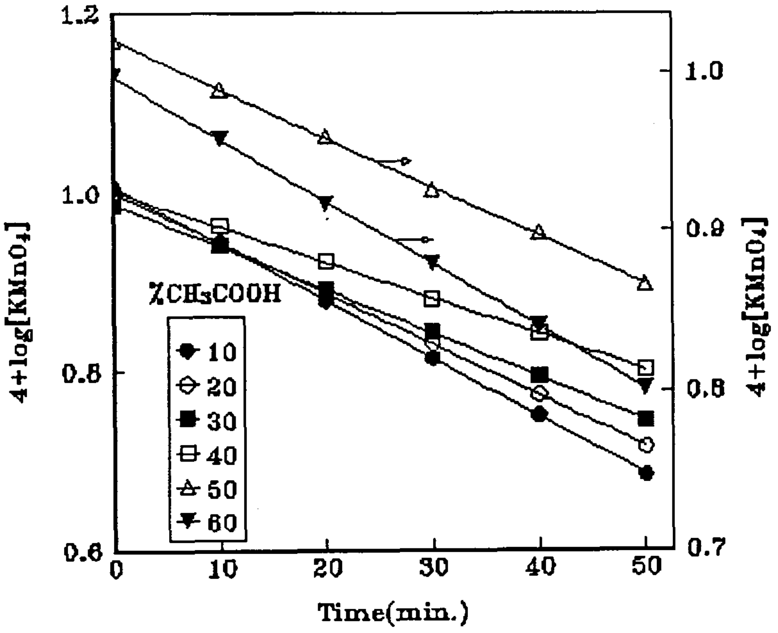


Fig 3.34 Effect of polarity of the medium on the rate of oxidation of 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

3.15.6 Effect of temperature on the rate of oxidation 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

The effect of temperature on the kinetics of the oxidation of 1-phenyl ethanol in 40% acetic acid was studied by varying the temperature from 303K to 318K under identical conditions. In all the cases the pseudo-first order condition was maintained by keeping the [alcohol] > [$KMnO_4$] (fig 3.35). The results are tabulated in table 3.28.

Table 3.28

Effect of temperature on the rate of oxidation 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

[$KMnO_4$] = 1.0 10^{-3} mol dm^{-3} [1-phenyl ethanol] = 1.0 x 10^{-2} mol dm^{-3}

Medium - 40% aq HOAc (v/v)

Temperature K	$10^3 k_2$ ($dm^3mol^{-1}s^{-1}$)	Correlation
303	15.23	0.9990
308	22.72	0.9995
313	30.00	0.9996
318	39.16	0.9998

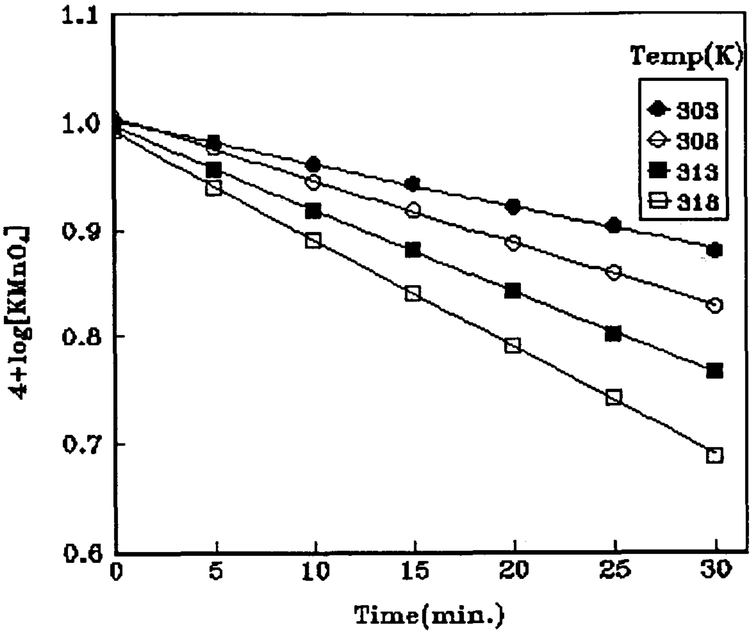


Fig 3.35 Effect of temperature on the rate of oxidation 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

3.15.7 Effect of the addition of acrylonitrile to the reaction mixture

To the reaction mixture containing 1.0 x 10^{-2} mol dm^{-3} 1-phenyl ethanol and 1.0 x 10^{-3} mol dm^{-3} $KMnO_4$ in 40% aqueous acetic acid, 5 ml acrylonitrile was added. The system was kept over night in the dark. The absence of white precipitate ruled out the possibility of polymerisation.

3.16 Effect of substituents on the rate of oxidation of 1-phenyl ethanol using $KMnO_4$ in aqueous acetic acid medium

The effect of substituents on the phenyl ring of 1-phenyl ethanol was studied using p-Me, p-Cl, p-OMe and p-NO_2 phenyl ethanols. The kinetics were studied under pseudo-first order condition by keeping all other conditions the same. The results are presented in table 3.29 and figure 3.36.

Table 3.29

Effect of substituents on the rate of oxidation using $KMnO_4$ in aqueous acetic acid medium

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [Carbinols] = 1.0×10^{-2} mol dm^{-3}
Medium - 40% aq HOAc (v/v) T = 303K

Carbinols	**$10^3 K_2$ ($dm^3 mol^{-1}s^{-1}$)**	**Corr. Coeff**
$PhCHOHCH_3$	15.23	0.9995
p-Me $PhCHOHCH_3$	24.65	0.9978
p-Cl $PhCHOHCH_3$	16.10	0.9985
p-OMe$PhCHOHCH_3$	84.52	0.9990
p-NO_2 $PhCHOHCH_3$	28.80	0.9989

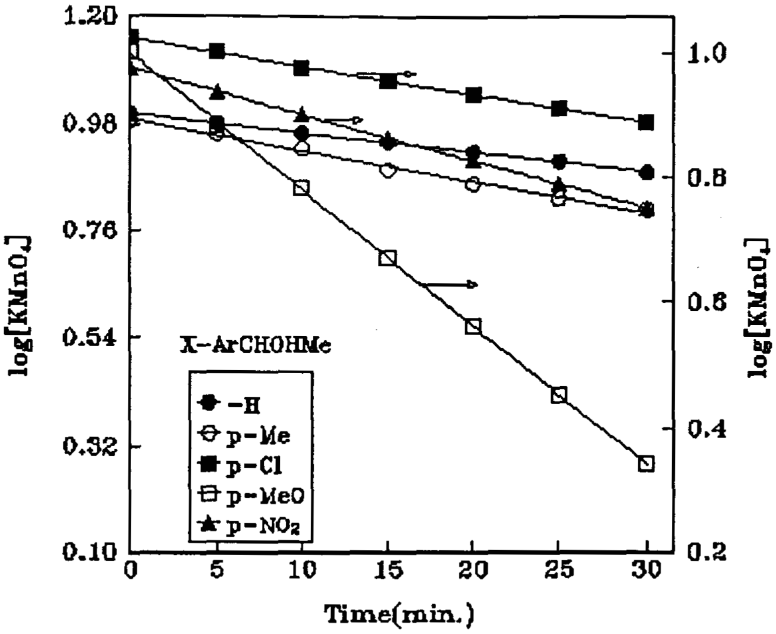


Fig 3.36 Effect of substituents on the rate of oxidation using $KMnO_4$ in aqueous acetic acid medium

3.16.1 Effect of temperature on the rate of oxidation of susbtituted 1-phenyl ethanol using $KMnO_4$ in aqueous acetic acid medium

The influence of temperature on the rate of oxidation of p-Me, p-Cl, p-OMe and p-NO_2 phenyl ethanols were studied at the temperature range varied from 303K to 318K under pseudo-first order condition and the rate constants were determined (table 3.30(a) to 3.30 (d) and (figure 3.37 to 3.40).

Table 3.30(a)

Effect of temperature on the rate of oxidation p-Me 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p-Me $PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium - 40% aq HOAc (v/v)

Temperature K	10^3 k_2 (dm^{3}mol^{-1}s^{-1})	Correlation
303	24.65	0.9978
308	34.82	0.9989
313	47.65	0.9989
318	63.50	0.9990

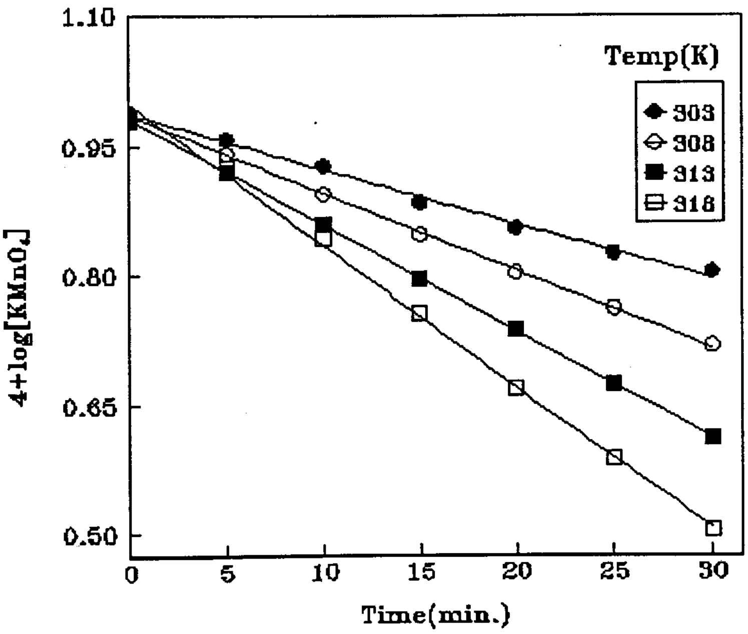


Fig 3.37 Effect of temperature on the rate of oxidation p-Me 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

Table 3.30(b)

Effect of temperature on the rate of oxidation p-Cl 1- phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p-Cl $PhCHOHCH_3$] $= 1.0 \times 10^{-2}$ mol dm^{-3}

Medium - 40% aq HOAc (v/v)

Temperature K	$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	Correlation
303	16.25	0.9985
308	23.61	0.9964
313	32.95	0.9990
318	44.04	0.9987

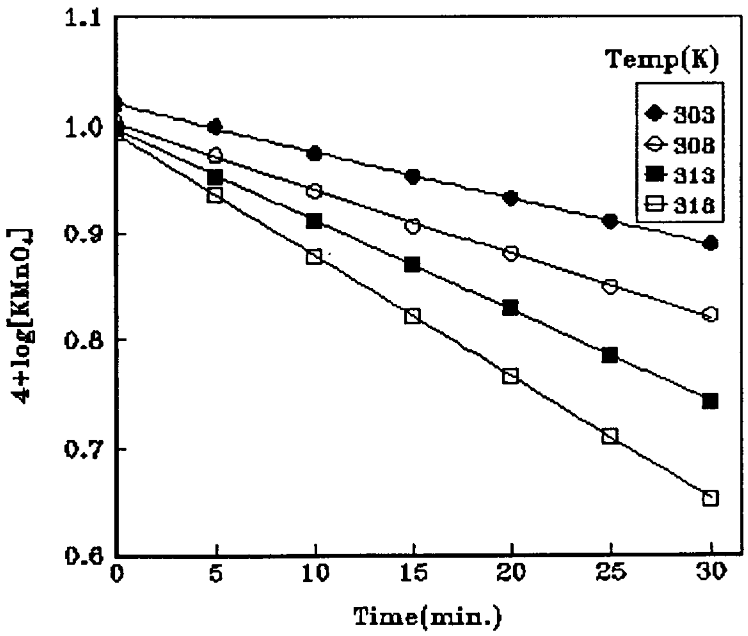


Fig 3.38 Effect of temperature on the rate of oxidation p-Cl phenyl ethanol in aqueous acetic acid using $KMnO_4$

Table 3.30(c)

Effect of temperature on the rate of oxidation p-OMe 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p-OMe $PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium - 40% aq HOAc (v/v)

Temperature K	10^3 k_2 ($dm^3mol^{-1}s^{-1}$)	Correlation
303	84.52	0.9989
308	134.34	0.9956
313	210.39	0.9975
318	324.86	0.9990

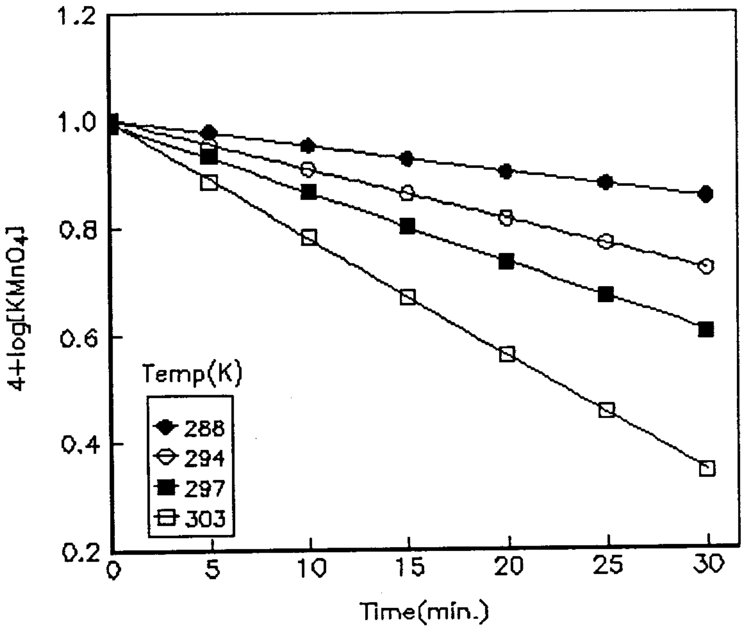


Fig. 3.39 Effect of temperature on the rate of oxidation p-OMe phenyl ethanol in aqueous acetic acid using $KMnO_4$

Table 3.30(d)

Effect of temperature on the rate of oxidation p-NO_2 1-phenyl ethanol in aqueous acetic acid using $KMnO_4$

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p-NO_2 $PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium - 40% aq HOAc (v/v)

Temperature K	$10^3 k_2$ (dm^{3}mol^{-1}s^{-1})	Correlation
303	28.88	0.9985
308	43.03	0.9978
313	66.41	0.9990
318	88.61	0.9947

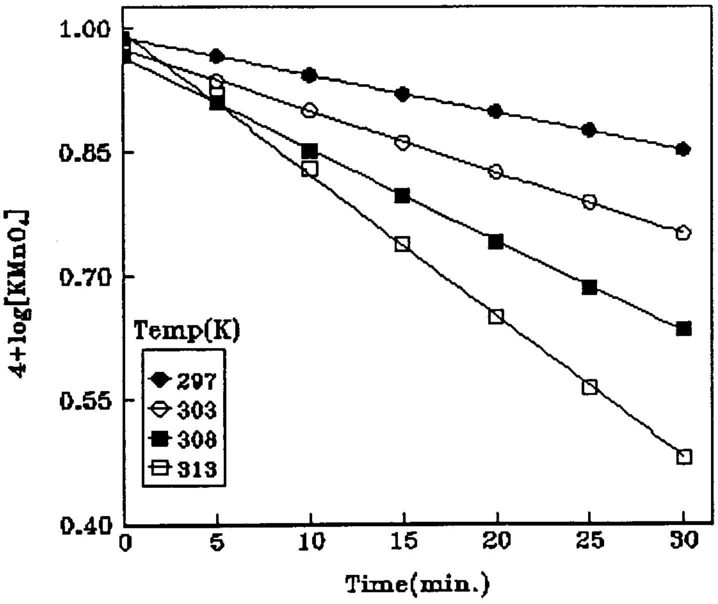


Fig.3.40 Effect of temperature on the rate of oxidation p-NO_2 phenyl ethanol in aqueous acetic acid using $KMnO_4$

CHAPTER IV

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

4.0 The experimental results on the kinetic investigation on the oxidation of 1-phenyl ethanol and its p-CH_3, p-OCH_3, p-Cl, p-NO_2 derivatives in benzene using phase transferred permanganate were presented and discussed in this chapter. Results on similar investigations on the oxidation of cyclohexanol and benzhydrol are also given in this chapter. Studies on the permanganate oxidation of 1-phenyl ethanol its p-CH_3, p-OCH_3, p-Cl and p-NO_2 derivatives in aqueous acetic acid medium have been carried out and are given separately. A comparison of the rate data and data on activation parameters of the catalysed reaction and the one taking place in aqueous solvent without catalyst would reveal the effect of the phase transfer catalytic activity.

4.1 Oxidation of 1-phenyl ethanol and other secondary alcohols using phase transferred permanganate (TBAP & TCMAP) in benzene

The experimental results on the kinetic investigation on the oxidation of 1-phenyl ethanol and its p-CH_3, p-OCH_3, p-Cl, p-NO_2 derivatives, other secondary carbinols like benzhydrol and cyclohexanol carried out separately in benzene using phase transferred permanganate with tetrabutylammonium bromide (TBAB) and tricapryl methylammonium chloride (TCMAC) as PT catalyst are presented and discussed in this section. Eventhough the oxidation of these carbinols can be carried out in heterogeneous condition with benzene solution of the carbinol and aqueous solution of the oxidant mixed with PT catalyst, the measurement of rates of phase transferred reactions are more convenient in homogenous condition. Hence the oxidant was first phase transferred into the non-polar organic solvents. Other solvents such as carbon tetrachloride, toluene, chloroform, chlorobenzene, methylene chloride etc. were also used for the studies of the oxidation of 1-phenyl ethanol by phase transferred permanganate. The effects of these solvents in relation to their specific properties such as dielectric constant are presented and discussed appropriately.

4.1.1 Soichiometry and the product of the oxidation

The experiments for the determination of the soichiometry of the reaction were conducted under the condition [$QMnO_4$]> [Carbinol] using TBAP & TCMAP as oxidants and 1-phenyl ethanol as substrate. The ratio of [Carbinol] : [$QMnO_4$] = 3:2 found experimentally conformed to a stoichiometry as given by the equation.

$$3ArCHOHCH_3+2QMnO_4\rightarrow 3ArCOCH_3+2MnO_2+2Q(OH)+2H_2O$$

where Q=TBA^+ or $TCMA^+$

The product of the reaction was ascertained to be acetophenone from the formation of corresponding 2,4-dinitro phenyl hydrazone(DNP) both with respect to TCMAP and TBAP as oxidant. This is also evident from spectral data (See fig. 3.8).

4.1.2 Kinetic studies

4.1.2.1 Effect of concentration of the oxidant ($QMnO_4$) on the rate of oxidation

The oxidation of 1-phenyl ethanol were carried out with different initial concentration of oxidants using TBAB and TCMAC as PT catalyst and rates were measured under the condition [carbinol]> >[$QMnO_4$]. The plot of log (Abosorbance) of $QMnO_4$ verses time gave linear relation at all concentration of the oxidant. Hence there is a first order dependence of the reaction on the oxidant concentration. The results of these investigations are consolidated in Table 4.1.

Table. 4.1

Effect of oxidant concentration, on the rate of oxidation of 1-phenyl ethanol using TBABand TCMAC as catalyst

$[PhCHOHCH_3] = 1.245 \times 10^{-2}$ mol dm^{-3} T= 303K

Solvent - benzene

Oxidant ($QMnO_4$)		$10^5 k_{obs} (s^{-1})$	$10^3 k_2$ ($dm^3 mol^{-1} s^{-1}$)
[TBAP] x 10^4 (mol dm^{-3})	[TCMAP] x 10^4 (mol dm^{-3})		
2.43	-	4.22	3.38
5.12	-	3.92	3.14
7.60	-	4.16	3.32
12.20	-	4.11	3.29
-	2.43	5.83	4.68
-	5.12	5.89	4.72
-	7.60	6.33	5.08
-	12.20	6.06	4.87

4.1.2.2 Effect of the concentration of substrate on the rate of oxidation

Rate measurements of the oxidation were carried out with different initial concentration of the substrate. The observed rate constant increased linearly with the increase in the concentration of the carbinol with both the catalysts used to phase transfer the oxidant. Further the second order rate constants, k_2 obtained by dividing the k_{obs} value by the respective carbinol concentration were almost constant indicating first order behaviour with respect to carbinol concentration. 1-phenyl ethanol was used as the substrate. The results are presented in table 4.2

Table 4.2

Effect of substrate concentration on the rate of oxidation

T= 303K Solvent - benzene

Oxidant ($QMnO_4$)		10^2 [carbinol] (mol dm^{-3})	$10^5k_{obs}(s^{-1})$	10^3k_2 (dm^3 $mol^{-1}s^{-1}$)
[TBAP] x 10^4 (mol dm^{-3})	[TCMAP] x 10^4 (mol dm^{-3})			
5.12	-	1.245	3.92	3.14
5.12	-	2.490	8.10	3.25
5.12	-	3.750	11.48	3.06
5.12	-	4.980	15.58	3.13
-	5.12	1.245	5.87	4.72
-	5.12	2.490	11.55	4.63
-	5.12	3.750	18.30	4.90
-	5.12	4.980	22.37	4.59

The first order dependence of the carbinol concentration is further confirmed by the double logarithemic plot viz that of log k_{obs} vs log [carbinol] which is linear with slope equal to unity (Fig. 4.1 (a & b)). The second order rate constants are practically constant for the same catalyst. The above table also indicates that TCMAC is a better catalyst for these types of oxidation as there are almost a fifty percentage of enhancements on the reaction rate with TCMAC. This better efficiency of the catalyst is due to the greater organophilicity of the cationic part of the catalyst.

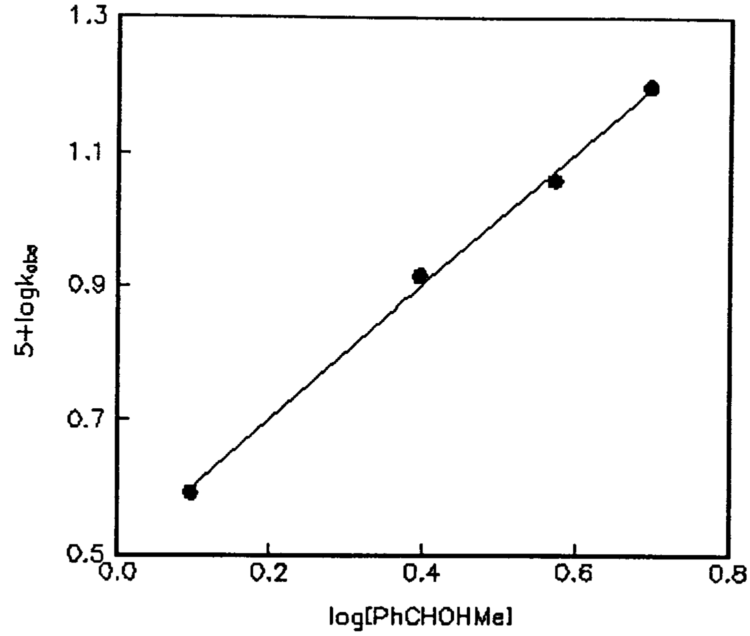


Figure 4.1 (a)

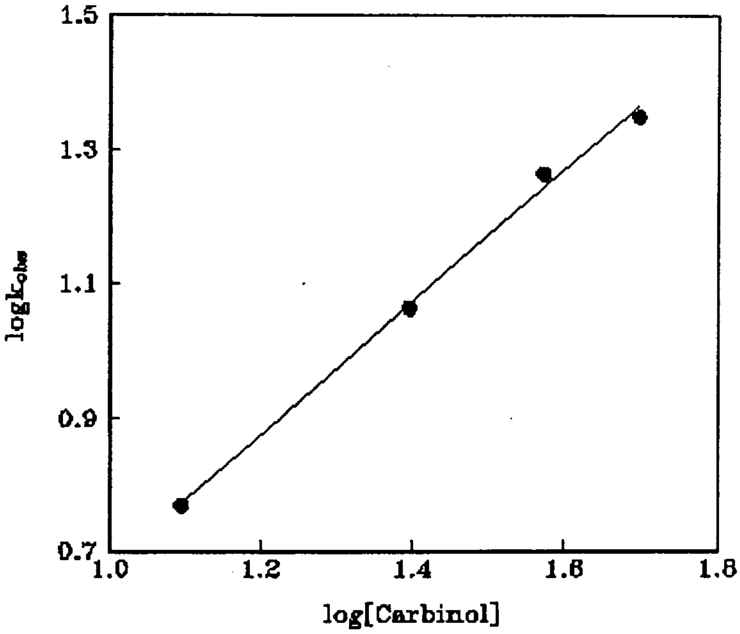


Fig. 4.1 (b)

Fig. 4.1 plot of log k$_{obs}$ vs log [carbinol], (a) using TBAP (b) using TCMAP

The double reciprocal plots, the plot of $1/k_{obs}$ vs. 1/[carbinol] is linear passing through the origin both in the case of TBAB and TCMAP as oxidant (Fig. 4.2 (a & b)). This ruled out the formation of a long-lived intermediate. However, the progress of the reaction through a transient complex during the permanganate oxidation cannot be ruled out[125]. The formation of a short lived manganate (v) ester intermediate whose the rate of formation as well as the rate of decomposition dependent on the substrate concentration was predicted by Ogino T *et al*[151] during the studies on the permanganate oxidation of endo-Dicyclopentadiene in methylene chloride using quaternary salts as PT catalysts. A first order dependence of the decay of the intermediate on the alkene concentration has been established.

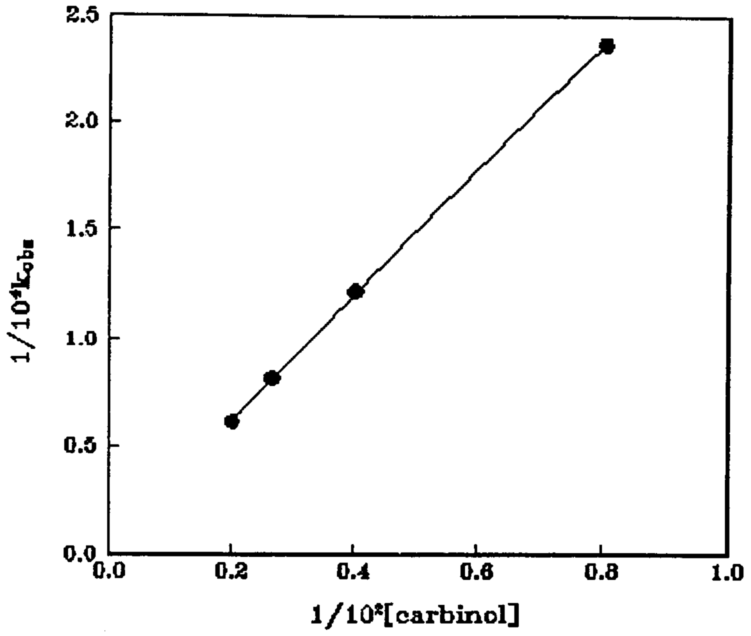


Fig. 4.2 (a)

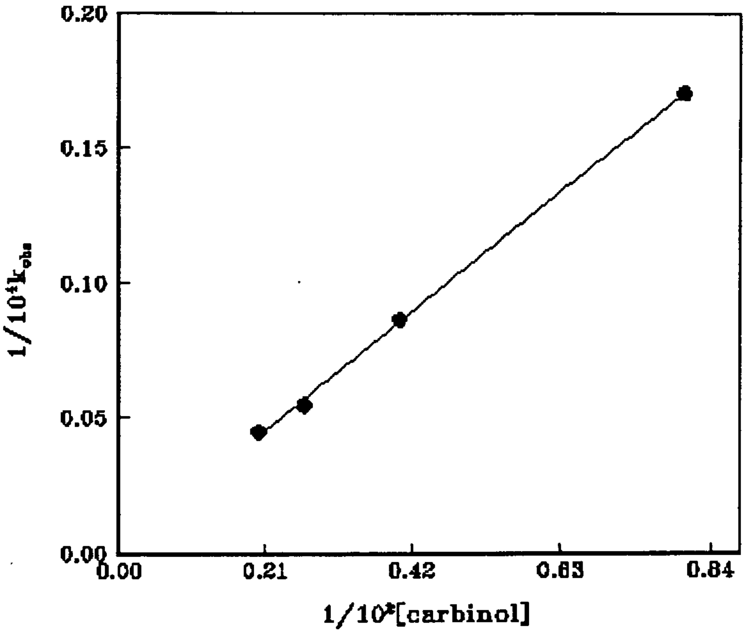


Fig. 4.2 (b)

Fig. 4.2 Plot of $1/k_{obs}$ vs 1/[substrate], (a) using TBAP (b) using TCMAP

4.1.2.3 Effect of adding TBAB into the reaction system (salt effect)

The effect of addition of TBAB into the reaction system did not produce any change in the value of rate constant for the oxidation of 1-phenyl ethanol in benzene both with respect to TBAP and TCMAP as the oxidants (Table 4.3). It is indicative of the fact that the reaction rate is unaffected by changes in ionic strength of the medium. Moreover, the catalytic efficiency of both the $QMnO_4$ are also not affected.

Table 4.3

Effect of adding TBAB into the reaction system (salt effect)

$[QMnO_4] = 5.12 \times 10^{-4}$ mol dm^{-3} T= 303K
$[PhCHOHCH_3] = 1.245 \times 10^{-2}$ mol dm^{-3} Solvent - benzene

Oxidant ($QMnO_4$)	TBAP		TCMAP	
[TBAP] 10^2 (mol dm^{-3})	$10^5k_{obs}(s^{-1})$	10^3k_2 (dm^3 mol^{-1}s^{-1})	$10^5k_{obs}(s^{-1})$	10^3k_2 (dm^3 mol^{-1}s^{-1})
0	3.92	3.14	5.87	4.72
1	4.22	3.38	5.71	4.59
2	3.87	3.12	5.95	4.78
3	4.03	3.32	6.06	4.87
4	3.92	3.14	5.75	4.62

The addition of TBAB to the reaction system in benzene medium can be treated as the addition of a salt to see any influence of one similar to the ionic strength[165-167] on the rate of oxidation. Since there is no appreciable change in the value of rate constant, as is evident from the table 4.3, it can be assumed that the rate-determining step involves the interaction of a dipole or a neutral molecule with an ion or another polar entity.

4.1.2.4 Effect of the dielectric constant of the solvent on the rate of oxidation

The influence of various solvents with different dielectric constant on the rate of the oxidation of 1-phenyl ethanol is given as shown in table 4.4. The results show that the rate of oxidation increased with increase in the dielectric constant of the organic solvent employed. The order of reactivity in various organic solvents is given as carbon tetrachloride <benzene<toluene<chlorobenzene<chloroform<methylene chloride. The plot of log k_2 vs 1/D of the solvent is almost linear with negative slope with correlation coefficient 0.997 (Fig. 4.3). It is indicative of the interaction between an anion and a dipole according to Amis equation[168,169]. The possibility of greater charge separation in the transition state compared to the ground state is also evident.

Table. 4.4

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

$[QMnO_4] = 5.12 \times 10^{-4}$ mol dm^{-3} T= 303K

$[PhCHOHCH_3] = 1.245 \times 10^{-2}$ mol dm^{-3}

Solvent	dielectric constant	10^3k_2 (dm^3 mol^{-1}s^{-1}) TBAP	TCMAP
CCl_4	2.22	2.99	3.79
C_6H_6	2.27	3.14	4.72
$C_6H_5CH_3$	2.40	3.63	5.02
C_6H_5Cl	5.62	5.42	6.07
$CHCl_3$	4.70	6.32	7.40
CH_2 Cl_2	9.08	7.86	10.60

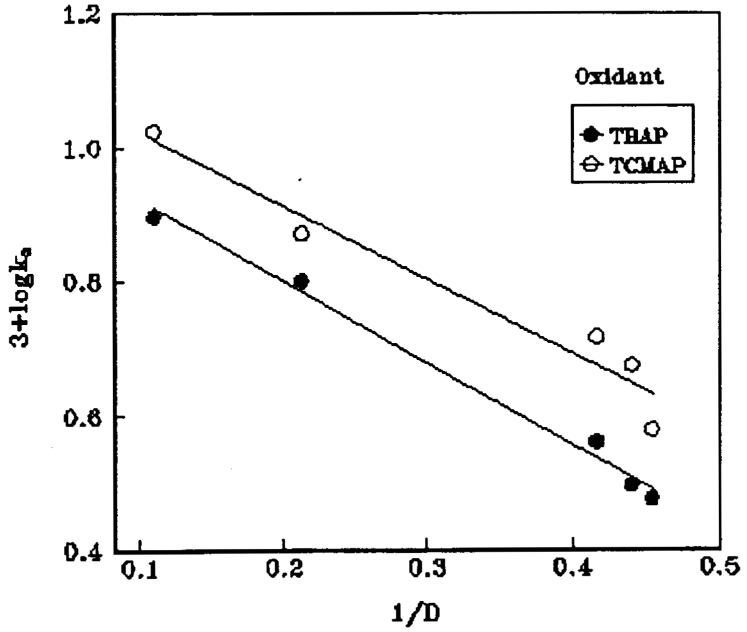


Fig 4.3 Solvent effects on the rate of oxidation of 1-phenyl ethanol using TBAP and TCMAP

4.1.2.5 Effect of substituents on the rate of oxidation of 1-phenyl ethanol

The effect of substituents on the permanganate oxidation of 1-phenyl ethanol under PTC condition has been investigated. The substituents chosen were methyl, methoxy, chloro and nitro for studying their effect when they are present at the para position of 1-phenyl ethanol. The results of such studies with TBAP and TCMAP in benzene gave unique and interesting results. Both the electron-releasing group and the electron-withdrawing groups enhanced the rate in comparison with the unsubstituted 1-phenyl ethanol. The results are represented in table 4.5.

Table 4.5

Effect of substituents on the rate of oxidation of 1-phenyl ethanol by $QMnO_4$

$[QMnO_4]$= 5.12 x 10^{-4} mol dm^{-3} T= 303K

[substrate] = 1.245 x 10^{-2} mol dm^{-3} solvent – Benzene

Substrate	k_2 x 10^3 (dm^3 $mol^{-1}s^{-1}$)	
	$QMnO_4$=TBAP	$QMnO_4$=TCMAP
$PhCHOHCH_3$	3.14	4.72
p-Me $PhCHOHCH_3$	4.41	5.73
p-Cl $PhCHOHCH_3$	6.47	8.42
p-OMe $PhCHOHCH_3$	16.60	22.59
p-NO_2 $PhCHOHCH_3$	29.25	32.57

The rate constants do not fit linearly with the substitutent constants as demanded by Hammett[169,170] equation. However the various points for the electron releasing groups and the electron withdrawing groups in the plot of log k_2 vs σ can be resolved in to two linear fits, one for electron releasing groups and the other for electron withdrawing groups separately (Fig.4.4). This is quite unique and is a reflection of the mechanism of the process. This has been found to be true both with respect to TBAB and TCMAC. The order of reactivity of the various substituents is -H<p-Me< p-Cl <p-MeO < p-NO_2 with respect to the oxidants.

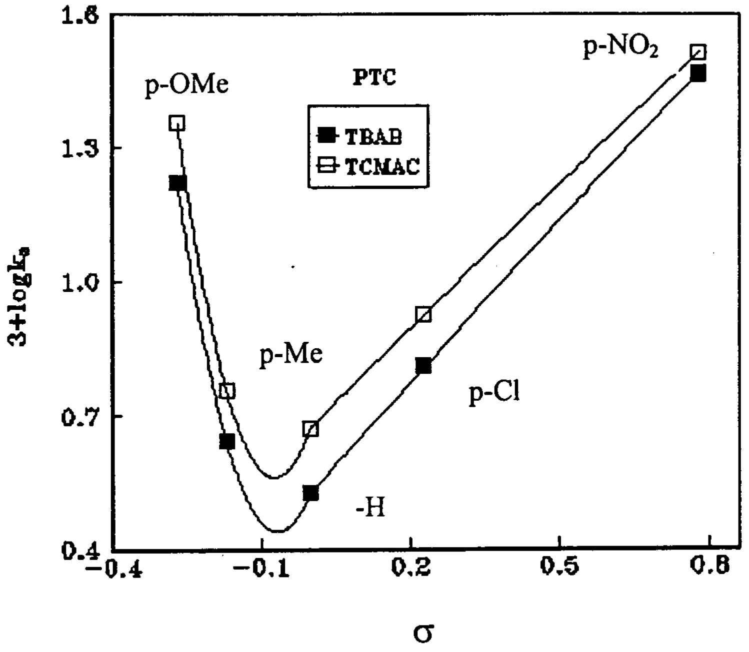


Fig. 4.4 Hammett plot for the oxidation of 1-phenyl ethanols

4.1.2.6 Effect of temperature on the rate of oxidation of the carbinols by $QMnO_4$ in benzene

The influence of temperature on the rate of oxidation of 1-phenyl ethanol and some of the substituted 1-phenyl ethanols were studied under phase transfer catalysis by TBAP and TCMAP as oxidants in the temperature range of 303K to 318 K. The activation parameters for the oxidation of respective carbinols were determined using the Arrhenius equation $k= A\ e^{-Ea}/^{RT}$. The plot of log k_2 vs 1/T and log k_2/T vs 1/T were used for the purpose[171]. (Fig. 4.5 to 4.9 (a&b)). Excellent linear fits were obtained in all the cases. The influence of temperature on the rate of oxidation of benzhydrol and cyclohexanol were also studied in the temperature range of 303K to 318K using TBAP and TCMAP as oxidants. The activation parameters were computed from the plot of log k_2 vs 1/T and log k_2/T vs 1/T (4.10 (a) & (b), 4.11 (a) & (b)).

The effect of temperature on the rate of oxidation of these different carbinols using TBAP and TCMAP as oxidants are given in table 4.6.

Table 4.6

Effect of temperature on the rate of oxidation of the various secondary alcohols by TBAP and TCMAP

$[QMnO_4) = 5.12 \times 10^{-4}$ mol dm^{-3} Medium-benzene

[substrate] = 1.245×10^{-2} mol dm^{-3}

Oxidant ($QMnO_4$)	TBAP				TCMAP			
	$k_2 \times 10^3$ at temperature (dm^3 mol^{-1}s^{-1})				$k_2 \times 10^3$ at T (dm^3 mol^{-1}s^{-1})			
Substrate	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
$PhCHOHCH_3$	3.14	5.55	9.62	13.32	4.72	7.49	12.27	17.82
pMe $PhCHOHCH_3$	4.41	7.37	11.53	16.65	5.73	9.17	13.66	21.01
p-Cl $PhCHOHCH_3$	6.47	10.14	15.30	23.30	8.42	13.38	20.59	30.12
p-OMe $PhOCHOHCH_3$	16.60	25.70	37.70	55.20	22.59	33.20	49.87	72.71
p-NO_2 $PhCHOHCH_3$	29.25	42.40	60.80	86.32	32.57	46.22	64.85	90.01
Benzhydrol	7.92	12.39	16.24	24.70	10.79	15.19	22.54	29.40
Cyclohexanol	2.86	5.36	7.39	12.64	3.92	6.53	10.12	15.69

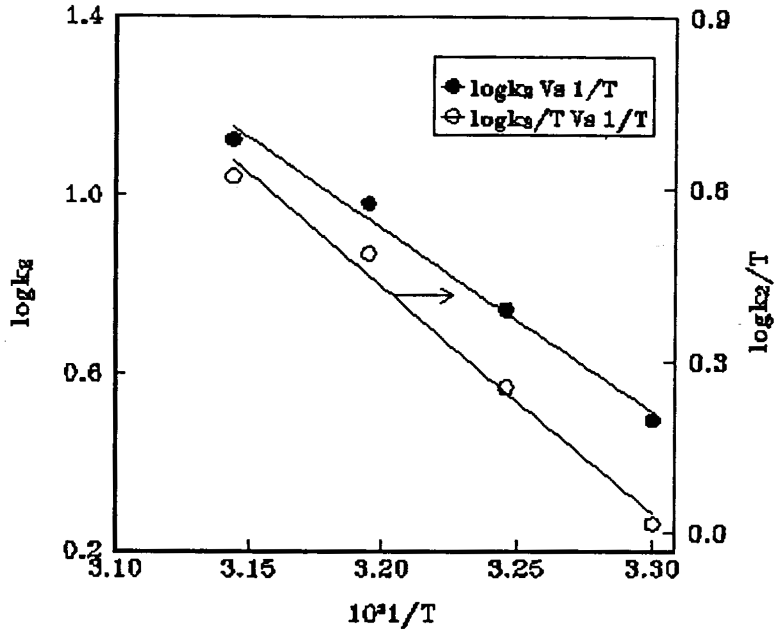


Fig 4.5 (a)

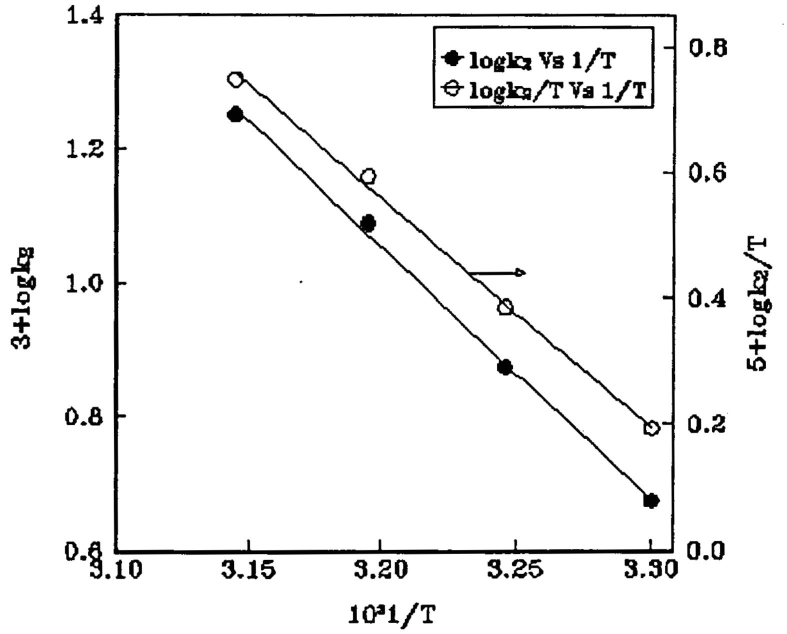


Fig 4.5 (b)

Fig 4.5 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T of PhCHOHCH$_3$ (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9940 & 0.9989 respectively)

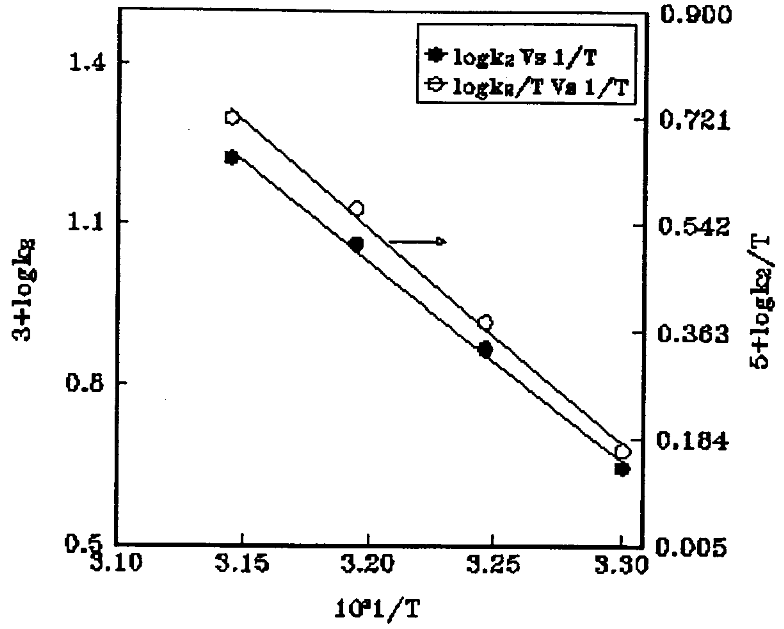


Fig 4.6 (a)

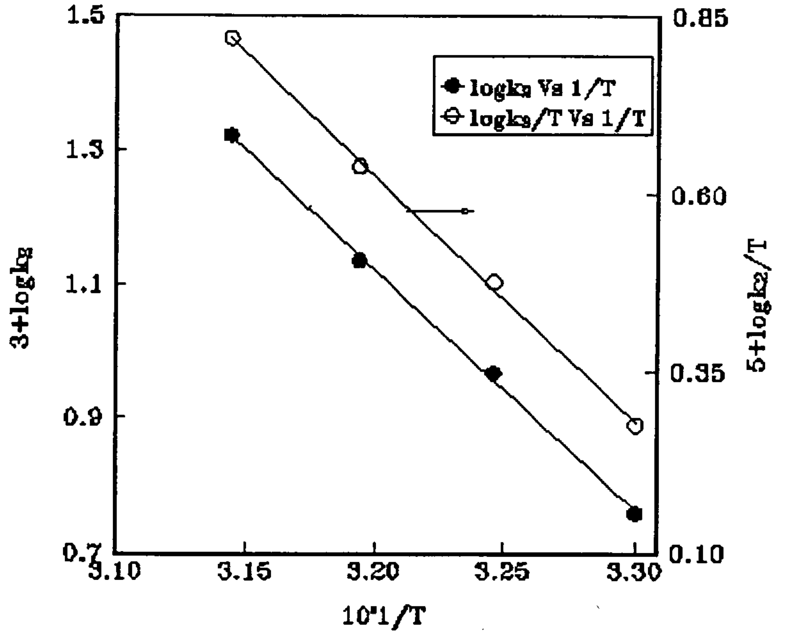


Fig 4.6 (b)

Fig 4.6 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of p-Me PhCHOHCH$_3$ (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9984 & 0.9997 respectively)

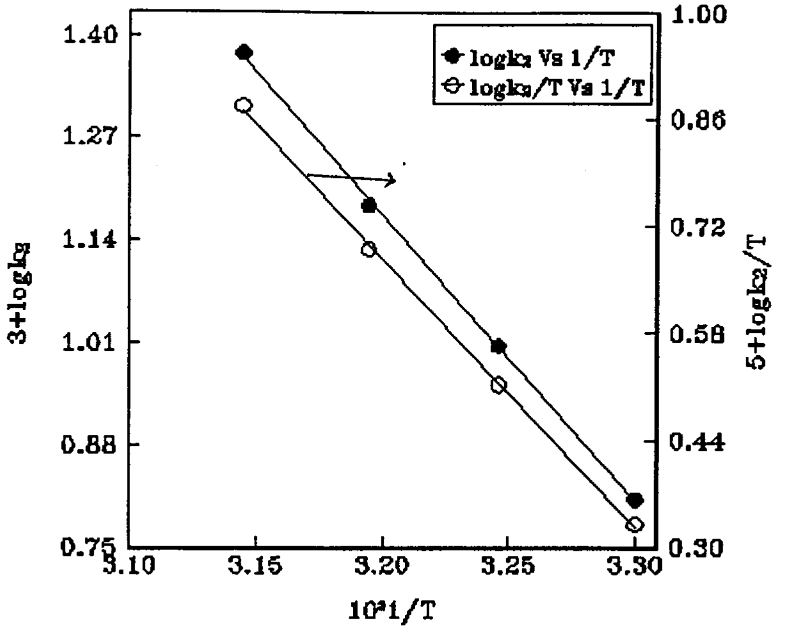


Fig 4.7 (a)

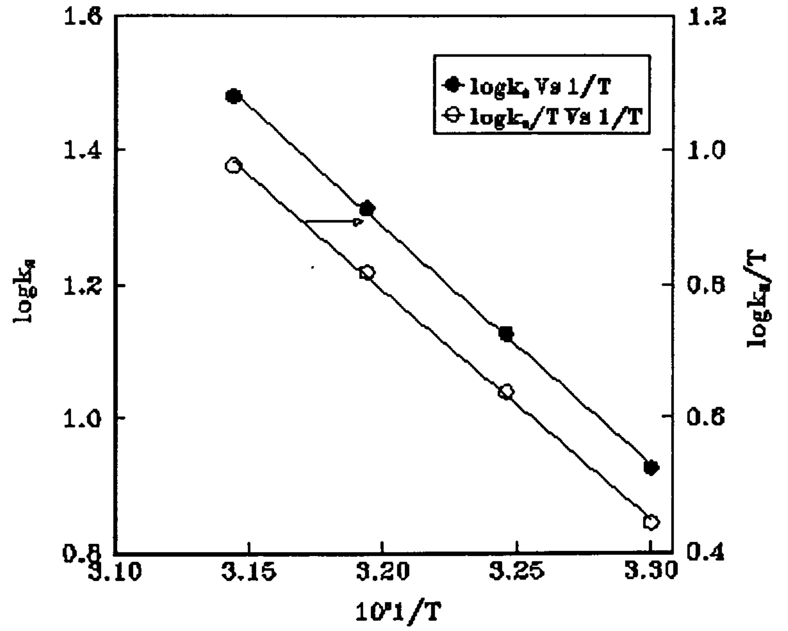


Fig 4.7 (b)

Fig. 4.7 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of p-Cl PhCHOHCH$_3$ (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9997 & 0.9996 respectively)

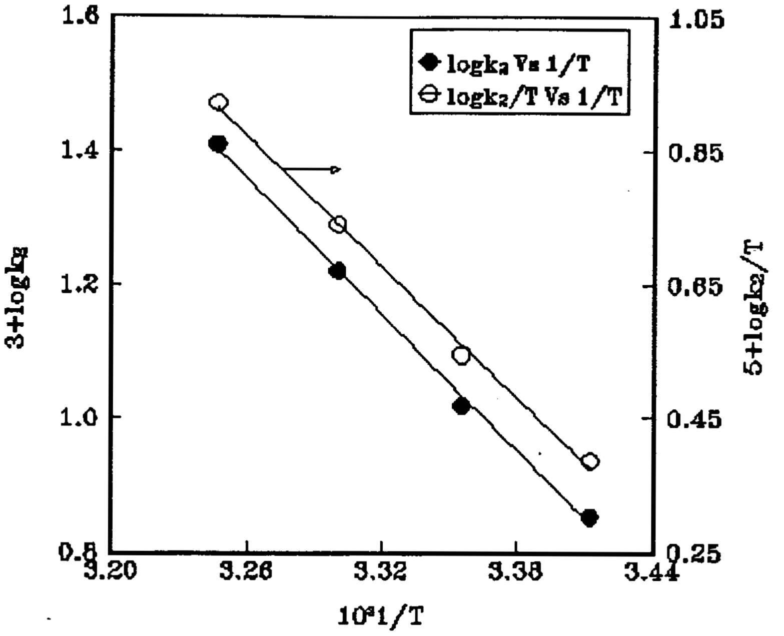


Fig 4.8 (a)

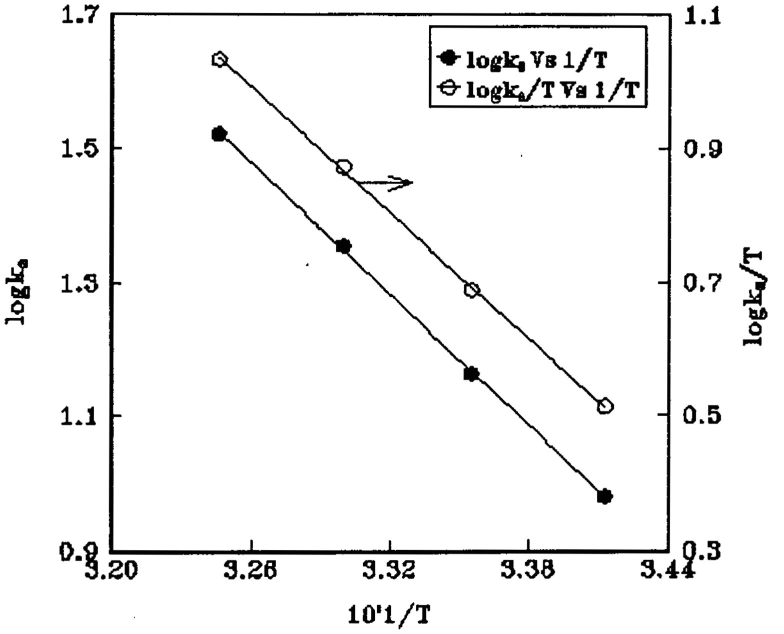


Fig 4.8 (b)

Fig 4.8 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of p-OMe PhCHOHCH$_3$ (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9980 & 0.9998 respectively)

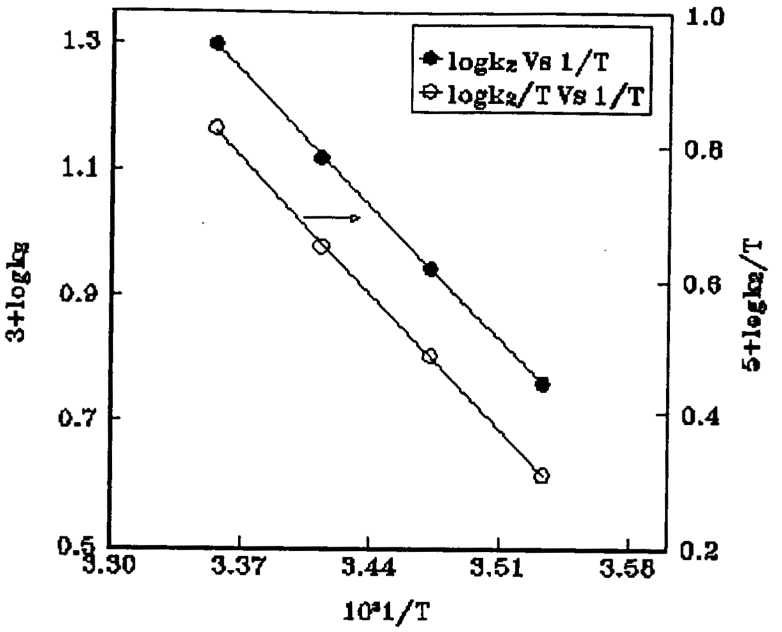


Fig. 4.9 (a)

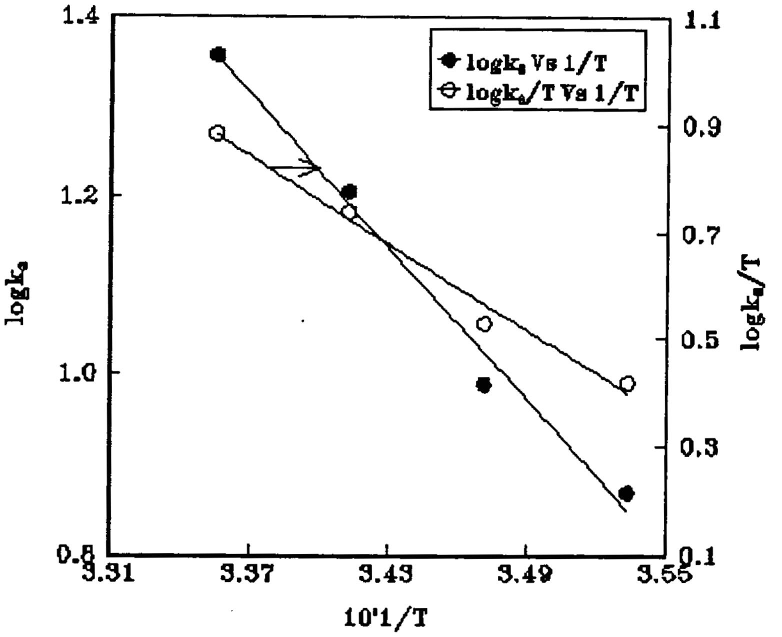


Fig 4.9 (b)

Fig 4.9 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of p-NO$_2$ PhCHOHCH$_3$ (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9980 & 0.9978 respectively)

The results show that the rate of the oxidation is quite sensitive to temperature charge. In the case of 1-phenyl ethanol the second order rate content k_2 increases from 3.14×10^{-3} to 13.82×10^{-3} $dm^3\ mol^{-1}s^{-1}$ when the temperature changes from 303K to 318K when TBAP was used as the oxidant. Similarly the second order constant k_2 increases form 4.72×10^{-3} to 17.82×10^{-3} $dm^3\ mol^{-1}s^{-1}$ with TCMP as oxidant. In the case of benzhydrol the second order constant increases from 7.92×10^{-3} to 24.70×10^{-3} $dm^3\ mol^{-1}s^{-1}$ when the temperature changes from 303K to 318K for TBAP was used as oxidant, while the values are 10.79×10^{-3} to 29.40×10^{-3} $dm^3\ mol^{-1}s^{-1}$ for TCMAP as the oxidant. The rate of oxidation of benzhydrol by phase transferred permanganate is found to be greater than that of 1-phenyl ethanol.

The activation parameters computed[171] for the various carbinols with TBAB and TCMAP as oxidants are given in Table 4.7 (a)& (b).

Table 4.7 (a)

Activation parameter for the oxidation of alcohols in benzene oxidant - TBAP

Carbinols	TBAP				
	K_2 x10^{3}at 303K (dm^3 mol^{-1} s^{-1})	Ea kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ Jmol^{-1}K	$\Delta G^{\#}$ kJmol^{-1}
PhCHOHCH$_3$	3.14	78.76	75.66	-43.30	88.78
p-Me PhCHOHCH$_3$	4.41	71.28	68.60	-63.72	87.90
p-Cl PhCHOHCH$_3$	6.47	69.55	67.17	-65.35	86.90
p-OMe PhCHOHCH$_3$	16.60	64.73	62.20	-73.80	84.90
p-NO$_2$ PhCHOHCH$_3$	29.25	57.75	55.35	-91.99	83.20
Benzhydrol	7.92	59.17	56.62	-98.58	86.46
Cyclohexanol	2.86	76.79	74.13	-49.42	89.02

Table 4.7 (b)

Activation parameter for the oxidation of alcohols in benzene TCMAP as oxidant

Carbinols	TCMAP				
	K_2 x10^{3}at 303K (dm^3 mol^{-1} s^{-1})	Ea kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ Jmol^{-1}K	$\Delta G^{\#}$ kJmol^{-1}
PhCHOHCH$_3$	4.72	72.01	69.39	-60.60	87.80
pMe PhCHOHCH$_3$	5.73	69.88	67.40	-65.60	87.30
p-Cl PhCHOHCH$_3$	8.42	68.06	65.50	-68.60	86.30
p-OMe PhCHOHCH$_3$	22.59	62.44	59.95	-78.80	83.80
p-NO$_2$ PhCHOHCH$_3$	32.57	54.29	51.78	-102.70	82.89
Benzhydrol	10.79	54.42	51.90	-111.48	85.68
Cyclohexanol	3.92	73.49	70.99	-56.91	88.23

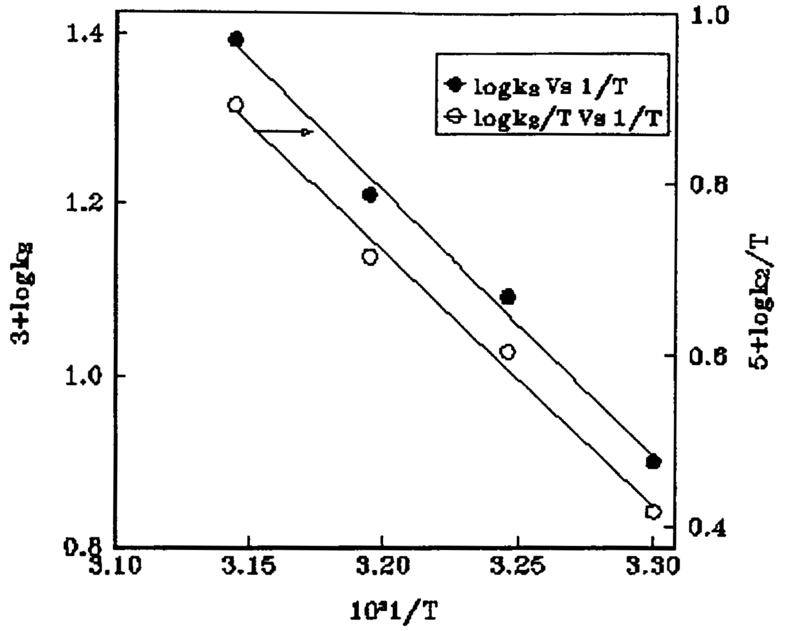


Fig 4.10 (a)

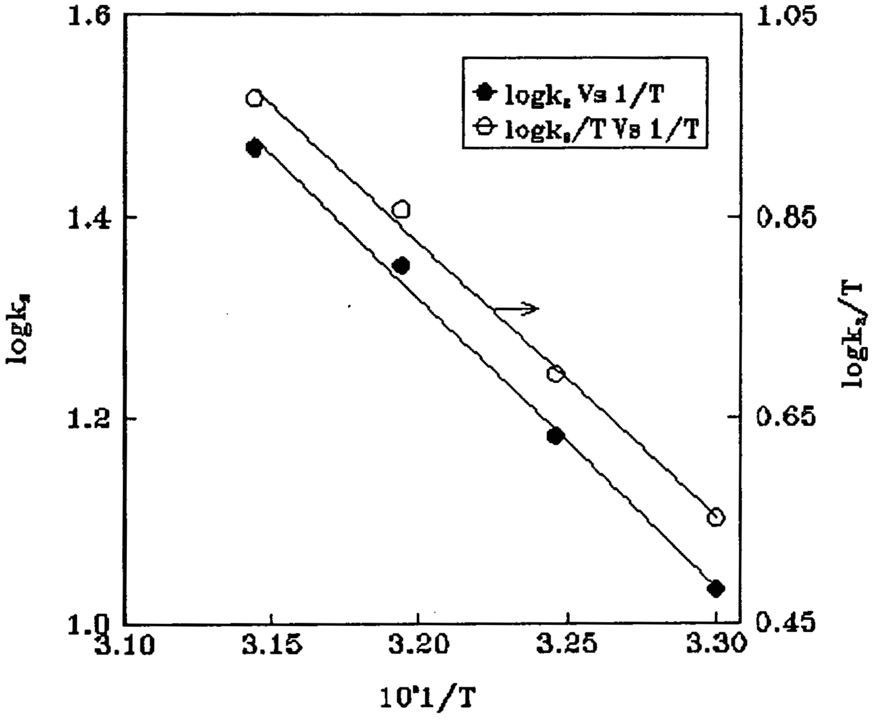


Fig 4.10 (b)

Fig 4.10 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of benzhydrol (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9964 & 0.9967 respectively)

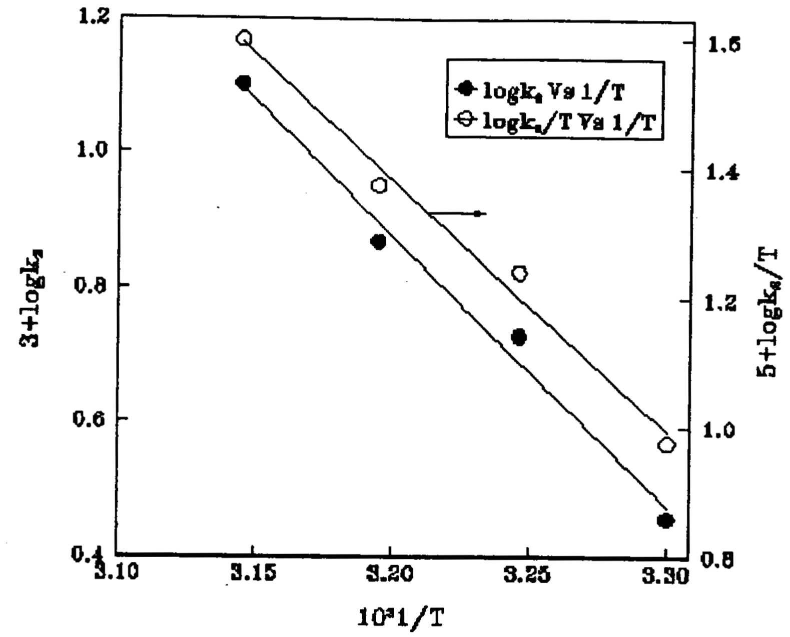


Fig 4.11 (a)

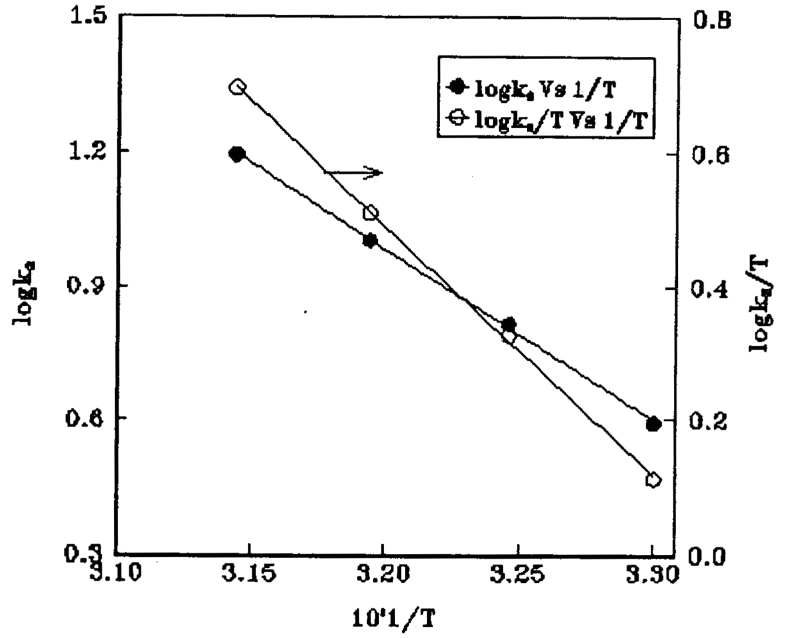


Fig 4.11 (b)

Fig 4.11 Plot of logk$_2$ vs 1/T & log k$_2$/T vs 1/T for the oxidation of cyclohexanol (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9948 & 0.9997 respectively)

4.1.2.7 Effect of organic structure of the catalyst on the rate of the oxidation

The effects of catalystic structure, i.e. The organic structure of the cationic part of the quarternary ammonium permanganate were studied using tetrabutyl ammonium bromide (TBAB) and tricaprylmethyl ammonium Chloride (TCMAC) as the catalysts. The kinetics of the oxidation were studied in benzene at 303K and at three other temperatures. The results represented in tables 4.7(a) and 4.7(b) indicate that TCMAP is such more efficient for effecting oxidation of carbinols than TBAP. The increase in the rate of oxidation with respect to TCMAP as compared to TBAP can be explained on the basis of an increase in the reactivity of the oxidant when it is present in combination with the cationic part with greater organophilicity. The better solubility of the cationic part in benzene inspite of its larger bulk and consequent possible steric hindrance enabled efficient reaction rate as it is more effective in transporting and holding the MnO_4^- ions in the non-polar media. Besides as suggested by Ugelstad and co-workers,[89] bulkier the cationic part of $QMnO_4$, greater the steric hindrance suffered by MnO_4- around that centre which in turn reduces the cation-anion interaction energy and hence increased anionic reactivity (See section, 1.4.1).

Another probable argument is that the bulkeir the cationic part of the catalyst, greater the organophilicity[172] of the reagent ($Q^+MnO_4^-$) and hence an increased anionic reactivity in organic solvents. The increase in the reactivity of TCMAP compared to TBAP is reflected in the reduction in the free energy of activation for the oxidation (Table 4.7(a)& (b)).

4.1.3 Discussion

Determination of the stoichiometry of the oxidation process and characteristics of the product revealed that the product of oxidation is acetophenone. The formation of acetophenone in quantitative amounts as ascertained from the yield of the 2,4 dinitrophenyl hydrazone derivative confirms the above. The sequential scan of the absorption spectra for the oxidation of 1-phenyl ethanol using $QMnO_4$ (Q= TBA^+) in benzene at regular intervals of time (Fig. 4.12) showed isosbestic point at 489 nm. This is in accordance with the assumption that within the measured time interval, only two absorption species are present, namely MnO_4^- and MnO_2[173]. This is also suggestive of a single product and rules out any complicated sequence of events during oxidation process[105, 109, 148-151, 174].

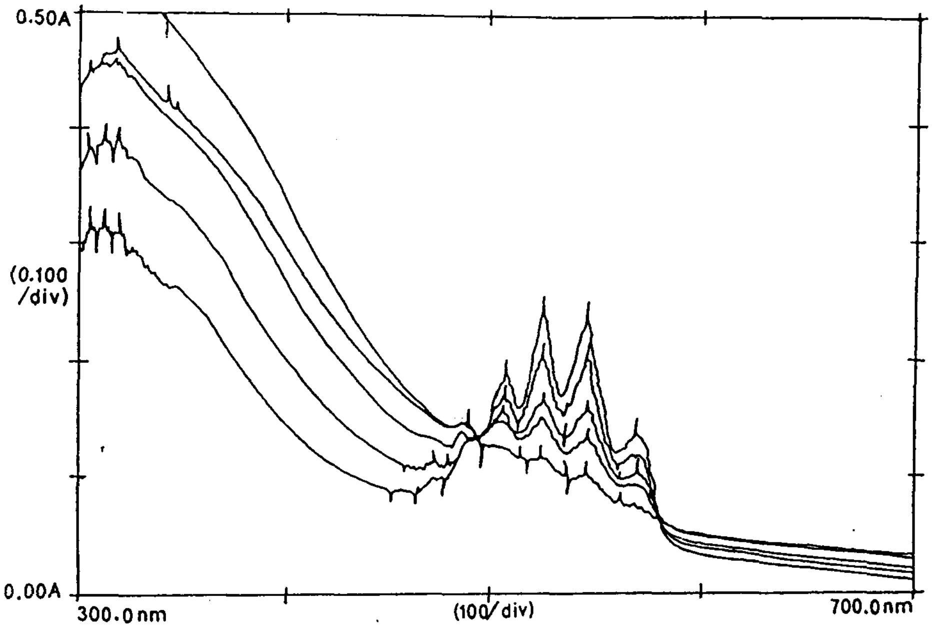


Fig 4.12 Sequential scan of the absorption spectrum of the kinetics of the oxidation of 1-phenyl ethanol by $QMnO_4$ ($Q = TBA^+$) in benzene at 40^0 [Isosbestic point 489nm]

The reaction conforms to first order kinetics with respect to the concentration of oxidant (TBAP or TCMAP) as well as with respect to the carbinol concentration. The rates of oxidation of the carbinol in various solvents were found to increase with increase in the dielectric constant of the organic solvents employed. This is in agreement with the possible interaction between a negative ion (MnO_4^-)and a dipole[168] (carbinol) as evidenced by the linear correlation of the plot of (correlation coefficient 0.995) $\log k_2$ verses 1/D with a negative slope (Fig 4.3). Further, the addition of TBAB into the reaction system did not produce any change in the value of rate constant. Hence there is absence of the primary salt effect which in turn rules out the possibility of ion-ion type interaction. The reaction mixture for the oxidation of 1-phenyl ethanol with phase transferred permangante failed to induce the polymerisation of acrylonitrile. Thus a one-electron oxidation give rise to free radicals is unlikely. Hence the reaction could very well be the consequence of an ion-dipole interaction or dipole-dipole interaction.

The influence of substituents at the para position of the benzene ring of 1-phenyl ethanol is quite unique in that both the electron-releasing and electron-withdrawing groups increase the rate of the reaction (Table 4.5). The plots of log k_2 vs substituent constant σ did not give linear relationship with all the substitutents instead, the relation can be resolved into two parts one for the electron-withdrawing group (linear) and the other for electron releasing groups (curved). This type of Hammett plot is quite unique and is indicative of a transition state undergoing variation depending on the electronic demand from the substituents[170, 175-177] (See Fig. 4.4).

Inspite of the observed uniqueness in the effect of substituents on rates, there exists an isokinetic relationship for the oxidation of these alcohols and this is evident from the plot of $\Delta H^{\#}$ vs $\Delta S^{\#}$ (Leffler Grunwald Plot).[177] The plots are linear with correlation coefficient (0.9819 & 0. 9830) respectively for TBAP and TCMAP (Fig 4.13(a)& (b)).

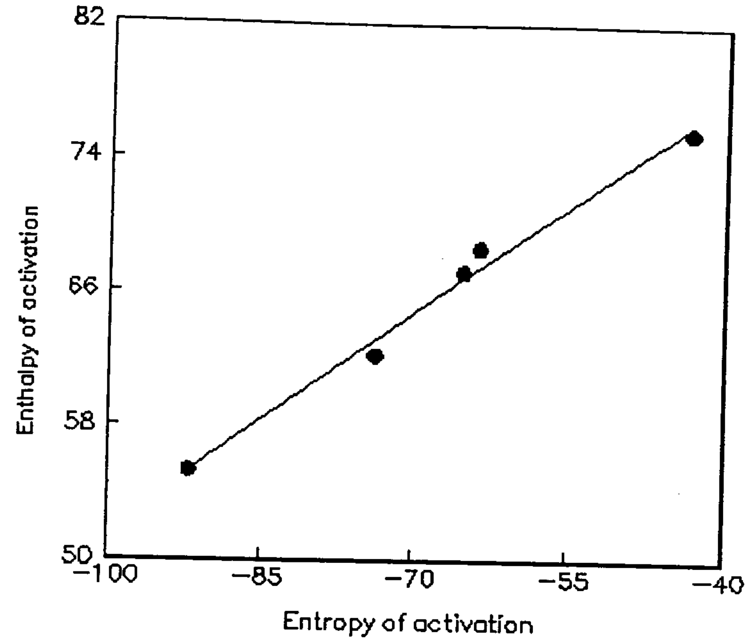


Fig 4.13 (a)

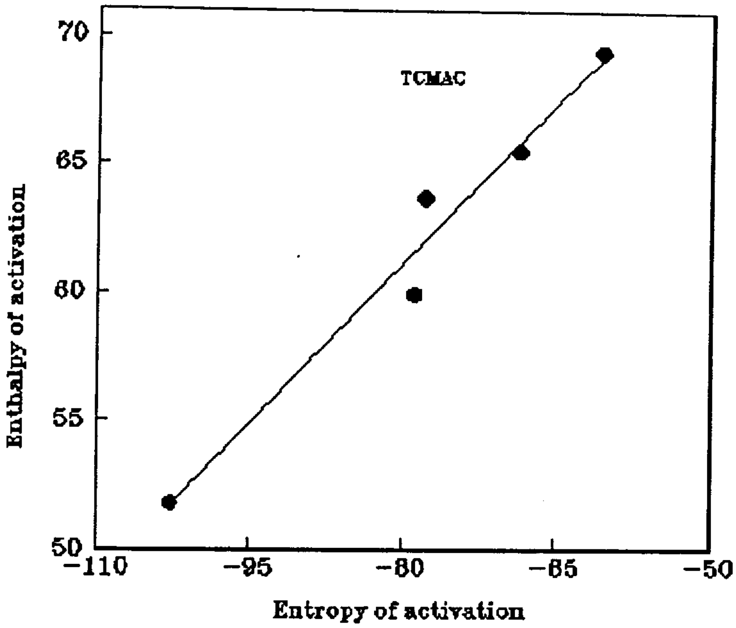


Fig 4.13 (b)

Fig 4.13 Isokinetic Plot for the oxidation of carbinols (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9948 & 0.9997 respectively)

Similarly the plot of logk$_2$ at 318 K vs logk$_2$ at 303K (Exners Plot)[178] is linear both with respect to TBAP and TCMAP (with correlation coefficient 0.9995 and 0.997 respectively (Fig.4.14 (a) & (b).

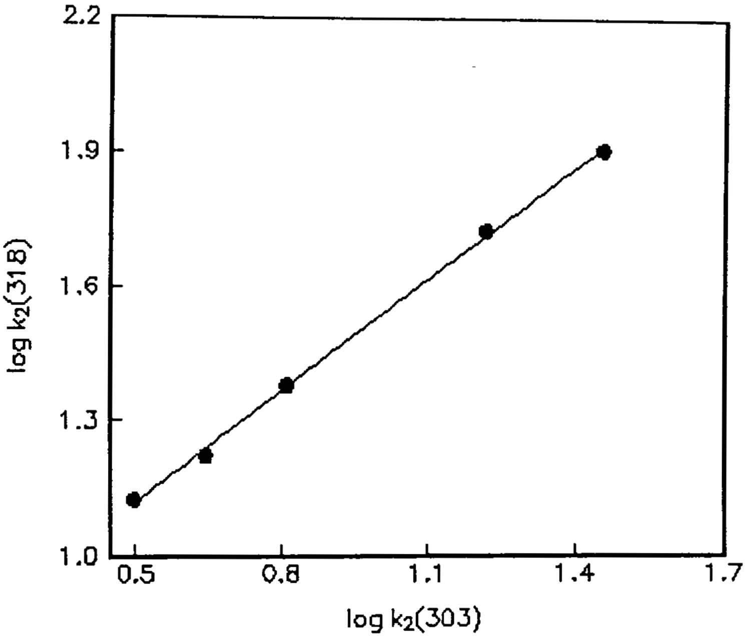


Fig 4.14 (a)

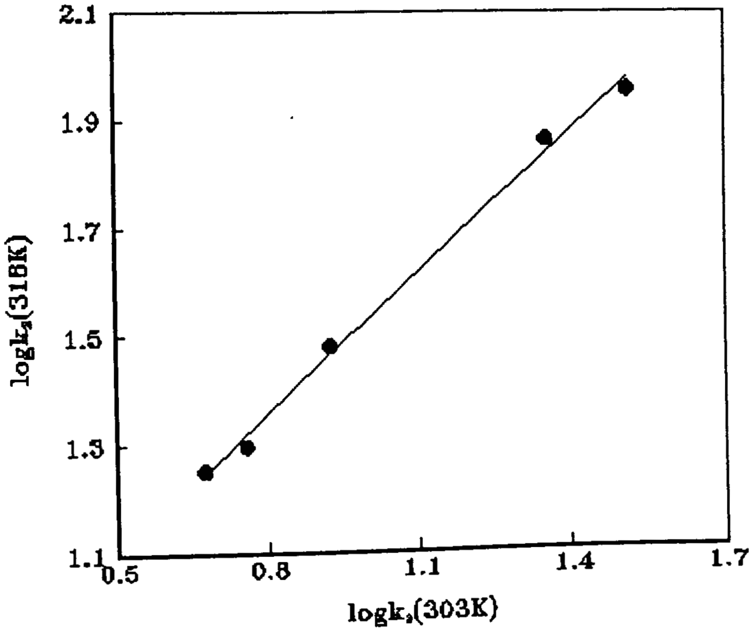


Fig 4.14 (b)

Fig 4.14 Exners' plot for the oxidation of carbinols (a) using TBAP (b) using TCMAP (Correlation coefficient = 0.9996 & 0.9977 respectively)

The isokinetic temperature is 424K when TBAP is used as oxidant and 478K when TCMAP is used as oxidant. These results are suggestive of the operation of a similar mechanism for the oxidation of all the secondary alcohols, which in further confirmed by the almost constant value of the free energy of activation ($\Delta G^{\#} \approx 85$ kJ mol^{-1}) (Table 4.7 (a)&(b)). The behaviour could be explained on the basis of the ambiphilicity of the permanganate ion.

The ambiphilicity of the permanganate ion during the oxidation of alkene has already been reported[179,180,192]. An ambiphilic or dipolar permanganate ion is expected to exhibit a parabolic dependence on alkene π electron availability that is characterised by high reactivity towards both the electron-poor and electron-rich alkene and low reactivity towards alkene of intermediate electronic character. This amphiphilicity of permanganate ion has been observed in the rate of oxidation of vinyl ethers, which is accelerated by both electron-withdrawing and electron-attracting groups. A concave upward Hammett plot for the permanganate oxidation of substituted stilbenes in dioxane has been reported[179, 180]. A positive slope is observed when electron-withdrawing substituents are present and a negative slope when electron-donating substituents are present. Apparently the reaction can proceed through the same intermediate, but via the electron-rich or an electron-deficient transition state, depending on the specific demands of the substituents. The nature of the transition state is controlled by the electronic effects of the substituents either to stabilize the positive or negative charges in the transition state configuration[148-150, 192].

Similar results in which both the electron-releasing groups and electron-withdrawing groups accelerate the rate of the reaction was reported by Lee DG *etal*[156] during the studies on the permanganate oxidation of para-substituted benzyl alcohols and benzyl ethers under phase transfer catalysis (PTC) condition in methylene chloride. Both the alcohols and the ethers responded to an identical way to the unique substituents effects caused by the introduction of various substituents at the para position of phenyl ring. In order account for this uniqueness, they suggested a mechanism that is guided by a consideration of frontier molecular orbital theory.[181-183] According to this approach the reaction is initiated by an interaction of the HOMO of the reductant (carbionl or ethers) with the LUMO of the oxidant to form an active complex. This is followed by a rate limiting decomposition of the complex involving αC-H bond cleavage and O→Mn bond cleavage. This conclusion has been arrived at in attempt to theoretically model reactions in which alcohols are oxidised by high valent transition metal oxo compounds.[184] The reaction between high-valent transition metal oxides and organic compound take place through the formation of active complexes or intermediates have been reported by several workers[148-151, 184-186, 192-194]

The results of the present works are in perfect agreement with the work of Lee *et al*[156] as mentioned earlier. That a similar mechanism is also operative in the present case has been confirmed by the excellent correlation (correlation coeff. 0.997) of the plot of the rate coefficients of the present investigation with those for the similarly substituted benzyl alcohols (Fig 4.15).

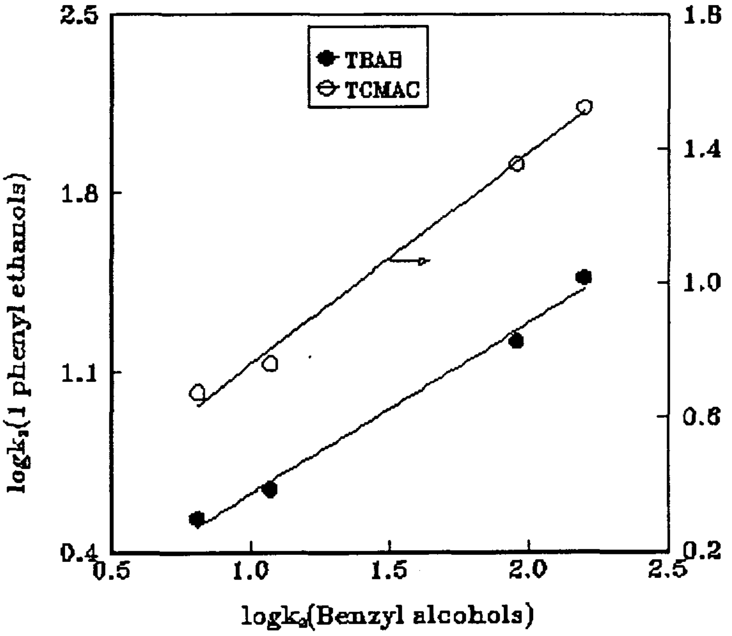
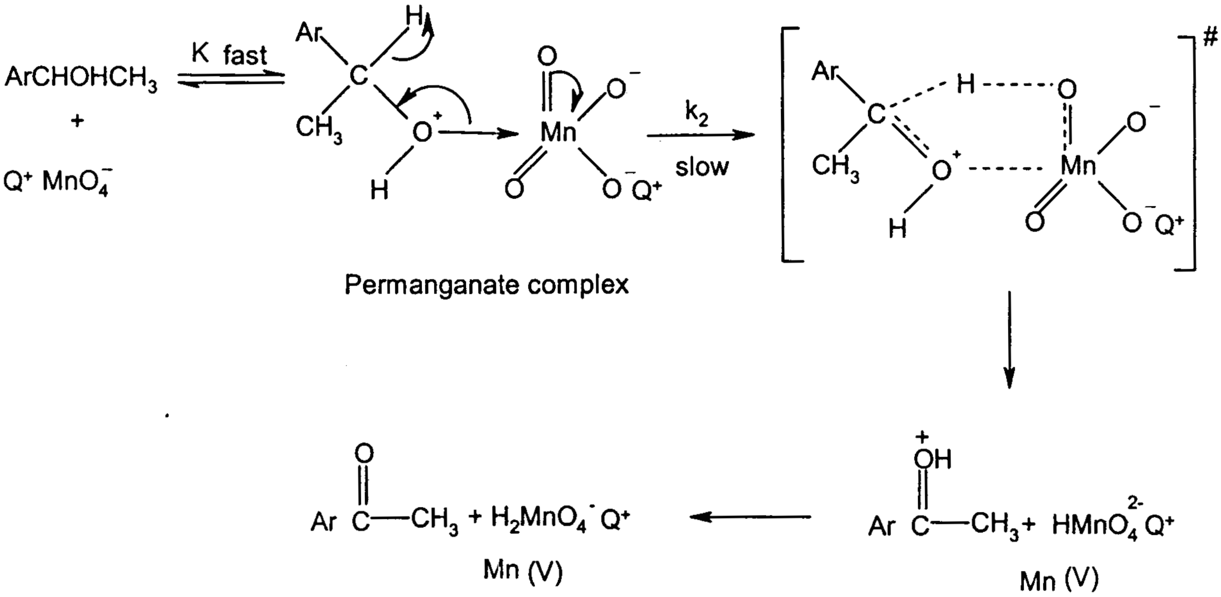


Fig 4.15

Fig 4.15 Correlation of rate constants for the oxidation of 1-phenyl ethanols with the similarly substituted benzyl alcohols under PTC condition (Correlation coefficient = 0.9956 & 0.9968 for TBAP & TCMAP respectively)

Accordingly the reaction is initiated by the interaction of the 2p electron on the HOMO of the oxygen of the alcohol with the LUMO of the permanganate (2e antibonding molecular orbital located primarily on manganese) to form a complex in a fast pre-equilibrium step. This is followed by the rate limiting decomposition of the complex via a cyclic transition state leading to the product as shown in scheme 4.1 Depending on the electronic demands from the substituents either the α C-H bond cleavage or Mn→O bond cleavage is favoured for the reaction. It seems that the electron-releasing substituents enhance the rate by favouring the cleavage of α C-H bond and while electron-withdrawing groups enhance the rate by aiding the cleavage of O→Mn bond. The fact that the cleavage of α C-H bond in the rate-determining step during the permanganate oxidation of alcohol has been established by labelled studies using isotopically labeled substrate with α C-D instead of α C-H.[101,125,156,187] According to this scheme the higher rate of oxidation of benzhydrol compared to 1-phenyl ethanol can be attributed due to the greater weakening of O→Mn bond leading to its easier cleavage resulting from the –M effect of the phenyl ring of benzhydrol in the transition state.



Scheme 4.1 Mechanism of the oxidation of alcohol

The manganes (V) formed in the reaction being unstable in neutral benzene undergoes fast disproportionation to manganese (IV), the experimentally observed product[1,101,156,191] as given by the equation 4.2

$$\underset{\text{Mn (V)}}{3H_2MnO_4^- Q^+} \rightarrow \underset{\text{Mn (IV)}}{2MnO_2} + \underset{\text{Mn(VII)}}{Q^+MnO_4^-} + Q^+(OH)^- + 2H_2O \quad (4.2)$$

A suitable rate expression for the oxidation of alcohols in consistant with the above mechanism can be given by the equation 4.3

$$-d\,[MnO_4^-]\,/dt = k_2\,[\text{complex}]$$

$$= Kk_2\,[ArCHOHCH_3]\,[MnO^-_4] \qquad (4.3)$$

4.2 Kinetics of oxidation of 1-phenyl ethanol using $KMnO_4$ in aqueous acetic acid medium

The results obtained on the kinetics of oxidation 1-phenyl ethanol, its p-CH_3, p-Cl, p-OCH_3 and p-NO_2 derivatives in aqueous acetic acid medium with $KMnO_4$ are presented and discussed in this section. An attempt has also been made to compare the results with that of the oxidation under PTC condition.

4.2.1 Stoichiometry and the product of the reaction

The oxidation of 1-phenyl ethanol in 40% aqueous acetic acid using $KMnO_4$ was carried out as mentioned in the section 3.14.1 The ratio of [carbinol]: [$KMnO_4$] = 3:2 was obtained which is in agreement with the stoichiometry as given in the equation

$$3\ ArCHOHCH_3 + 2Mn\ (VII) \rightarrow 3\ ArCOCH_3 + 2Mn(IV) + 6H^+$$

The product of the oxidation was ascertained to be acetophenone from the formation of the corresponding 2,4 dinitro phenyl hydrazone (DNP). The DNP was found to be identical with the DNP of authentic sample of acetophenone.

4.2.2 Kinetic Study

The rate constants for oxidation of 1-phenyl ethanol in aqueous acetic acid with $KMnO_4$ were determined under different experimental conditions of concentration of oxidant, concentration of substrate, ionic strength, different solvent, temperature etc. and are presented and discussed in detail.

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

The plots of log [$KMnO_4$] vs time are linear showing first order dependence on the oxidant concentration. Further the psuedo-first order rate constant (k_{obs}) is independent for the initial concentration $KMnO_4$ (Table 4.8).

4.2.2.2 Effect of substrate concentration on the rate of oxidation of 1-phenyl ethanol

The pseudo-first order rate constants determined under the experimental conditions were directly proportional to the concentration of the carbinol. The second order constants (k_2) obtained by dividing k_{obs} by [carbinol] are almost constant. The first order dependence of the carbinol concentration is further confirmed by the plot of log k_{obs} vs log [carbinol] which is linear passing through origin with a slope =1.02 (Fig 4.16). The results are presented in table 4.8.

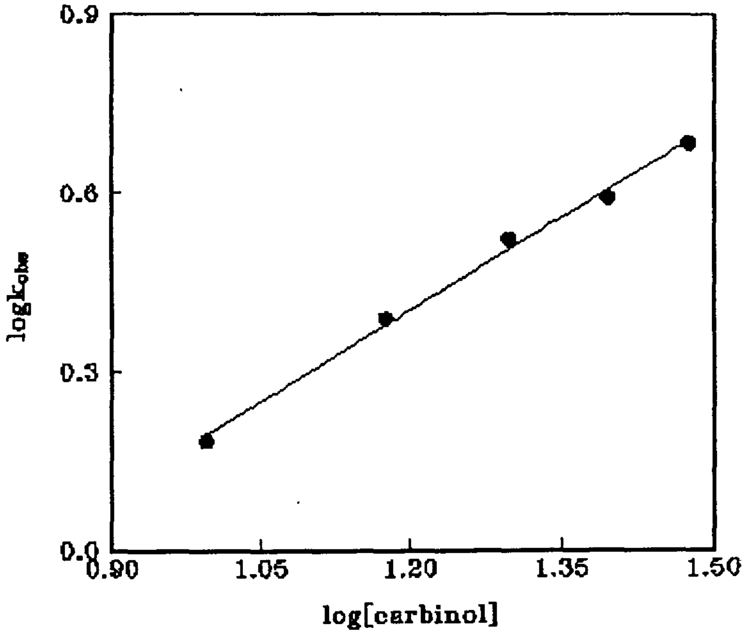


Fig 4.16

Fig 4.16 Plot of log k_{obs} vs log [substrate] (Correlation coefficient = 0.9977)

Table 4.8

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

Medium - 40% aq HOAc (v/v) T = 303K

$[KMnO_4] \times 10^3$ (mol dm^{-3})	$[PhCHOHCH_3] \times 10^2$ (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})	$10^3 k_2$ (dm^3 mol^{-1} s^{-1})
0.50	1.00	15.62	15.62
0.75	1.00	15.69	15.69
1.00	1.00	15.23	15.23
1.25	1.00	15.54	15.54
1.00	1.50	22.72	15.14
1.00	2.00	31.47	15.73
1.00	2.50	39.15	15.68
1.00	3.00	46.06	15.35

The plot $1/k_{obs}$ vs 1/ [carbinol] is also linear passing through the origin and this rules out the formation of a long-lived intermediate. (Fig 4.17) However it may be considered that the substrate interacts with the oxidant and form a transient complex, which immediately decomposes and the rate is controlled by the interaction of the carbinol with the oxidant.

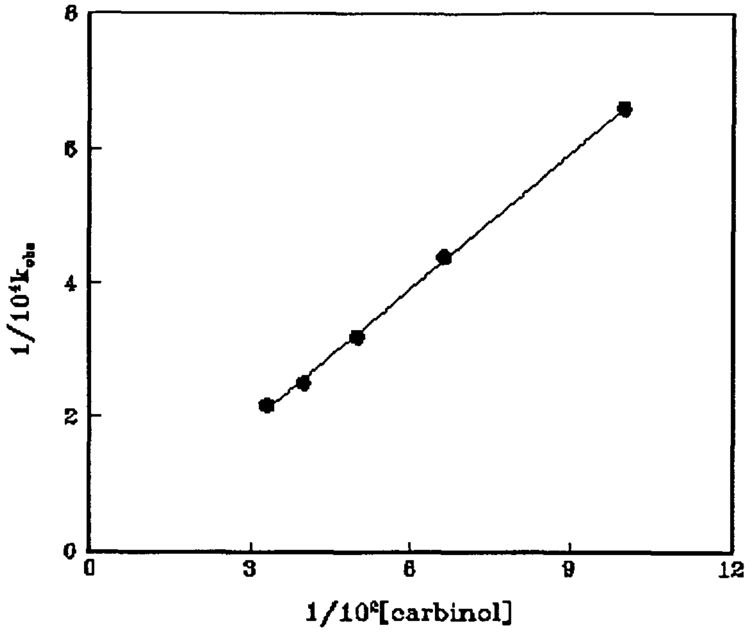


Fig 4.17 Plot $1/k_{obs}$ vs 1/[substrate] (Correlation coefficient = 0.9978)

4.2.2.3 Influence of ionic strength on the rate of oxidation of 1 phenyl ethanol - Influence of the added salt

Table 3.25 (in section 3.15.3) showed that the addition of salt did not produce any primary kinetic salt effect. The rate constant remained practically constant with the different concentrations of NaCl added. It suggests the absence of any ion-ion type interaction and hence the possibility could be that of an ion and a dipole or that between two dipolar entities.[165-167]

4.2.2.4 Effect of added mineral acids (H^+) on the rate of oxidation

Addition of different amount of acid increased the rate of oxidation as can be seen from the table 4.9. By varying the concentration of H_2SO_4

from 0.0227 to 0.1590 mol dm^{-3}, the observed rate constant, k_{obs} was found to vary from 15.23 x 10^{-5} to 32.97 x 10^{-5} s^{-1} (Table 4.9).

Table 4.9
Influence of addition of H_2SO_4 on the rate of oxidation
$[KMnO_4]=1.0x10^{-3}$ mol dm-^{3} $[PhCHOHCH_3]$ =1.0 x 10^{-2} mol dm-^{3}
T = 303K, medium – 40% aq HOAc(v/v)

$[H_2SO_4]$ x 10^2 (mol dm-^{3})	10^5 k_{obs} (s^{-1})
2.270	17.27
6.820	20.84
11.360	27.15
15.90	32.97

The plot of k_{obs} vs log $[H_2SO_4]$ is not linear but concave upwards with an intercepts on the Y axix. (Fig.4.18). This is suggestive of a complex order with respect to $[H^+]$. This observation leads to the conclusion that the reaction is acid catalysed and follows a path involving singly protonated and doubly protonated form of the reactive species at moderate and higher concentration of acid respectively[125]. Another argument for the concave upward shape of the plot can be given as follows. There are some additional factors assisting the oxidation at higher concentration of acids. This may probably arise from larger protonation of the carbinol and the oxidant in the pre-equilibrium step at the higher concentration of mineral acids which in turn assists the oxidation. Therefore the plot would be concave upwards instead of the expected linear one. Similar results have been reported by Banerjee *et al*[125] on the kinetics of the oxidation of secondary alcohol using bis2,2(bipyridyl) Cu (II) permanganate in aqueous acetic acid medium.

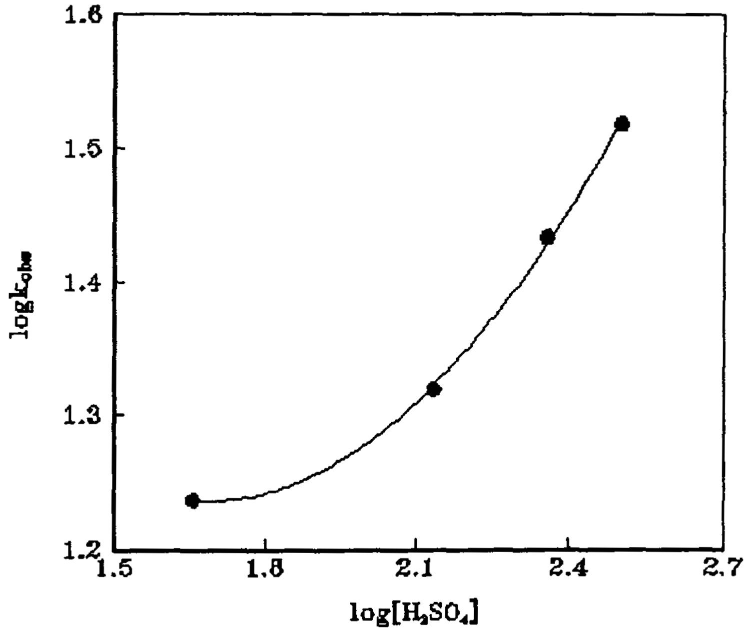


Fig 4.18 Effect of added mineral acids – plot of log k_{obs} vs log $[H_2SO_4]$

4.2.2.5 Effect of changing the polarity of the medium

The studies on the effect of changing the percentage composition of acetic acid in the aqueous acetic acid medium led to quite interesting results. The rate of oxidation decreased as the percentage composition of acetic acid was increased up to a concentration of 50 percentage v/v. Beyond the increase in the percentage acetic acid (> 50%) the rate is found to be increased. (See table 3.27 in section 3.15.5). A plot of log k_2 vs 1/D of the medium is linear with negative slope up to 50% composition of acetic acid, (Corr. Coeff. 0.998) which is in accordance with the Amis equation for an ion-dipole interaction [168, 188]. (Fig 4.19) The dielectric constant values used above were obtained according to the literature[189].

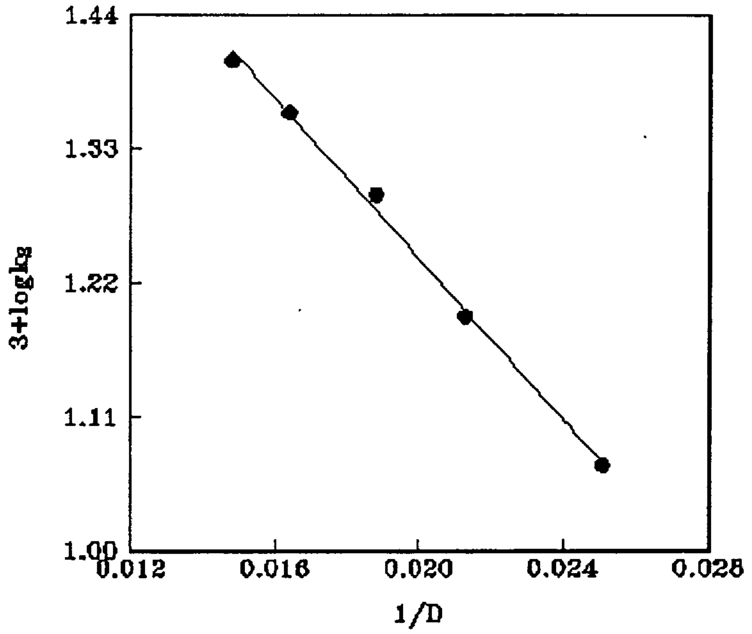


Fig 4.19 Effect of changing the polarity of the medium – Plot log k_2 vs 1/D (Correlation coefficient = 0.9980)

The increase in the rate of oxidation when the % composition of acetic acid larger than 50 could be due to increase in the acidity of medium and the subsequent catalytic effect from the involvement of a more powerful oxidising agent, $HMnO_4$[101] at that stage.

4.2.2.6 Effect of substituents on the benzene ring of 1-phenyl ethanol on the rate of oxidation

The introduction of various substituents like $-CH_3$, $-Cl$, $-OCH_3$, $-NO_2$ at the para position of the phenyl ring of 1-phenyl ethanol gave results different from the normal trend. Both the electron-releasing groups and the electron-withdrawing groups enhanced the rate with respect to the parent carbinol. (see table 3.29 in section 3.16). The reactivity increased in the order –H > p-Cl >p-Me >, p-NO_2, >p-MeO.

The plot of log k_2 vs σ is not linear and is not in conformity with the requirements of Hammett equation. Fig 4.20

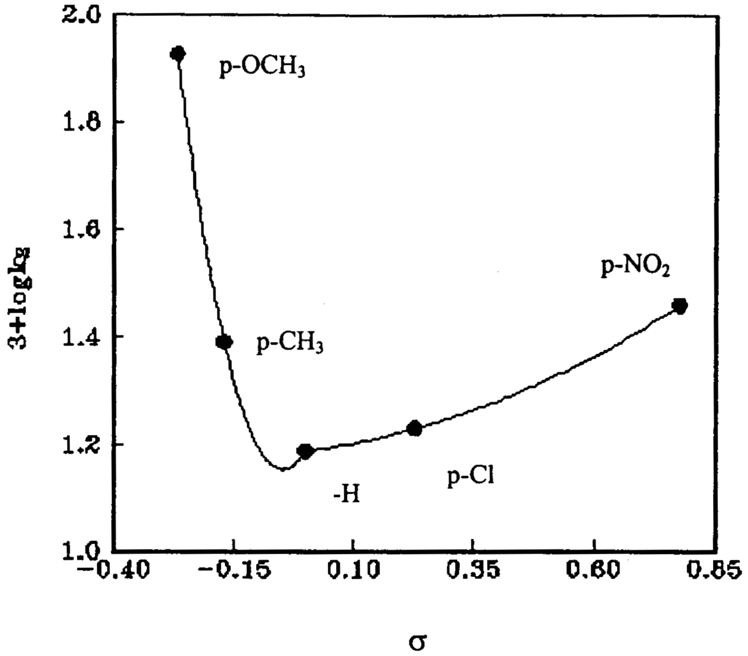


Fig 4.20 Hammett plot for the oxidation of 1-phenyl ethanols using $KMnO_4$ 40% HOAc

4.2.2.7 Influence of temperature on the rate of oxidation of the carbinols

The influence of temperature on the rate of oxidation of 1-phenyl ethanol and its substituents were studied using $KMnO_4$ in 40% aqueous acetic acid at a temperature range of 303K to 318 K. The activation parameters were computed from the plot of log k_2 vs 1/T and log k_2 /T vs 1/T. (Fig 4.21 to 4.25).

The influence of temperature on the rate of oxidation of various carbinols using $KMnO_4$ as oxidant in 40% acetic acid is presented in table 4.10

Table 4.10

Influence of temperature on the rate of oxidation 1-phenyl ethanols by $KMnO_4$

[carbinol] = 1.0×10^{-2} mol dm^{-3}
[$KMnO_4$] = 1.0×10^{-3} mol dm^{-3}

Carbinols	$k_2 \times 10^3$ at temperature(K) (dm^3 mol^{-1}s^{-1})			
	303K	308K	313K	318K
$PhCHOHCH_3$	15.23	22.72	30.00	39.16
p-Me $PhCHOHCH_3$	24.65	34.82	47.65	63.50
p-Cl $PhCHOHCH_3$	16.98	23.61	32.95	44.04
p-OMe $PhCHOHCH_3$	84.52	134.34	210.39	324.86
p-NO_2 $PhCHOHCH_3$	28.88	43.03	66.41	88.61

In case of 1-phenyl ethanol the second-order rate constant k_2 increased from 15.23×10^{-3} to 39.16×10^{-3} dm^3 mol^{-1}s^{-1} for a temperature variation from 303 K to 318 K. The data have been used for calculating activation parameters for the oxidation of the carbinol in aqueous acetic acid by permanganate. The activation parameters computed for the various p-substituted phenyl ethanols are given in table 4.11.

Table 4.11

Activation parameters of the oxidation of various 1-phenyl ethanols by $KMnO_4$ in 40% aq. HOAc

Carbinols	K_2 x10^3at 303K (dm^3 mol^{-1} s^{-1})	Ea kJmol^{-1}	$\Delta H^\#$ kJmol^{-1}	$\Delta S^\#$ Jmol^{-1}K	$\Delta G^\#$ kJmol^{-1}
$PhCHOHCH_3$	15.23	49.30	46.73	-125.59	84.78
p-Me $PhCHOHCH_3$	24.65	50.42	47.82	-118.09	83.59
p-Cl $PhCHOHCH_3$	16.98	51.08	48.49	-118.97	84.54
p-OMe $PhCHOHCH_3$	84.52	71.92	69.46	-36.42	80.50
p-NO_2 $PhCHOHCH_3$	28.88	63.29	60.72	-74.21	83.20

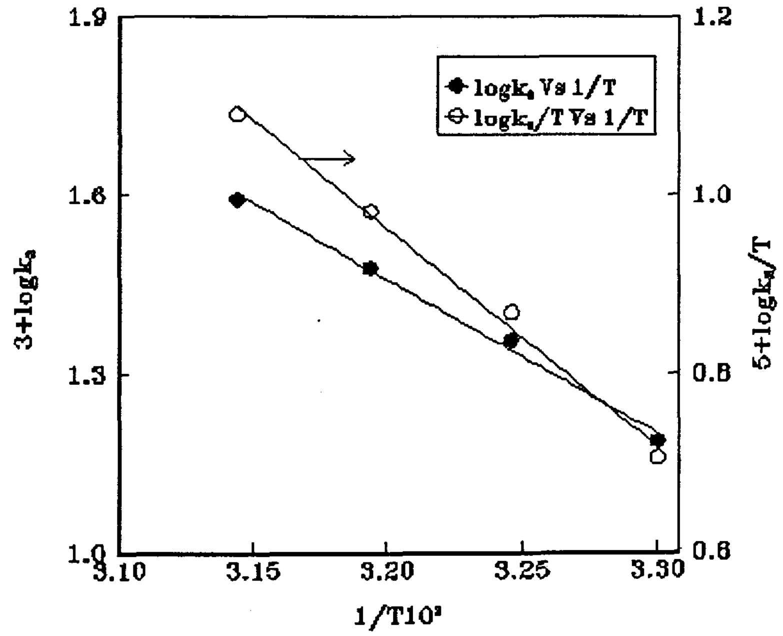


Fig 4.21 Plot of log k_2 vs 1/T & log k_2/T vs 1/T for the oxidation of 1-phenyl ethanol (Correlation coefficient = 0.9968)

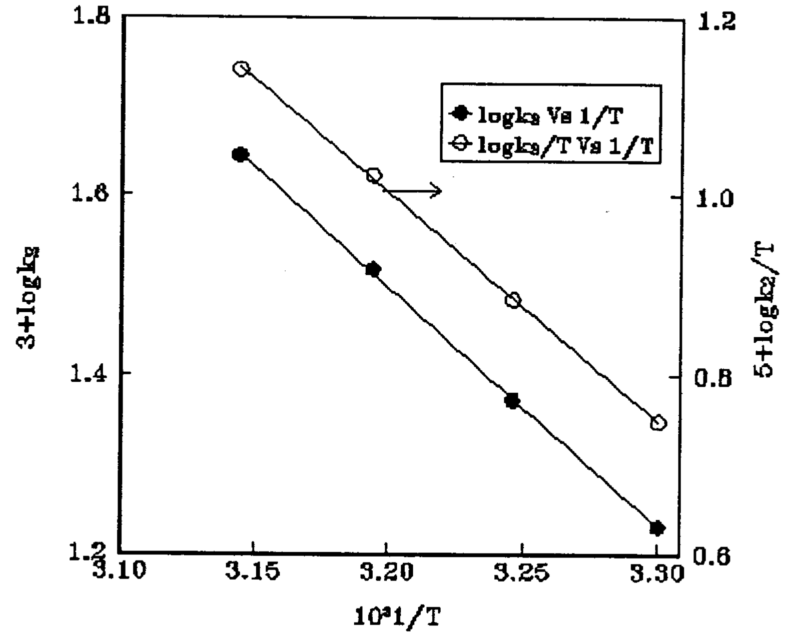


Fig 4.22 Plot of log k_2 vs 1/T & log k_2/T vs 1/T for the oxidation of p-Cl phenyl ethanol (Correlation coefficient = 0.9998)

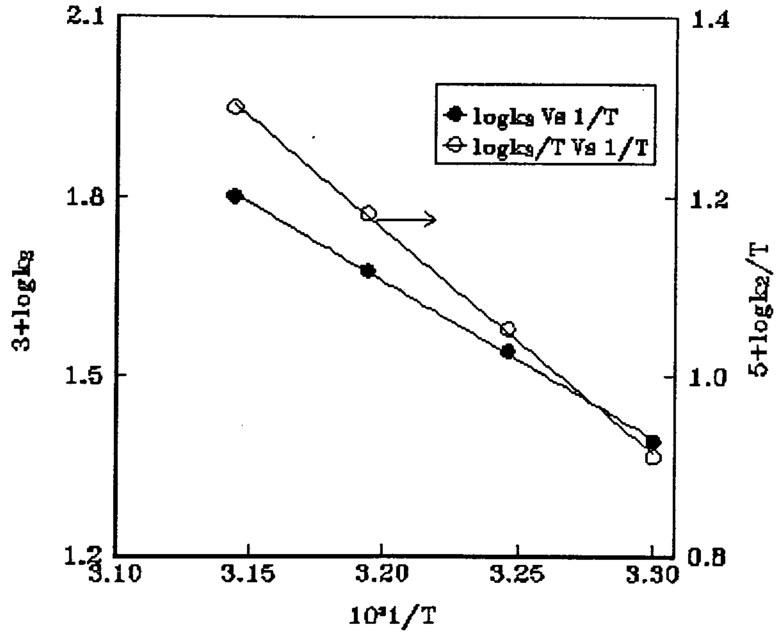


Fig 4.23 Plot of log k_2 vs 1/T & log k_2/T vs 1/T for the oxidation of p-Me phenyl ethanol (Correlation coefficient = 0.9997)

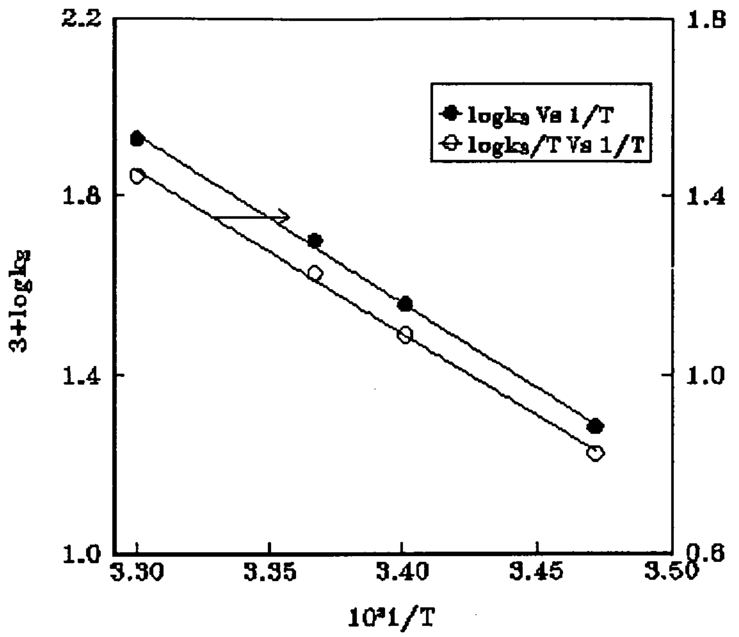


Fig 4.24 Plot of log k_2 vs 1/T & log k_2/T vs 1/T for the oxidation of p-OMe phenyl ethanol (Correlation coefficient = 0.9992)

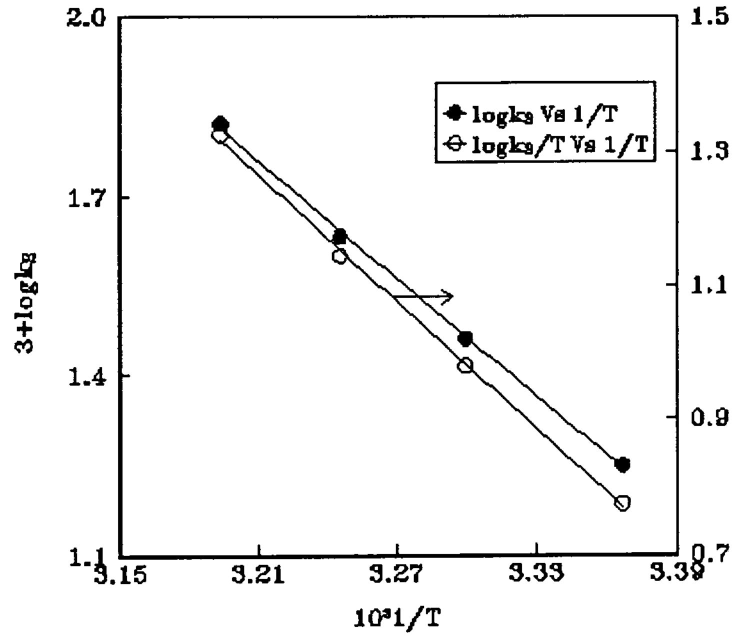


Fig 4.25

Fig 4.25 Plot of log k_2 vs 1/T & log k_2/T vs 1/T for the oxidation of p-NO_2 phenyl ethanol (Correlation coefficient = 0.9995)

4.2.3 DISCUSSION

The product of the oxidation of 1-phenyl ethanol by $KMnO_4$ in 40% aqueous acetic acid was ascertained to be acetophenone and stoichiometry was determined to be 3:2 carbinol : $KMnO_4$. The reaction conformed to first order kinetics with respect to oxidant concentration as well as with carbinol concentration. The sequential scan of the absorption spectrum for the kinetics of the system at regular time intervals showed isosbestic point at 482.5nm. (Fig 4.26)

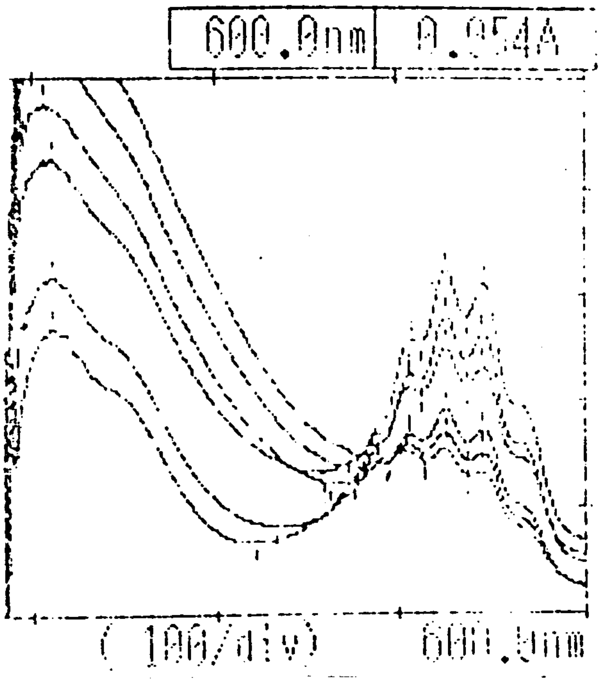


Fig 4.26 Sequential scan of the absorption spectrum of the kinetics of the oxidation of 1-phenyl ethanol by $KMnO_4$ in 40% aqueous acetic acid at 30°C. (Isosbestic point 482.2nm)

This is suggestive of a single product and rules out any complicated sequence of events during the oxidation.[148-150,174] The influence of mineral acid revealed that the reaction followed an initial acid-independent path and subsequent acid-dependent path involving singly protonated and doubly protonated forms of the reactive species at moderate and higher concentration of the mineral acid respectively. The effect of polarity of the medium indicates that the interaction is between a negative ion and a dipole. The added salt had no influence on the rate of the reaction and this ruled out the possibility of interaction between two charged species. Since the addition of acrylonitrile failed to induce polymerisation the involvement of free radicals during oxidation can be ruled out.

The influence of the substituents at the para position of phenyl ring of 1-phenyl ethanol was quite unique in that both electron-withdrawing and electron-releasing groups enhanced the reaction rate. The plot of log k_2 vs σ (Hammett plot)[170] did not give a single linear relation. However it can be resolved into two approximate linear relations, one for electron-releasing groups and the other for electron-withdrawing groups. This type of plot is suggestive of a transition state undergoing structural variation depending on the specific electronic environment available from the substituents in the making and breaking of the bonds[148,170,175-177,179,180,192].

The plot of $\Delta H^{\#}$ Vs $\Delta S^{\#}$ (Leffler-Grunwald plot)[177] is linear with correlation coefficient of 0.998 and value of isokinetic temperature is 260K (Fig 4.27). Similarly the plot of log k_2 at 318K vs log k_2 at 303K (Exners plot)[178] is also linear with a correlation coefficient of 0.9960 with isokinetic temperature of 252 K. (Fig 4.28)

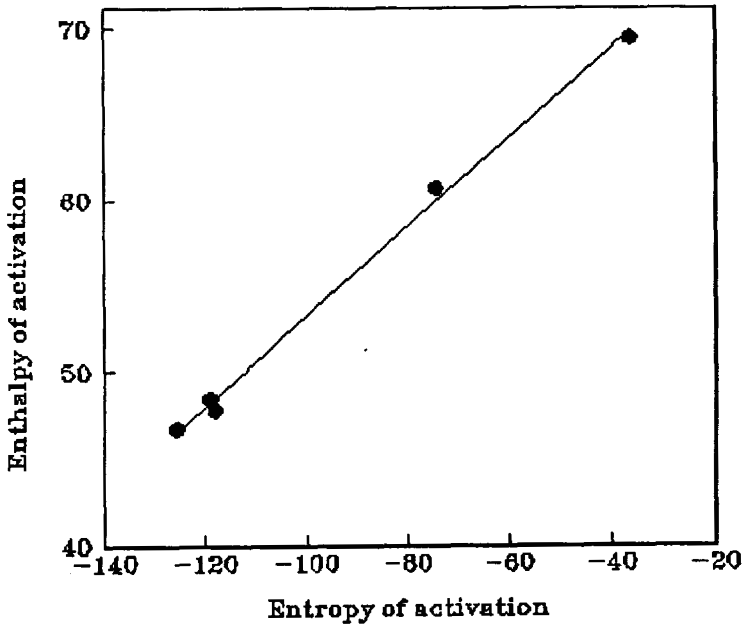


Fig 4.27 Isokinetic plot for the oxidation of carbinols (Correlation coefficient = 0.9980)

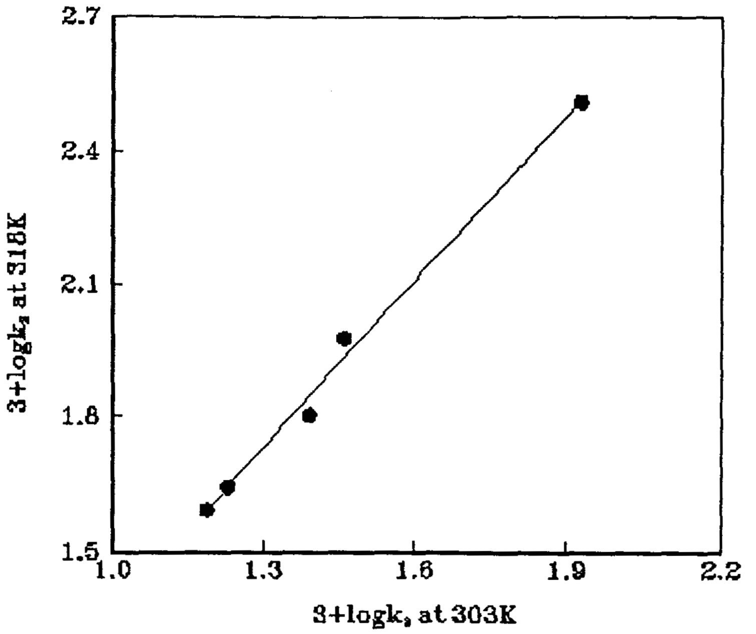
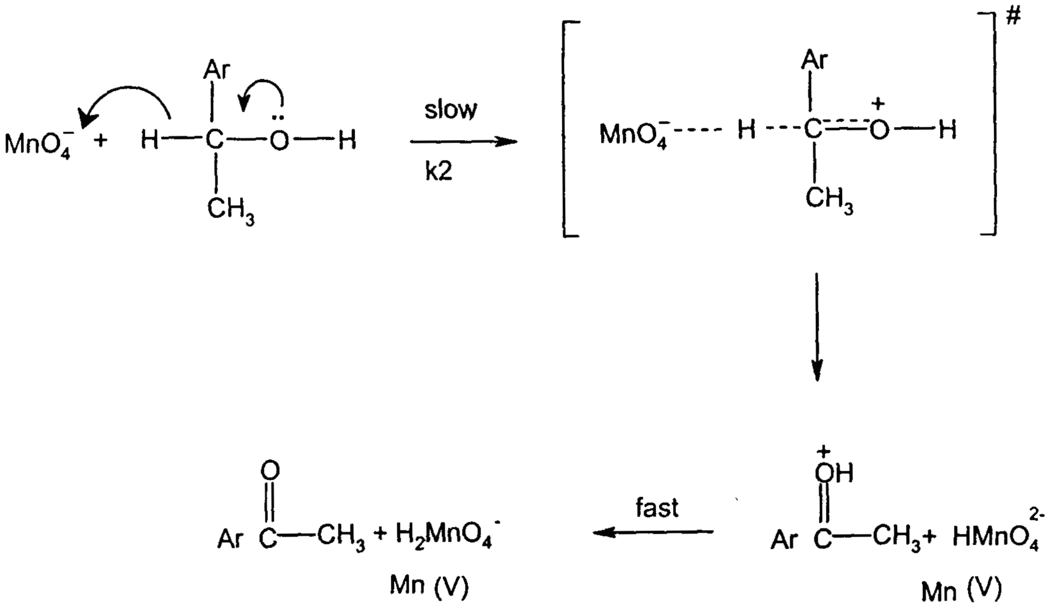


Fig 4.28 Exners plot for the oxidation of carbinols
(Correlattion coefficient = 0.9960)

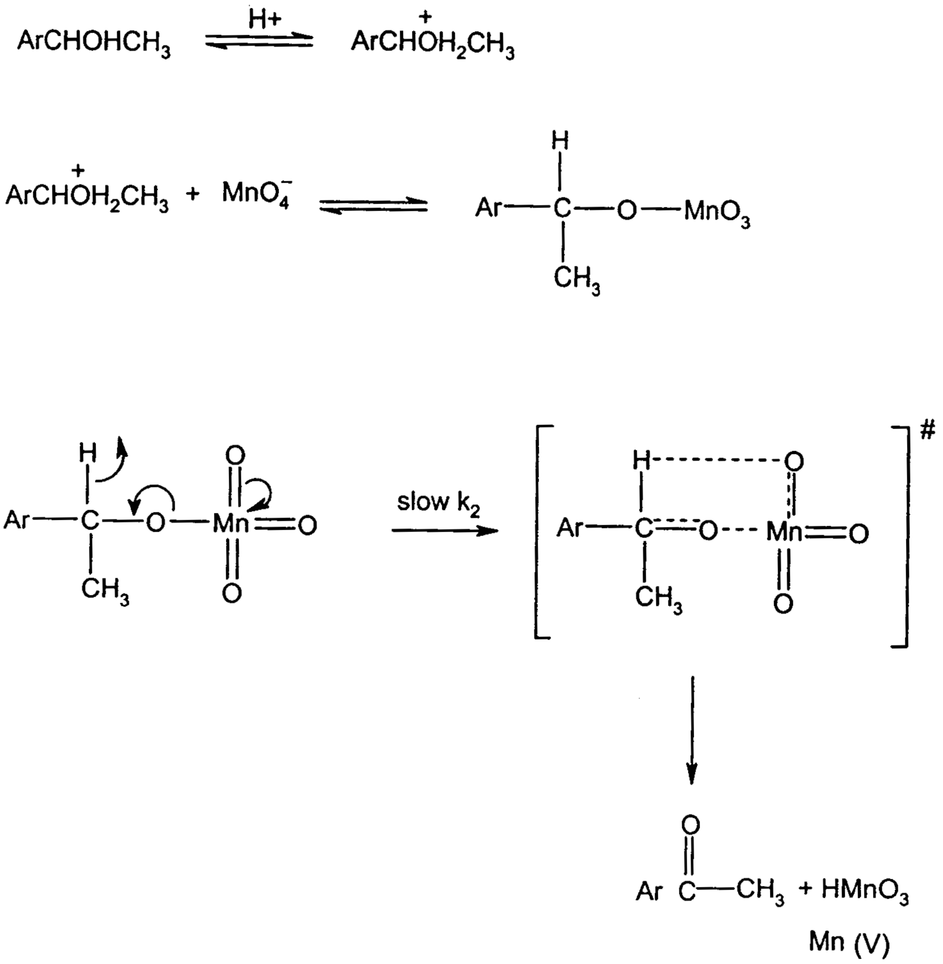
The existence of the isokinetic temperature together with the constancy in the value of free energy of activation ($\Delta G^{\#}$ = 83 kJ mol^{-1}) are suggestive of the operation of a similar mechanism for the oxidation of all the alcohols by $KMnO_4$ in aqueous acetic acid.

Almost similar results in which electron-withdrawing groups as well as electron-releasing groups enhance the rate with respect to the parent compound was reported by Henbest *et al*[180] during the oxidation of substituted stilbenes by permanganate in aqueous dioxane. Careful examination of the rate data for the oxidation of the substituted stilbenes indicated that the Hammett plot is concave upwards. A positive slope is observed when electron-withdrawing groups are present and a negative slope when electron-releasing groups are present. That such a plot is indicative of the fact that apparently the reaction can proceed via an electron deficient or an electron- rich transition state[148,192], depending on the demands of the reaction centre from the substituents. The reaction between high-valent transition metal oxides and organic compounds via formation of active complexes or intermediate have appeared abundantly in literature.[105,125,148-151,185,186,192-194]

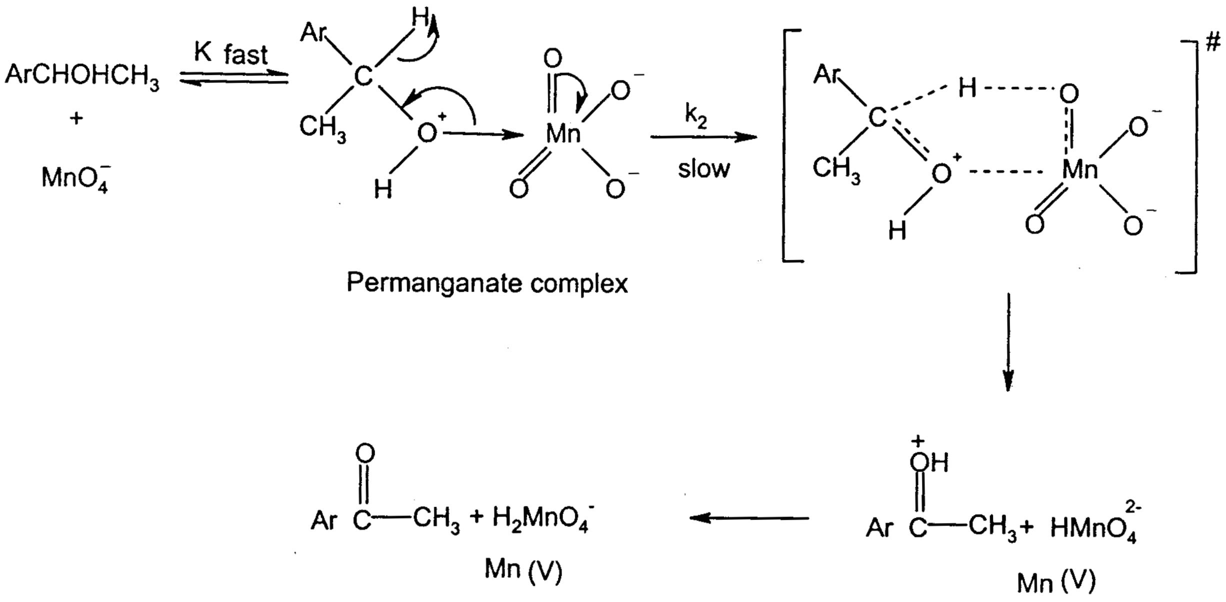
The probable mechanism for the oxidation of secondary alcohols by permanganate in aqueous acetic acid medium can therefore be formulated according to following schemes.



Scheme 1


ArCHOHCH$_3$
H+
ArCHOH$_2$CH$_3$
ArCHOH$_2$CH$_3$ + MnO$_4^-$
Ar—C—O—MnO$_3$
slow k$_2$
#
Ar C—CH$_3$ + HMnO$_3$
Mn (V)

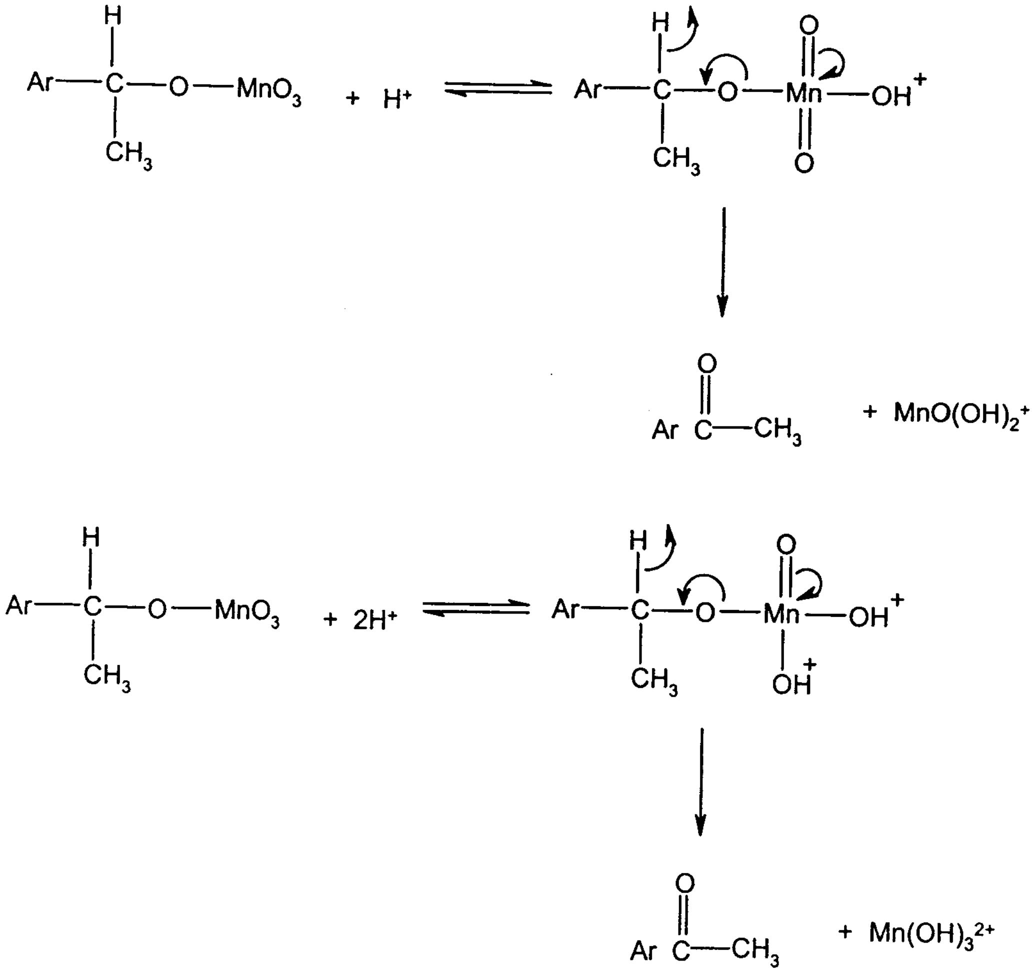
Scheme 2



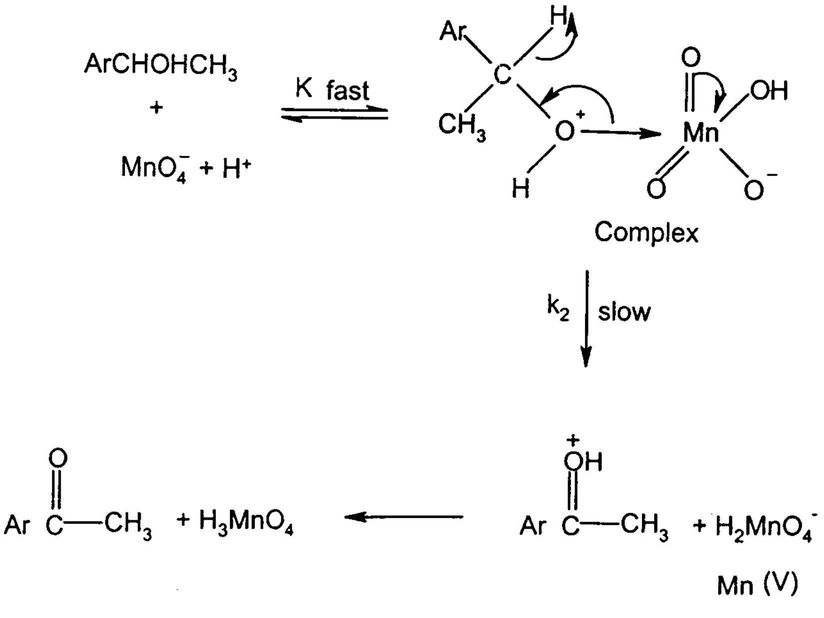
$$3\mathrm{Mn(V)} \rightarrow 2\mathrm{Mn(IV)} + \mathrm{Mn(VII)}$$

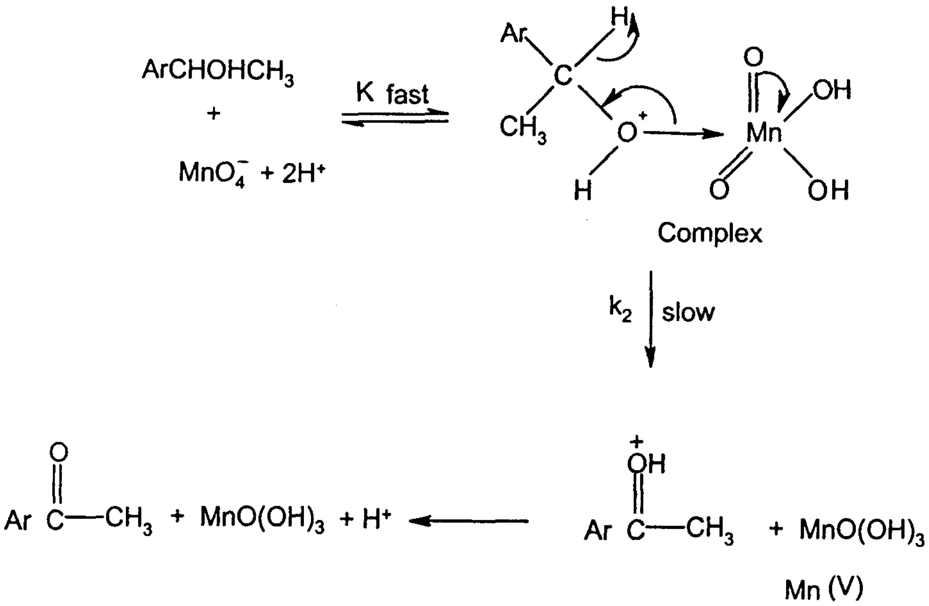
Scheme 3

In the presence of mineral acids the schemes 2 and 3 can be modified by assuming a rate-determining step involving singly protonated and doubly protonated reactive complexes[125] corresponding to two acid-dependent paths as shown in scheme 2.1 and 3.1 respectively.


Ar
H
C
O
MnO3
CH3
+ H+
Mn
OH+
+ MnO(OH)2+
+ 2H+
+ Mn(OH)3 2+

Scheme 2.1


ArCHOHCH3
+
MnO4- + H+
K fast
Complex
k2
slow
+ H3MnO4
+ H2MnO4-
Mn (V)



Scheme 3.1

In all the cases Mn(V) disproportionate into Mn(IV) the experimentally observed product[1,101,156,191] as 3Mn(V) → 2Mn(IV) + Mn(VII)

The scheme (1) suggested by Littler and Barter appears[101] to be quite straightforward. The findings account for an electron-deficient transition state as a result of hydride ion shift from carbinol to oxidant, which is favoured if electron-releasing groups are present at the para position of the benzene ring of the carbinol. However, the observed increase in the rate by electron-withdrawing substituents cannot be explained by the above argument. Further, the probability of the transfer of hydride ion via an acyclic one-step bimolecular process was questioned by Bordwell.[189] It is now well established that the transfer of hydrogen takes place only through the involvement of cyclic transition state and that is a truly symmetrical processes involving a linear hydride ion transfer (Woodward and Hoffman)[190].

According to scheme 2 the reaction is initiated by the formation of permanganate ester complex by the interaction between protonated alcohol and permanganate, which is followed by the rate limiting decomposition of the complex involving α C-H bond clevage and O-Mn bond cleavage through a cyclic-transition state. It appears that the electron releasing substituents enhance the rate by favouring the cleavage of α C-H bond while electron-withdrawing substituents accelerate the rate by aiding the cleavage of O-Mn bond. Protonation of alcohol is possible in aqueous acetic acid medium. The main drawback of the scheme is its inqbility to account for the comparable rate of oxidation of carbinols with ethers[156], both having the same electronic environment around the α carbon atom to which the functional groups are attached. A similar ester formation is unlikely in the case of ethers.

The results on the kinetic studies on the oxidation of 1-phenyl ethanol and its para-substituted derivatives in aqueous acetic acid medium by potassium permanganate are almost comparable to that of the oxidation taking place in benzene under PTC condition as can be seen in the table 4.12.

Table 4.12

Activation parameters for the permanganate oxidation of 1-phenyl ethanol and its substituents in aqueous acetic acid medium and in benzene under PTC condition

Medium	Aq. HOAc (40% v/v)				Benzene using phase transferred MnO_4^-, PT Catalyst = TBAB			
Substrate	10^3 x k_2 (dm^3 $mol^{-1}s^{-1}$)	$\Delta H^{\neq}$(k $Jmol^{-1}$	$\Delta S^{\neq}$(JK^{-1} mol^{-1}	$\Delta G^{\neq}$(k $Jmol^{-1}$	10^3 x k_2 (dm^3 $mol^{-1}s^{-1}$)	$\Delta H^{\neq}$(kJ mol^{-1}	$\Delta S^{\neq}$(J K^{-1} mol^{-1}	$\Delta G^{\neq}$(k $Jmol^{-1}$
PhCHOH CH_3	15.23	46.73	-125.59	84.78	3.14	75.66	-43.30	88.78
p-Me PhCHOH CH_3	24.65	47.82	-118.09	83.59	4.41	68.60	-63.72	87.90
p-OMe PhCHOH CH_3	84.52	69.46	-36.42	80.50	16.60	62.20	-73.80	84.90
p-Cl PhCHOH CH_3	16.98	48.49	-118.97	84.54	6.47	67.17	-65.35	86.90
p-NO_2 PhCHOH CH_3	28.88	60.72	-74.21	83.20	29.25	55.35	-91.99	83.20

A comparison of the $\Delta G^{\neq}$ values according to the table 4.12 for the oxidation in aqueous acetic acid and in non-polar organic media would indicate that there is practically no change in mechanism in either solvent systems as expected. In the case of the unsubstituted substrate viz 1-phenyl ethanol the entropy of activation in the aqueous medium is largely negative indicating a better solvated and hence more ordered transition state in that media. However, for the same substrate a change over of solvent to a non-polar medium like benzene makes the entropy of activation less negative and this is evidence for the likely destabilization of the transition state configuration in the organic phase. With groups, which have greater electronic effects like the p-OMe and the p-NO_2, there is reversal in the activation entropy values. That is the entropy of activation in the aqueous medium are less negative compared to those in the organic media. The larger electronic effects of the para substitutents enable the transition state in the non-polar media to be stabilized better over that conferred by solvation in polar aqueous media.

The existence of almost close isosbestic point in the sequential scan of the absorption spectrum of the oxidation (482.5nm in aqueous acetic and 489nm in PTC condition in benzene), the almost same trend of the substituents in effecting the rate of oxidation, the comparable value of free energy of activation, the almost identical dielectric effect of the solvents, identical salt effect etc. revealed that the mechanism operating in aqueous acetic acid medium and that under PTC condition in benzene are comparable. Hence a mechanism guided by frontier molecular orbital theory as shown in the scheme 3 is suggested.

Accordingly the reaction is initiated by the interaction of the 2p electron on the HOMO of the oxygen of the alcohol with the LUMO of the permanganate (2e antibonding molecular orbital located primarily on manganeese) to form a complex in a fast pre-equilibrium step. This is followed by the rate limiting decomposition of the complex via a cyclic transition state leading to the product as shown in scheme 3.Depending on the electronic demands from the substituents either the α C-H bond cleavage or Mn→O bond cleavage is favoured for the reaction. It seems that the electron-releasing substituents enhance the rate by favouring the cleavage of α C-H bond and while electron-withdrawing groups enhance the rate by aiding the cleavage of O→Mn bond. The fact that the cleavage of α C-H bond in the rate-determining step during the permanganate oxidation of alcohol has been established by labelled studies using isotopically labeled substrate with α C-D instead of α C-H.[101,125,156,187]

This mechanism would account for the kinetic observations made. The order of the reaction, the influence of mineral acids, the effects of the dielectric constant of the medium, the salt effect, the substituent effects etc. can very well be explained by this mechanism.

A slight decrease in the slope of the Hammett plot as compared to that under PTC method was found in aqueous acetic acid medium. This may probably arise from the slight change in the electronic effect of the substituents due to the change in the polarity of the medium.

A suitable rate expression for the oxidation of the carbinols in accordance with the above mechanism can be given by the equation 4.4.

$$-d\,[MnO_4]\,/dt = k_2\,[\text{complex}]$$

$$= Kk_2\,[ArCHOHCH_3]\,[MnO^-_4] \qquad (4.4)$$

CONCLUSION

The oxidation of 1- phenyl ethanol and some of its para-substituted derivatives by phase transferred permanganate occurred smoothly in benzene and in a few other non-polar organic solvents with appreciable rate. The carbinols were oxidised to the corresponding ketones. Tricaprylmethyl ammonium chloride (TCMAC) was found to be a better phase transfer catalyst than tetrabutylammonium bromide (TBAB) for the extraction of MnO_4^- ions from the aqueous phase to organic phase and also for effecting oxidation. The values of the second order rate constants (k_2) are 4.72×10^{-3} dm^3mol^{-1} s^{-1} and 3.14×10^{-3} dm^3mol^{-1} s^{-1} for TCMAC and TBAB respectively. Of the various organic solvents employed, dichloromethane and chloroform were found to be the best solvents for effecting oxidation.

The values of the activation parameters obtained for the various secondary carbinols under PTC condition in benzene are comparable to similar oxidation in aqueous acetic acid media. The introduction of substituents in the para-position of the benzene ring of 1- phenyl ethanol produced a unique substituent effect in which both the electron-releasing groups and electron-withdrawing groups enhanced the reaction rate. Although the same trend of substituent effect were observed in aqueous acetic acid medium, there was a marked reduction in the electronic effect of the substituents in the aqueous medium compared to the organic medium. In general it may be seen that the phase transferred permanganate oxidizes these substrates quite easily. Further, the electronic effect of the structural modifications of the substituents are more clearly and unambiguously brought about in the phase transferred reaction conditions. The reaction practically did not occur in the absence of the catalyst in the organic media employed. Thus the phase transfer catalysis technique offers a convenient route to study the kinetics and mechanism of the oxidation of organic compounds in organic media.

SUMMARY

SUMMARY

Kinetics of the oxidation of 1-phenyl ethanol, its para-substituted derivatives like p-Me, p-Cl, p-OMe and p-NO_2, other secondary alcohols like benzhydrol and cylcohexanol have been carried out in benzene using phase transferred permanganate. Tricaprylmethyl ammonium chloride (TCMAC) and tetrabutylammonium bromide (TBAB) were used as phase transfer catalysts. For carrying out the kinetic studies the permanganate ions from the aqueous phase were first extracted into an organic phase with the help of the PT catalyst. Though both the catalysts were equally good for the extraction of permanganate ion in to the organic medium, the former (TCMAC) was found to be superior over the latter (TBAB) on account of its greater organophilicity. This phase transferred permanganate called purple benzene was found to be relatively stable for effecting the oxidation of carbinols under homogeneous condition.

The effect of [oxidant], [substrate], solvents, ionic strength and temperature were studied using TBAB and TCMAC as PT catalysts and activation parameters were computed for all the carbinols. The reaction was found to be first order with respect to the oxidant concentration as well as with respect to the carbinol concentration. Stoichiometry was found to be 3:2 [carbinol] : [MnO_4^-]. The product of the oxidation was

ascertained to be the corresponding ketones. The rate of oxidation increased with increase in the polarity of the organic solvents employed. The effect of the substituents in the para position of the benzene ring of 1-phenyl ethanol was quite unique in that both the electron-releasing and electron-withdrawing groups increased the reaction rate. The Hammett plot was not linear, instead it can be resolved into two approximate linear fits respectively for electron withdrawing groups and electron releasing groups. The rate of oxidation is greater with TCMAC than with TBAB as the PT catalyst. The values of the activation parameters are comparable to similar oxidations in aqueous media.

The kinetics of the oxidation of 1-phenyl ethanol and its para-substituted derivatives were also studied in 40% aqueous acetic acid medium using $KMnO_4$. Although the same trend of substituent effect were observed in aqueous acetic acid medium, there was a marked reduction in the electronic effect of the substituents in the aqueous medium compared to the organic medium. Thus phase transfer technique offers a convenient route to study the kinetics and mechanism of the water insoluble organic compound in organic medium. The simplicity of the operation, the rapidity reaction rate, the high selectivity and the generally high yield of the product ensure that the technique will find wide application in industrial field.

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APPENDIX

Oxidation of 1-phenyl ethanol by permanganate is benzene using tetrabutylammonium bromide (TBAB) as phase transfer catalyst.

Table 3.5

Effect of varying concentration of oxidant, $[QMnO_4]$ on the rate of oxidations of 1-phenylethanol.

$[PhCHOHCH_3] = 1.245\times10^{-3}$ mol dm^{-3} T- 303K

Solvent - Benzene PTC-TBAB.

$[QMnO_4]\times10^4$ (mol dm^{-3})	2.450	5.120	7.500	12.200
Time (min.)	1+log(Absorption of $QMnO_4$ at 528nm)			
0	0.7815	1.1100	1.2800	1.4800
10	0.7715	1.1000	1.2710	1.4700
20	0.7635	1.0880	1.2620	1.4580
30	0.7495	1.0790	1.2480	1.4490
40	0.7390	1.0700	1.2380	1.4380
50	0.7275	1.0585	1.2260	1.4260
− Slope	0.00110	0.00102	0.00108	0.00107
$k_{ob}\times10^5(s^{-1})$	4.22	3.92	4.15	4.12
Correlation coefficient	0.9993	0.9991	.9990	0.9998

Table 3.6

Effect of varying concentration of substrate on the rate of oxidation

$[QMnO_4] = 5.12 \times 10^{-4}$ mol dm^{-3} T = 303K

Medium - Benzene PTC = TBAB.

$10^2[PhCHOHCH_3]$ (mol dm^{-3})	1.245	2.490	3.740	4.980
Time (min.)	1 + log Absorbance of $QMnO_4$ at 528nm			
0	1.1100	1.1020	1.1100	1.1020
10	1.1000	1.0809	1.0780	1.0600
20	1.0880	1.0580	1.0490	1.0220
30	1.0790	1.0400	1.0180	0.9760
40	1.0700	1.0160	0.9900	0.9380
50	1.0585	0.9960	0.9600	0.9000
-Slope	0.00102	0.00211	0.00299	.00406
$k_{ob} \times 10^5$ (s^{-1})	3.92	8.09	11.48	15.58
$k_2 \times 10^3$ (dm^{3}mol^{-1}s^{-1})	3.14	3.25	3.07	3.13
Corr:Coefft	0.9991	0.9995	0.9998	0.9996

Table 3.7

Effect of addition of tetrabutyl ammonium bromide (TBAB) on the rate of oxidation (Salt effect).

$[PhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Temp = 303K

$[QMnO_4] = 5\times10^{-4}$ mol dm^{-3} Medium - Benzene

$[Q = TBA^+]$ PTC = TBAB.

10^2[TBAB] (mol dm^{-3})	0	1	2	3	4
Time (min.)	1+log Absorbance of $QMnO_4$ at 528nm.				
0	1.1100	1.0930	1.1100	1.0900	1.0800
10	1.1000	1.0820	1.1000	1.0800	1.0680
20	1.0880	1.0700	1.0880	1.0680	1.0580
30	1.0790	1.0610	1.0790	1.0580	1.0500
40	1.0700	1.0480	1.0700	1.0460	1.0385
50	1.0585	1.0370	1.0590	1.0340	1.0280
-Slope	0.00102	0.00111	0.00101	0.00112	0.00102
$k_{ob}\times10^5$ (s^{-1})	3.92	4.26	3.87	4.29	3.92
$k_2\times10^3$ (dm^{3}mol^{-1}s^{-1})	3.14	3.42	3.11	3.44	3.14
Correlation Coefficient	0.9991	0.9993	0.9992	.9990	0.9998

Table 3.8

Effect of solvent on the rate of oxidation of 1-phenyl ethanol.

$[PhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} T = 303K

$[QMnO_4] = 5.12\times10^{-4}$ mol dm^{-3} PTC = TBAB.

Solvent	Carbon tetrachloride	Toluene	Chloroform	Chloro benzene	Methylene chloride.
Time (min.)	1+log Absorbance of $QMnO_4$ at 528nm.				
0	1.1070	1.0780	1.0780	1.1000	1.0940
10	1.0960	1.0640	1.0600	1.0830	1.0700
20	1.0860	1.0520	1.0380	1.0640	1.0430
30	1.0770	1.0410	1.0180	1.0480	1.0180
40	1.0688	1.0300	0.9970	1.0300	0.9920
50	1.0580	1.0180	0.9765	1.0120	0.9670
-Slope	0.00097	0.00118	0.00205	0.00176	0.00255
$k_{ob}\times10^5(s^{-1})$	3.72	4.53	7.80	6.75	9.78
$k_2\times10^3$ $(dm^3mol^{-1}s^{-1})$	2.99	3.63	6.32	5.42	7.86
Correlation coefficient	0.9994	0.9995	0.9996	0.9990	0.9997

Table 3.9

Effect of Temperature on the rate of oxidation of 1-phenyl ethanol by $QMnO_4$ ($Q=TBA^+$) in benzene.

$[PhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Medium - Benzene

$[QMnO_4] = 5.12\times10^{-4}$ moldm^{-3} PTC = TBAB.

Temp. (K)	303	308	313	318
Time (min.)	1+log Absorbance of $QMnO_4$ at 528nm.			
0	1.1100	1.1160	1.1160	1.1061
10	1.1000	1.1000	1.0860	1.0700
20	1.0880	1.0780	1.0540	1.0243
30	1.0790	1.0630	1.0220	0.9780
40	1.0700	1.0440	0.9880	0.9350
50	1.0585	1.0260	0.9600	0.8940
-Slope	0.00102	0.0018	0.00311	0.00432
$k_{ob}\times10^5$ (s^{-1})	3.92	6.91	11.94	16.58
$k_2\times10^3$ ($dm^3mol^{-1}s^{-1}$)	3.14	5.55	9.56	13.32
Correlation Coefft	0.9991	0.9998	0.9990	0.9995

Table 3.10

Effect of Substituents on the rate of oxidation of 1-phenyl ethanol by $QMnO_4$ ($Q=TBA^+$) using TBAB as PTC

[Substrate] = 1.245×10^{-2} mol dm^{-3} T = 303K

[$QMnO_4$] = 5.12×10^{-4} mol dm^{-3} Medium - Benzene.

Substrate	1-phenyl ethanol	p-methyl 1-phenyl ethanol	p-chloro 1-phenyl ethanol	p-methoxy 1-phenyl ethanol	p-nitro. 1-phenyl ethanol
Time (min.)	1+log Absorbance of $QMnO_4$ at 528nm.				
0	1.1100	1.1090	1.1020	1.1020	1.0981
10	1.1000	1.0980	1.0800	1.0470	0.9905
20	1.0880	1.0830	1.0590	0.9950	0.9021
30	1.0790	1.0720	1.0400	0.9400	0.8055
40	1.0700	1.0550	1.0180	0.8860	0.7048
50	1.0585	1.0390	0.9975	0.8330	0.6045
-Slope	0.00102	0.00143	0.00210	0.00538	0.00952
$k_{ob} \times 10^5$ (s^{-1})	3.92	5.49	8.06	20.65	36.54
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	3.14	4.40	6.47	16.78	29.25
Corr.Coefft	0.9991	0.9975	0.9998	0.9997	0.9994

Table 3.11 (a)

Effect of temperature on the rate of oxidation of p-nitro 1-phenyl ethanol by $QMnO_4$ ($Q=TBA^+$)

$[p\text{-}NO_2PhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Solvent - Benzene

$[QMnO_4] = 5.12\times10^{-4}$ mol dm^{-3} PTC = TBAB.

Temp(K)	283	288	293	298
Time (min.)	1+log (Absorbance of $Q^+MnO_4^-$) at 528nm.			
0	1.1000	1.0920	1.0920	1.0942
5	1.0900	1.0780	1.0700	1.0605
10	1.0810	1.0620	1.0500	1.0301
15	1.0720	1.0490	1.0280	0.9980
20	1.0620	1.0350	1.0060	0.9660
25	1.0530	1.0200	0.9851	0.9320
30	1.0440	1.0060	0.9642	0.9000
(-Slope)	0.00187	0.00286	0.00427	0.00645
$k_{ob}\times10^5(s^{-1})$	7.18	10.97	16.38	24.75
$k_2\times10^3$ $(dm^3mol^{-1}s^{-1})$	5.76	8.82	13.16	19.88
Corr.Coefft	0.9994	0.9996	0.9995	0.9997

Note: The k_2 values at temperatures 303K, 308K, 313K and 318K are determined with the help of Arrhenius equation by knowing the values of the Ea and taking the value of k_2 at 298K as reference.

Table 3.11 (b)

Effect of temperature on the rate of oxidation of p-chloro 1-phenyl ethanol by $QMnO_4$ ($Q=TBA^+$)

$[p\text{-}ClPhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Solvent - Benzene

$[Q^+MnO_4^-] = 5.12\times10^{-4}$ mol dm^{-3} PTC = TBAB.

Temp(K)	303	308	313	318
Time (min.)	1+log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1020	1.1000	1.1060	1.0900
10	1.0800	1.0682	1.0540	1.0122
20	1.0590	1.0130	1.0041	0.9360
30	1.0401	1.0000	0.9570	0.8600
40	1.0182	0.9650	0.9040	0.7801
50	0.9975	0.9341	0.8562	0.7011
-Slope	0.00210	0.00329	0.00499	0.00776
$k_{ob}\times10^5(s^{-1})$	8.06	12.77	19.15	29.78
$k_2\times10^3$ ($dm^3mol^{-1}s^{-1}$)	6.47	10.14	15.30	23.90
Corre: Coefft.	0.9998	0.9929	0.9998	0.9998

Table 3.11 (c)

Effect of temperature on the rate of oxidation of p-methyl 1-phenyl ethanol by $QMnO_4$ ($Q=TBA^+$)

$[p\text{-}MePhCHOHCH_3] = 1.245x10^{-2}$mol dm^{-3} Solvent - Benzene

$[Q^+MnO_4] = 5.12x10^{-4}$mol dm^{-3} PTC = TBAB.

Temp(K)	303	308	313	318
Time (min.)	1+log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1090	1.1120	1.1130	1.1070
10	1.0980	1.0880	1.0750	1.0501
20	1.0832	1.0621	1.0380	0.9920
30	1.0721	1.0401	1.0000	0.9380
40	1.0550	1.0160	0.9631	0.8820
50	1.0390	0.9920	0.9260	0.8240
-Slope	0.00143	0.00239	0.00374	0.00564
$k_{ob}x10^5(s^{-1})$	5.48	9.17	14.35	20.73
k_2x10^3 ($dm^3mol^{-1}s^{-1}$)	4.41	7.37	11.53	16.65
Corre. Coefft.	0.9974	0.9996	0.9997	0.9995

x

Table 3.11 (d)

Effect of temperature on the rate of oxidation of p-methoxy 1-phenyl ethanol by $Q^+MnO^-_4$ ($Q=TBA^+$)

$[p\text{-}OMePhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Solvent - Benzene

$[QMnO_4]=5.12\times10^{-4}$ mol dm^{-3} PTC=TBAB.

Temp(K)	290	298	303	308
Time (min.)	1+log (Absorbance of $QMnO_4$) at 528nm.			
0	1.0851	1.0880	1.1020	1.1020
5	1.0801	1.0720	1.0760	1.0630
10	1.0680	1.0580	1.0470	1.0180
15	1.0560	1.0401	1.0220	0.9761
20	1.0442	1.0230	0.9950	0.9350
25	1.0320	1.0040	0.9661	0.8940
30	1.0201	0.9870	0.9400	0.8520
-Slope	0.00231	0.00339	0.00541	0.00836
$k_{ob}\times10^5(s^{-1})$	8.86	13.01	20.75	32.08
$k_2\times10^3$ ($dm^3mol^{-1}s^{-1}$)	7.12	10.45	16.60	25.70
Corre. Coefft.	0.9977	0.9984	0.9997	0.9998

Note: k_2 values at 313K and 318K were calculated with the help of Arrhenius equation by knowing the value of Ea and taking k_2 value at 303K as reference.

Table 3.12

Effect of temperature on the rate of oxidation of benzhydrol by $QMnO_4$ ($Q=TBA^+$)

[PhCHOHPh] = 1.245×10^{-2} mol dm^{-3} Solvent - Benzene

[$QMnO_4$] = 5.12×10^{-4} mol dm^{-3} PTC=TBAB.

Temp(K)	303	308	313	318
Time (min.)	1+log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1180	1.1175	1.0980	1.1080
10	1.0920	1.0780	1.0480	1.0200
20	1.0680	1.0380	0.9940	0.9300
30	1.0421	0.9981	0.9420	0.8420
40	1.0160	0.9560	0.8901	0.7580
50	0.9901	0.9170	0.8340	0.7215
-Slope	0.00255	0.00402	0.00527	0.00802
$k_{obs} \times 10^5$ (s^{-1})	9.86	14.58	20.21	30.66
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	7.92	12.39	16.24	24.70
Corre: Coefft.	0.9993	0.9995	0.9998	0.9948

Table 3.13

Effect of temperature on the rate of oxidation of cyclohexanol by $QMnO_4$ ($Q=TBA^+$)

[Cyclohexanol] = $1.245\text{x}10^{-2}$mol dm^{-3} Solvent - Benzene

[$QMnO_4$]=$5.12\text{x}10^{-4}$mol dm^{-3} PTC-TBAB.

Temp(K)	303	308	313	318
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.0940	1.1080	1.1100	1.1160
10	1.0860	1.0920	1.0860	1.0795
20	1.0760	1.0730	1.0615	1.0401
30	1.0665	1.0570	1.0380	1.0020
40	1.0570	1.0390	1.0140	0.9640
50	1.0480	1.0215	0.9901	0.9281
-Slope	0.0093	0.00174	0.00240	0.00410
$k_{ob}\text{x}10^5$ (s^{-1})	3.56	6.66	9.22	15.73
$K_2\text{x}10^3$ ($dm^3mol^{-1}s^{-1}$)	2.86	5.36	7.39	12.64
Corr: Coefft.	0.9996	0.9998	.9990	0.9994

Oxidation of 1-phenylethanol by $QMnO_4$ in benzene using TCMAC as PT catalyst

Table 3.14

Effect of varying the concentration of oxidant (TCMAP) on the rate of oxidation of 1-phenyl ethanol.

[$PhCHOHCH_3$] = 1.245×10^{-2} mol dm^{-3} Temp = 303K

Solvent - Benzene PTC - TCMC

[TCMAP]$\times 10^4$ (mol dm^{-3})	2.5	5.12	7.5	12.15
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	0.7810	1.0940	1.2800	1.4901
10	0.7660	1.0801	1.2600	1.4760
20	0.7500	1.0650	1.2450	1.4600
30	0.7360	1.0480	1.2280	1.4400
40	0.7200	1.0340	1.2120	1.4250
50	.07050	1.0180	1.1960	1.4060
-Slope	0.00152	0.00154	0.00158	.00156
$K_{ob} \times 10^5$ (s^{-1})	5.83	5.91	6.06	5.98
Correlation Coefft.	0.9981	0.9996	0.9993	0.9997

Table 3.15

Effect of varying the concentration substrate on the rate of oxidation of 1-phenyl ethanol by TCMAP.

[TCMAP] = 5.12x10^{-4}mol dm^{-3} Temp = 303K

Solvent - Benzene PTC = TCMAC

[$PhCHOHCH_3$] (mol dm^{-3})	1.245	2.490	3.745	4.980
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.0940	1.0950	1.0840	1.0920
10	1.0801	1.0640	1.0360	1.0331
20	1.0650	1.0350	0.9901	0.9750
30	1.0480	1.0040	0.9435	0.9160
40	1.0340	0.9745	0.8960	0.8580
50	1.0180	0.9440	0.8480	0.8001
-Slope	0.00153	0.00301	0.00478	0.00583
k_{ob}x10^5 (s^{-1})	5.87	11.55	18.3	22.37
k_2x10^3 (dm^{3}mol^{-1}s^{-1})	4.72	4.63	4.90	4.59
Corr: Coefft.	0.9996	0.9997	0.9996	0.9996

Table 3.16

Effect of adding TBAB on the rate of oxidation of 1-phenyl ethanol by TCMAP.

[Ph CH OH CH_3] = 1.245×10^{-2} mol dm^{-3} Solvent - Benzene

[TCMAP] = 5.12×10^{-4} mol dm^{-3} Temp = 303K.

PTC - TCMAC

[TBAB] x 10^2 (mol dm^{-3})	1	2	3	4
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.0860	1.0940	1.0921	1.1000
10	1.0720	1.0801	1.0760	1.0840
20	1.0560	1.0650	1.0600	1.0701
30	1.0420	1.0480	1.0450	1.0566
40	1.0260	1.0341	1.0280	1.0401
50	1.0120	1.0180	1.0131	1.0240
-Slope	0.00149	0.00155	0.00158	0.00150
$k_{ob} \times 10^5$ (s^{-1})	5.72	5.94	6.06	5.75
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	4.59	4.77	4.87	4.62
Correlation Coefft.	0.9998	0.9993	0.9998	0.9997

Table 3.17

Effect of Solvent on the rate of oxidation of 1-phenyl ethanol by TCMAP.

[Ph CHOH CH_3] = 1.245×10^{-2} mol dm^{-3} T = 303K.

[TCMAP] = 5.12×10^{-4} mol dm^{-3} PTC - TCMAC

Solvent	CCl_4	$C_6H_5CH_3$	$CHCl_3$	C_6H_5Cl	CH_2Cl_2
Time (min.)	1+log Absorbance of $QMnO_4$ at 528nm.				
0	1.1070	1.1040	1.0820	1.0820	1.0940
10	1.0941	1.0901	1.0601	1.0630	1.0620
20	1.0860	1.0780	1.0360	1.0350	1.0261
30	1.0680	1.0601	1.0120	1.0240	0.9960
40	1.0571	1.0460	0.9865	1.0040	0.9560
50	1.0460	1.0320	0.9620	0.9820	0.9230
-Slope	0.00123	0.00160	0.00241	0.00197	0.00344
$k_{ob} \times 10^5$	4.72	6.14	9.25	7.56	13.20
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	3.79	4.93	7.43	6.07	10.60
Corre.Coefft	0.9995	0.9990	0.9997	0.9959	0.9994

Table 3.18

Effect of temperature on the rate of oxidation of 1-phenyl ethanol using TCMAP.

[Ph CH OH CH_3] = 1.245x10^{-2}mol dm^{-3} Medium-benzene

[$^{-}$QMnO_4] = 5.12x10^{-4}mol dm^{-3} PTC=TCMAC

Q^+ = $TCMA^+$

Temp(K)	303	308	313	318
Time (min.)	1 + log (Absorbance of QMnO_4) at 528nm.			
0	1.0940	1.0920	1.0920	1.0920
10	1.0801	1.0680	1.0521	1.0321
20	1.0650	1.0440	1.0130	0.9740
30	1.0480	1.0210	0.9740	0.9141
40	1.0340	0.9960	0.9341	0.8560
50	1.0180	0.9701	0.89210	0.8050
-Slope	0.00153	0.00243	0.00398	0.00578
k_{ob}x10^5 (s^{-1})	5.87	9.33	15.27	22.18
k_2x10^3 (dm^{3}mol^{-1}s^{-1})	4.72	7.49	12.27	17.82
Corr. Coefft.	0.9996	0.9998	0.9997	0.9997

Table 3.19

Effect of substituents on the rate of oxidation of 1-phenyl ethanol by TCMAP.

[Carbinols] = 1.245×10^{-2} mol dm^{-3}	Temp = 303K
[$QMnO_4$] = 5.12×10^{-4} mol dm^{-3}	Solvent - Benzene
$Q^+ = TBA^+$	PTC - TCMAC

Substrate	1-phenyl ethanol	p-methyl 1-phenyl ethanol	p-chloro 1-phenyl ethanol	p-methoxy 1-phenyl ethanol	p-nitro 1-phenyl ethanol
Time (min.)	1+log (Absorbance of $QMnO_4$) at 528nm.				
0	1.0940	1.1001	1.1060	1.0950	1.0900
10	1.0801	1.0801	1.0800	1.0201	0.9822
20	1.0650	1.0625	1.0520	0.9472	0.8680
30	1.0480	1.0440	1.0240	0.8750	0.7568
40	1.0340	1.0260	0.9970	0.8051	0.6485
-Slope	0.00152	0.00184	0.00274	0.00724	0.01050
$k_{ob} \times 10^5 (s^{-1})$	5.83	7.05	10.52	27.78	40.30
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	4.68	5.67	8.42	22.59	32.57
Correlation Coefft	0.9996	0.9997	0.9995	0.9996	0.9993

Table 3.20 (a)

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

$[\text{p-MePhCHOHCH}_3] = 1.245\times10^{-2}\text{mol dm}^{-3}$ Solvent - Benzene

$[^{-}\text{QMnO}_4] = 5.12\times10^{-4}\text{mol dm}^{-3}$ PTC - TCMAC

$(\text{Q}^+ = \text{TCMA}^+)$

Temp(K)	303	308	313	318
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1000	1.0901	1.0860	1.0860
10	1.0801	1.0602	1.0401	1.0201
20	1.0630	1.0101	0.9965	0.9500
30	1.0440	1.0002	0.9520	0.8820
40	1.0260	0.9701	0.9081	0.8140
50	1.0060	0.9420	0.8630	0.7470
-Slope	0.00186	0.00300	0.00444	0.00680
$k_{ob}\times10^5 (s^{-1})$	7.13	11.51	16.88	26.10
$k_2\times10^2$ $(dm^3mol^{-1}s^{-1})$	5.73	9.17	13.68	20.96
Corr.coefft	0.9997	0.9989	0.9990	0.9995

Table 3.20 (b)

Effect of temperature on the rate of oxidation of p-chloro 1-pheyl ethanol by TCMAP.

[p-Cl $PhCHOHCH_3$] = 1.245×10^{-2} mol dm^{-3} Solvent - Benzene

[TCMAP] = 5.12×10^{-4} mol dm^{-3} PTC – TCMAC.

Temp(K)	303	308	313	318
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1060	1.1040	1.0880	1.0806
10	1.0800	1.0601	1.0201	0.9801
20	1.0520	1.0160	0.9530	0.8320
30	1.0240	0.9730	0.8860	0.7830
40	0.9970	0.9301	0.8200	0.6860
50	0.9701	0.8870	0.7540	0.5920
-Slope	0.00273	.00434	.00668	0.00977
$k_{ob} \times 10^5$ (s^{-1})	10.48	16.65	25.64	37.50
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	8.42	13.38	20.59	30.12
Correlation Coefft.	0.9995	0.9998	0.9997	0.9995

Table 3.20 (c)

Effect of temperature on the rate of oxidation of
p-methoxy 1-pheyl ethanol by TCMAP

$[p\text{-}MeOPhCHOHCH_3] = 1.245\times10^{-2}$ mol dm^{-3} Solvent - Benzene

$[TCMAP] = 5.12\times10^{-4}$ mol dm^{-3} PTC – TCMAC.

Temp(K)	293	298	303	308
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1090	1.1080	1.0950	1.0940
5	1.0940	1.0840	1.0580	1.0180
10	1.0790	1.0600	1.0201	0.9800
15	1.0630	1.0365	0.9840	0.9280
20	1.0480	1.0130	0.9470	0.8720
25	1.0320	0.9901	0.9115	0.8175
30	1.0160	0.9660	0.8750	0.7612
-Slope	0.00310	0.00472	0.00733	0.01077
$K_{ob}\times10^5$ (s^{-1})	11.89	18.11	28.13	41.13
$K_2\times10^3$ ($dm^3mol^{-1}s^{-1}$)	9.55	14.55	22.59	33.20
Corre: Coefft.	0.9999	0.9995	0.9996	0.9982

Note: The k_2 values at 313K and 318K are determined by employing Arrhenius equation by knowing the value of Ea, and by taking k_2 value at 303K as reference.

T_1(K)	T_2(K)	Ea (J mol^{-1})	10^3 x k_2 (T_1) (dm^3 mol^{-1}s^{-1})	10^3 x k_2 (T_2) (dm^3 mol^{-1}s^{-1})
303	313	62940	22.59	49.87
303	318	62940	22.59	72.71

Table 3.20 (d)

Effect of temperature on the rate of oxidation of p-nitro 1-pheyl ethanol by TCMAP.

[p- NO_2 $PhCHOHCH_3$] = 1.245×10^{-2} mol dm^{-3} Solvent - Benzene

[TCMAP] = 5.1×10^{-4} mol dm^{-3} PTC – TCMAC

Temp(K)	283	288	293	298
Time (min.)	1+ log (Absorbance of $QMnO_4$) at 528nm.			
0	1.1040	1.0920	1.1000	1.0920
5	1.0920	1.0760	1.0750	1.0550
10	1.0801	1.060	1.0480	1.0180
15	1.0670	1.0450	1.0215	0.9810
20	1.0561	1.0280	0.9960	0.9440
25	1.0440	1.0120	0.9701	0.9080
30	1.0320	0.9980	0.9440	0.8710
-Slope	0.00240	0.00316	0.00521	0.00736
$k_{ob} \times 10^5$ (s^{-1})	9.21	12.13	19.99	28.25
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	7.39	9.74	16.06	22.69
Correlation coefft.	0.9990	0.9998	0.9997	0.9998

Note: The k_2 values at 303K, 308K, 313K and 318K are determined with the help of Arrhenius equation by knowing Ea, and by taking k_2 value at 298K as reference.

T_1(K)	T_2(K)	Ea J mol^{-1}	10^3 k_2 (T_1) (dm^3 $mol^{-1} s^{-1}$)	10^3 k_2 (T_2) (dm^3 $mol^{-1} s^{-1}$)
298	303	54290	22.69	32.57
298	308	54290	22.69	46.22
298	313	54290	22.69	64.85
298	318	54290	22.69	90.01

Table 3.21

Effect of temperature on the rate of oxidation of benzhydrol using TCMAP as oxidant.

[Benzhydrol] = 1.245 x 10^{-2}mol dm^{-3} Solvent - benzene

[TCMAP] = 5.12 x 10^{-4}mol dm^{-3} PTC – TCMAC

Temp(k)	303	308	313	318
Time (min.)	1+ log Absorbance of $QMnO_4$ at 528nm.			
0	1.1060	1.0980	1.1001	1.0870
10	1.0710	1.0470	1.0240	0.9615
20	1.0360	0.9970	0.95101	0.8891
30	1.0001	0.9480	0.8780	0.7920
40	0.9960	0.8990	0.805	0.6950
50	0.9310	0.8515	0.734	0.5980
-Slope	0.00350	0.00493	0.0073	0.00955
$k_{ob}x10^5 (s^{-1})$	13.43	18.92	28.05	36.66
k_2x10^3 $(dm^3mol^{-1}s^{-1})$	10.79	15.20	22.54	29.44
Corr: Coefft.	0.9999	0.9998	0.9995	0.9988

Table 3.22

Effect of temperature on the rate of oxidation of cyclohexanol by TCMAP.

[Cyclohexanol] = 1.245×10^{-2}mol dm^{-3} Solvent - Benzene

[TCMAP] = 5.12×10^{-4}mol dm^{-3} PTC – TCMAC

Temp(k)	303	308	313	318
Time (min.)	1+ log Absorbance of $QMnO_4$ at 528nm.			
0	1.1001	1.1040	1.1040	1.1050
10	1.0880	1.0801	1.0710	1.0560
20	1.0725	1.0580	1.0390	1.0105
30	1.0620	1.0380	1.0070	0.9650
40	1.0501	1.0180	0.9755	0.9200
50	1.0360	0.9970	0.9450	0.8650
-Slope	0.00127	0.00212	0.00328	.00506
$k_{ob} x 10^5 (s^{-1})$	4.87	8.14	12.59	19.42
$k_2 x 10^3$ $(dm^3 mol^{-1} s^{-1})$	3.92	6.53	10.12	15.60
Corr: Coefft.	0.9998	0.9995	0.9994	0.9992

Oxidation of 1-phenyl ethanol by $KMnO_4$ in aqueous acetic acid

Table 3.23

Effect of [oxidant] on the rate of oxidation of
1-phenyl ethanol in aqueous acetic acid

$[PhCHOHCH_3] = 1.0 \times 10^{-2}$ mol dm^{-3} T = 303K

Medium – 40% aq. HOAc (v/v)

$[KMnO_4] \times 10^4$ (dm^3 mol^{-1} s^{-1})	5.5	7.5	10	12.5
Time (min.)	4 + log $[KMnO_4]$			
0	0.7500	0.8840	1.0000	1.0920
10	0.7200	0.8490	0.9620	1.0620
20	0.6740	0.8080	0.9220	1.0240
30	0.6365	0.7687	0.8810	0.9745
40	0.5980	0.7245	0.8400	0.9350
50	0.5460	0.6820	0.8000	0.8945
-Slope	0.00407	0.00409	0.00397	0.00405
$k_{ob} \times 10^5$ (s^{-1})	15.62	15.69	15.23	15.54
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	15.62	15.69	15.23	15.54
Corr: Coefft.	0.9980	0.9978	0.9990	0.9959

Table 3.24

Effect of [substrate] on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} T = 303K

Medium – 40% aq. HOAc (v/v)

$[PhCHOHCH_3] \times 10^2$ (dm^3 mol^{-1} s^{-1})	1	1.5	2	2.5	3
Time (min.)	4 + log $[KMnO_4]$				
0	1.0000	0.9880	0.9920	0.9840	0.9840
5	0.9820	0.9610	0.9500	0.9310	0.9180
10	0.9620	0.9320	0.9100	0.8780	0.8570
15	0.9440	0.9020	0.8680	0.8301	0.7940
20	0.9220	0.8730	0.8290	0.7760	0.7300
25	0.9040	0.8430	0.7880	0.72450	0.6670
30	0.8830	0.8215	0.7440	0.67250	0.6020
35	0.86380	0.7840	0.7050	0.6240	0.5400
40	0.8440	0.7540	0.6640	0.5740	0.4820
-Slope	0.00397	0.00592	0.00820	0.0102	0.0120
$k_{ob} \times 10^5$ (s^{-1})	15.23	22.72	31.47	39.15	46.06
$k_2 \times 10^3$ (dm^{3}mol^{-1}s^{-1})	15.23	15.15	15.73	15.66	15.35
Corr: Coefft.	0.9990	0.9989	0.9965	0.9978	0.9992

Table 3.25

Effect of ionic strength on the rate of oxidation of 1-phenyl ethanol in aqueous acetic acid

$[KMnO_4] = 1 \times 10^{-3}$ mol dm^{-3} $[PhCHOHCH_3] = 1.0 \times 10^{-2}$ mol dm^{-3}

Medium – 40% aq. HOAc (v/v) T = 303K

[NaCl] x 10^2 (dm^3 mol^{-1} s^{-1})	0	1.00	2.00	3.00	4.00
Time (min.)	4 + log $[KMnO_4]$				
0	1.0000	1.0270	1.0060	1.007	1.0260
10	0.9620	0.9840	0.9680	0.9690	0.9850
20	0.9220	0.9440	0.9280	0.9285	0.9450
30	0.8801	0.9020	0.8860	0.8870	0.9018
40	0.8400	0.8615	0.8460	0.8480	0.8620
50	0.8001	0.8200	0.8040	0.8060	0.8200
-Slope	0.00397	0.00405	0.00401	0.00402	0.00404
k_{ob}x10^5 (s^{-1})	15.23	15.54	15.39	15.43	15.50
k_2x10^3 (dm^{3}mol^{-1}s^{-1})	15.23	15.54	15.39	15.43	15.50
Corr: Coefft.	0.9990	0.9978	0.9985	0.9989	0.9975

Table 3.26

Effect of added mineral acid [H^+] on the kinetic of oxidation of 1.0-phenyl ethanol in aqueous acetic acid

[$KMnO_4$] = 1.0 x 10^{-3} mol dm^{-3} [$PhCHOHCH_3$] = 1.0x10^{-2} mol dm^{-3}

Medium – 40% aq. HOAc (v/v) T = 303K

[H_2SO_4] x 10^2 (dm^3 mol^{-1} s^{-1})	2.27	6.82	11.36	15.90
Time (min.)	4 + log [$KMnO_4$]			
0	1.0090	0.9980	1.0020	1.0000
10	0.9620	0.9420	0.9285	0.9200
20	0.9140	0.8900	0.8600	0.8280
30	0.8670	0.8300	0.7880	0.7390
40	0.8200	0.7815	0.7201	0.6480
50	0.7700	0.7260	0.6460	0.5800
-Slope	0.00450	0.00543	0.00708	0.00859
k_{ob}x10^5 (s^{-1})	17.27	20.84	27.17	32.97
k_2x10^3 ($dm^3mol^{-1}s^{-1}$)	17.27	20.84	27.17	32.97
Corr: Coefft.	0.9990	0.9981	0.9995	0.9968

Table 3.27

Effect of percentage variation of acetic acid (Change of polarity of medium) on the rate of oxidation of 1-phenyl ethanol

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} $[PhCHOHCH_3] = 1.0 \times 10^{-2}$ mol dm^{-3}

T = 303K

% HOAc	10	20	30	40	50	60	70	80
Time (Min)	4 + log ($KMnO_4$)							
0	1.0060	1.0000	0.9865	1.0000	1.0202	0.9980	0.9970	1.0000
10	0.9445	0.9435	0.9400	0.9625	0.9901	0.9589	0.9460	0.9440
20	0.8790	0.8865	0.8910	0.9224	0.9602	0.9280	0.9020	0.8672
30	0.8146	0.8310	0.8435	0.8801	0.9260	0.885	0.856	0.8315
40	0.7512	0.7740	0.7939	0.8412	0.8980	0.8470	0.8120	0.7750
50	0.6848	0.7160	0.7495	0.8010	0.8662	0.8091	0.7660	0.7178
Slope (-)	0.0642	0.00567	0.00485	0.00397	0.00309	0.00393	0.00458	0.00568
$k_{ob} \times 10^5$	25.03	21.76	18.61	15.23	11.94	15.08	17.57	21.80
Corre. Coefft.	0.9993	0.9997	0.9994	0.9996	0.9956	0.9990	0.9980	0.9986

Table 3.28

Effect of Temperature on the rate of oxidation of 1-phenyl ethanol in aqueous acetic medium

[$KMnO_4$] = 1.0×10^{-3} mol dm^{-3} [$PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium – 40% aq. HOAc (v/v)

Temp (K)	303	308	313	318
Time (min.)	4 + log [$KMnO_4$]			
0	1.0000	1.0040	0.9970	0.9920
5	0.9820	0.9770	0.9570	0.9401
10	0.9620	0.9460	0.9200	0.8920
15	0.9440	0.9190	0.8815	0.8415
20	0.9220	0.8880	0.8420	0.7901
25	0.9040	0.8601	0.8020	0.7420
30	0.8804	0.8280	0.7650	0.68650
-Slope	0.00397	0.00586	0.00774	0.01010
$k_{ob} \times 10^5$ (s^{-1})	15.23	22.72	30.00	39.16
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	15.23	22.72	30.00	39.16
Corr: Coefft.	0.9995	0.9995	0.9996	0.9998

Table 3.29

Effect of substituents on the kinetic of oxidation of 1-phenyl ethanol in aqueous acetic acid

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [Carbinol] = 1×10^{-2} mol dm^{-3}

Medium – 40% aq. HOAc (v/v) T = 303K

Substrate	1-phenyl ethanol	p-Me 1-phenyl ethanol	p-Cl 1-phenyl ethanol	p-OMe 1-phenyl ethanol	p-NO_2 1-phenyl ethanol
Time (min.)	4 + log $[KMnO_4]$				
0	1.000	0.9880	1.0220	1.0000	0.9750
5	0.982	0.9590	1.0000	0.8230	0.9360
10	0.962	0.9290	0.9750	0.7820	0.9000
15	0.944	0.8860	0.9540	0.6701	0.8620
20	0.9220	0.8560	0.9330	0.5625	0.8265
25	0.904	0.8200	0.9110	0.4520	0.7890
30	0.8802	0.8040	0.8890	0.342	0.7500
-Slope	0.00397	0.00636	0.00444	0.0218	0.00745
$k_{ob} x 10^5 (s^{-1})$	15.23	24.65	16.10	84.52	28.88
$k_2 x 10^3$ $(dm^3 mol^{-1} s^{-1})$	15.23	24.65	16.10	84.52	28.88
Corr: Coefft.	0.9995	0.9978	0.9985	0.9990	0.9989

Table 3.30 (a)

Effect of Temperature on the rate of oxidation of p-methyl phenyl ethanol in aqueous acetic medium

[$KMnO_4$] = 1.0 x 10^{-3} mol dm^{-3} [p-$MePhCHOHCH_3$] = 1.0 x10^{-2} mol dm^{-3}
Medium – 40% aq. HOAc (v/v)

Temp (K)	303	308	313	318
Time (min.)	4 + log [$KMnO_4$]			
0	0.9880	0.9880	0.980	0.9850
5	0.9590	0.9420	0.9220	0.9260
10	0.9290	0.8960	0.86150	0.8440
15	0.8860	0.8490	0.7980	0.7580
20	0.856	0.8040	0.7400	0.6700
25	0.826	0.7630	0.6750	0.5880
30	0.804	0.7190	0.6120	0.5050
-Slope	0.00636	0.00898	0.01229	0.01638
k_{ob}x10^5 (s^{-1})	24.65	34.82	47.65	63.50
k_2x10^3 ($dm^3mol^{-1}s^{-1}$)	24.65	34.82	47.65	63.50
Corr: Coefft.	0.9978	0.9989	0.9989	0.9990

Table 3.30 (b)

Effect of Temperature on the rate of oxidation of p-Cl phenyl ethanol in aqueous acetic medium

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p- Cl $PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium – 40% aq. HOAc (v/v)

Temp (K)	303	308	313	318
Time (min.)	$4 + \log [KMnO_4]$			
0	1.0220	1.0040	0.9980	0.9950
5	1.0000	0.9730	0.9540	0.9360
10	0.9750	0.9400	0.9130	0.8780
15	0.9540	0.9070	0.8700	0.8220
20	0.9330	0.8808	0.8290	0.7660
25	0.9110	0.8490	0.7850	0.7100
30	0.8890	0.8220	0.7420	0.6530
-Slope	0.00438	0.00609	0.00850	0.01136
$k_{ob} \times 10^5$ (s^{-1})	16.98	23.61	32.95	44.04
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	16.98	23.61	32.95	44.04
Corr: Coefft.	0.9985	0.9964	0.9990	0.9987

Table 3.30 (c)

Effect of Temperature on the rate of oxidation of p-OMe phenyl ethanol in aqueous acetic medium

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p- $OMePhCHOHCH_3] = 1.0 \times 10^{-2}$ mol dm^{-3}

Medium – 40% aq. HOAc (v/v)

Temp (K)	288	294	297	303
Time (min.)	4 + log $[KMnO_4]$			
0	1.0000	1.0000	0.9880	1.0000
5	0.9760	0.9540	0.9320	0.8830
10	0.9510	0.9080	0.8670	0.7820
15	0.9260	0.8600	0.8000	0.6700
20	0.9001	0.8140	0.7360	0.5620
25	0.8760	0.7680	0.6701	0.4520
30	0.8520	0.7200	0.6040	0.3420
-Slope	0.00496	0.00933	0.01291	0.02161
$k_{ob} \times 10^5$ (s^{-1})	19.23	36.17	50.05	84.52
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	19.23	36.17	50.05	84.52
Corr: Coefft.	0.9989	0.9956	0.9975	0.9990

Note:

k_2 at = 303 K = 84.52 x 10^3 $dm^3 mol^{-1} s^{-1}$

E_a = 69462 kJ mol^{-1}

k_2 at = 308 K = 134.34 x 10^3 $dm^3 mol^{-1} s^{-1}$

k_2 at = 313 K = 210.39 x 10^3 $dm^3 mol^{-1} s^{-1}$

k_2 at = 318 K = 324.86 x 10^3 $dm^3 mol^{-1} s^{-1}$

Table 3.30 (d)

Effect of Temperature on the rate of oxidation of p-NO_2 phenyl ethanol in aqueous acetic medium.

$[KMnO_4] = 1.0 \times 10^{-3}$ mol dm^{-3} [p- NO_2 $PhCHOHCH_3$] = 1.0×10^{-2} mol dm^{-3}

Medium – 40% aq. HOAc (v/v)

Temp (K)	297	303	308	313
Time (min.)	4 + log [KmnO$_4$]			
0	0.9880	0.9750	0.9660	0.9800
5	0.9660	0.9360	0.9100	0.9200
10	0.9430	0.9000	0.8520	0.8300
15	0.9200	0.8620	0.7970	0.7400
20	0.8980	0.8270	0.7420	0.6500
25	0.8750	0.7890	0.7860	0.5600
30	0.8510	0.7500	0.6340	0.4790
-Slope	0.00456	0.00745	0.0111	0.01713
$k_{ob} \times 10^5$ (s^{-1})	17.68	28.88	43.03	66.41
$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)	17.68	28.88	43.03	66.41
Corr: Coefft.	0.9989	0.9985	0.9978	0.9990