KINETIC STUDIES ON THE HYDROLYSIS OF ESTERS AND OXIDATION OF ALCOHOLS UNDER PHASE TRANSFER CATALYSIS

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forwarded

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Dedicated to

My Father, Prof. Shaji Govind,
Department of Chemistry, St. Mary's College,
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&

Mother, S. Sukumari Amma,
Department of Hindi, St. Mary's College,
Sultansbattery, Wayanad

who still encourages

DECLARATION

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

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CERTIFICATE

The thesis presented herewith embodies the observations on **Kinetic Studies on the Hydrolysis of Esters and Oxidation of Alcohols under Phase Transfer Catalysis**. This is an authentic record of the research work carried out by **S. Rana Pratap** 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. Radhakrishnan Nair

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LIST OF ABBREVIATIONS

PT : Phase Transfer
PTC : Phase Transfer Catalysis
TBAB : Tetrabutylammonium bromide
TBPB : Tetrabutylphosphonium bromide
TBAHS : Tetrabutylammonium hydrogen sulphate
$QMnO_4$: Quaternary ammonium permanganate
Q^+ : Quaternary ammonium or phosphonium cation
aq. HOAc : Aqueous acetic acid
TBAP : Tetrabutylammonium permanganate
TBPP : Tetrabutylphosphonium permanganate
2-phol : 2-phenyl ethanol
$Ph\text{-}CH_2\text{-}CH_2\text{-}OH$: 2-phenyl ethanol

CHAPTER I

INTRODUCTION

One hundred and fifty years of organic synthesis since Wohler's first successful experiment has provided the chemist with a very large arsenal of the sophisticated methods of organic synthesis. However on considering the ease with which living organisms produce complex structures in essentially aqueous surroundings at temperatures only a little different from room temperature, chemists come to realize that they have not been successful in and endeavors are being made continuously to the development of simpler and useful synthetic techniques. Thus they are constantly on the alert for faster, simpler and cheaper preparative methods of chemical synthesis. The development of chemistry has therefore witnessed novel techniques playing important roles in synthetic methods. Various innovative methods have been devised for speeding up reactions, for carrying out reactions in a continuous fashion, for separating complex mixtures and so on. These studies include development and application of different types of catalytic substances also.

When the organic substrate is soluble only in a water immiscible non polar organic solvent and the reagent for effecting the reaction is soluble only in water, proper reaction cannot take place, when these two are mixed. The two cannot react even if mixed and even if they react, the process will be very slow and the reaction proceeds only at the interface of the two solvent phases. The rate of such a reaction can however be increased by stirring the heterogeneous mixture. This situation can be solved to some extend by the use of polar aprotic solvents which can solvate cations thereby liberating reactive anions to enable the reaction to proceed faster. However such solvents are expensive and their removal is difficult. Many of these solvents are also toxic in nature. In many reactions very strong bases are required and the use of strong bases can create problems with solvents and side reactions also can take place. The use of materials known as 'Phase Transfer catalyst' (PTC) are soluble in water as well as in organic solvents, can be of great help under such circumstances. The developmental use of PTC has been a subject of recent origin starting from the mid seventies. Most of the research work connected with PTC in synthetic methods have been patented and hence the number of available publications are limited. The Phase transfer catalytic process can be conveniently carried out in a heterogeneous system of two immiscible liquids like water and a non polar solvent like benzene or methylene chloride or chloroform or toluene.

PTC has emerged as a powerful technique for conducting useful synthetic reactions in heterogeneous conditions. Synthesis in the fields of medicinal, pharmaceutical and bio-chemical areas have benefited from this convenient and cost effective method. This branch of science continues to stimulate further research in this area. Almost explosive growth of new knowledge and information regarding phase transfer catalysis has been emerging.

When a substrate present in an organic phase is to be reacted chemically with a reagent soluble only in aqueous medium forming another phase, reaction seldom takes place. In such a situation reaction is achieved by the transfer of the reactant in its active form from its normal phase of existence into the normal phase of existence of the substrate using PTC. The classical phase transfer catalysts are Crown Ethers which are toxic in nature and expensive. Quaternary ammonium and phosphonium salts are quite useful as phase transfer catalysts and can catalyze many reactions. These agents are capable of solubilizing or extracting the anionic reactant as ion pairs into the organic phase where the substrate is normally present and becomes quite reactive which helps the reaction to become faster.

Dipolar aprotic solvents like dimethyl sulfoxide, dimethylformamide, acetonitrile, hexamethylphosphoramide etc. were used as co-solvents with water for liberating an active 'naked' anion for effecting reactions before the use of PTC. But the use of such solvents is not advisable due to the high cost, larger toxicity and chances for side reactions to occur. The upkeep of these solvents in anhydrous state is also difficult. These solvents are also difficult to be purified.

When PTC's are used, the transferred onium ions are highly reactive and depending on the conditions they are also selective. Thus alkylation at C or O appears to be much more specific than in the usual alcoholic or aprotic solvents[1,2]. A number of PT agents like Quaternary salts[3], Phosphoramides, Crown ethers[4] and Cryptands have been used to catalyze various reactions. It has also been shown that linear Polyethylene glycol can complex with alkali metal ions and transfer the complex salt into the organic phase[5,6]. Polyethylene glycols known as "Poor Chemists Crown" are also found to perform the function of crown ethers [7-14].

The PT techniques become superior to the conventional methods in many respects. Some of the important advantages are as follows.

- Do not require vigorous conditions and the reactions are fast.
- Do not require expensive aprotic solvents.
- There is no need for anhydrous condition since water is used as one of the phases.
- At the same time it works under anhydrous condition also.
- In many cases the work up procedure is easier.
- Many reactions which require strong bases like alkoxide, sodamide, sodium hydride etc. can proceed with OH^- as it becomes strongly nucleophilic in the presence of PTC.
- Almost all reactions can be carried out under PTC conditions.
- The reactions which do not otherwise proceed can be made to proceed in good yield.
- The reaction can be carried out with selectivity and specificity in many cases.
- Higher yields are usually obtained through the suppression of side reactions by the use of PTC.

Phase transfer technique has also been found to be applicable for a wide variety of reactions like nucleophilic substitution[15-24], elimination[25-33], carbene reaction[34-45], alkylation[46-61], esterification[62-66], etherification[67-73], condensation[74-80], addition[81-84], polymerization[85-92], isomerisation[93-98], rearragements[99-100], hydrolysis[101-107], oxidation-reduction[108-114] reactions etc.

It has been found that PTC may function not only through liquid-liquid system but also with liquid-gas[115] ,liquid-solid[116-122], solid-gas and solid-solid system. Triphase catalysis is also a phase transfer process in which three phases viz. organic, aqueous and solid catalyst are present. The solid catalyst is generally on a polymer support and is not soluble in water or organic solvent. For eg. insolubilized ammonium and phosphonium compounds as catalyst. Quaternary ammonium and phosphonium salts conveniently attached to glass surface can also be used.

1.1. History of phase transfer catalysis

There are undoubtedly many early examples of the phenomenon now known as phase transfer catalysis and a presentation of all of them is neither relevant nor feasible. This novel technique was introduced by M. Makosza and later developed by Brandstorm and C.M. Starks. It was Starks who gave the name phase transfer catalysis. Earlier the phenomenon was known under the name "extractive alkylation". Makosza and co-workers published the first series of research papers in 1965[123]. Systematic exploration of the alkylation and other reactions in two phase systems containing alkali metal hydroxide were the earlier investigations. The descriptive terms used by them were 'catalytic two phase reactions,' 'catalytic alkylation of anions', 'catalytic generation of carbenes' etc. This work became more widely known with the discovery of dichloro carbene[34,35] Almost at the same period patents on the catalysis of heterogeneous reactions were issued to starks of the continental oil company in ponca city ,okhlahoma.[124]

At about the same time Arne Brandstorm developed a process which he called 'ion pair extraction.[125]' Brandstorms ion pair extraction technique logically leads to the technique of PTC. Brandstorms ion pair extraction technique is used to extract anions from an aqueous layer into the organic layer with the Quaternary ammonium or phosphonium as the cationic part. The ion pairs have a tendency to associate in the organic phase and hence to overcome the unfavorable extraction barriers.

In addition to the above examples a number of other publications and patents have appeared during that period. An important example of this is, the method reported by Gibson and Hosking in 1965.[126] They have shown that triphenylmethylarsonium permanganate could be prepared and isolated and dissolved in chloroform where it acts as an excellent oxidizing agent.

1.2. Types and requirements of phase transfer catalysis

Though one usually finds that a variety of PT agents work reasonably well, particularly in anion transfer systems, extensive use has been made of two types of catalysts only. They are:

1. Quaternary salts and
2. Macrocyclic ethers or Crown ethers.

There are two basic requirements for a PT catalyst. One is that it shall be able to transfer one of the reactants from its normal phase into the normal phase of the second reactant and secondly the transferred reagent in the new phase must be available in a highly reactive form.

Although the transfer of many species such as cations, anions, alcohols, ammonia, oxygen etc. from their normal phase to a second phase are known to occur, the bulk of literature on PTC is infact concerned with reactions involving anion transfer and activation. For this the PT catalyst must be cationic and must have enough organic structure so that the catalyst and the desired anion are substantially partitioned into the organic phase and again the cation - anion bonding must be loose enough to allow high anion reactivity to occur.

In addition to the above requirements several additional parameters like the stability of the catalyst under the reaction conditions, ease of preparation and availability of the catalyst, cost, ease of removal or recovery, selectivity in catalytic activity, whether or not anhydrous conditions are desirable are to be considered.

1.3. Nature of Quaternary salts in ion pair extraction

Numerous Quaternary ammonium, phosphonium, arsonium, bismuthonium and tertiary sulphonium salts have been claimed to be PTC. But in practice only a limited number of ammonium and phosphonium salts are being widely used[126,127,128]. This is because of certain factors involved in the selection of Quaternary salts as catalysts for anion transfer[129]. The simple notation $R_4N^+X^-$, $R_4P^+X^-$ etc. for Quaternary salts includes the structure and properties in this kind of PT catalyst.

1.4. Significance of the alkyl group of PTC

The primary requirement of the R group is that they must have sufficient organic structure to transfer the desired anion into the organic phase. The required organic structure will depend upon the anion transferred, the polarity of the organic phase, the concentration of inorganic reagent in the aqueous phase and to a certain extent, the presence of solvating organic compounds. It has been found that tetramethyl and tetraethyl ammonium salts do not have sufficient oleophilicity to function well as anion transfer catalyst.

Tetrabutylammonium salts are usually stable enough and sufficiently well partitioned into the organic phase (particularly if the organic phase is moderately polar) to be good catalyst for many reactions. This cation is frequently used since it is commercially available in association with a variety of anions and its salts are easily removed from the final product by diluting the organic phase with ether and washing with water.

Quaternary salts of the type $R\text{-}N^{+}(R')_3$ are frequently used because of their ease of preparation and commercial availability. Catalysts where R' = butyl or larger appear to activate anion more strongly because they provide near- maximum, cation - anion inter ionic distance. These catalysts are particularly useful when the organic phase reaction is relatively slow as in simple displacement reactions. The cheapest catalyst available is tricaprylmethyl ammonium chloride, a technical mixture containing C-C alkyl groups which is sold under the trade name Aliquate 336 (fluka AG, Buchs Switzerland; General mills Co. Kankasee, Illinouis, USA) or Andogen 464 (Aldrich Chemical Co. Mclwaukee, Wisconsin, USA) belong to this group.

Quaternary ammonium and phosphonium salts have been successfully used as PT catalyst although each has its own merits and demerits. Commercially ammonium salts are more widely available and are much less expensive. Moreover ingredients with which to prepare ammonium salts with a large variety of structures are also available. But phosphonium salts are more thermally stable than the corresponding ammonium salt in the same environment.. Phosphonium salts are reasonably stable upto temperatures of 150-170°C, whereas ammonium salts loose their activity rather rapidly at temperatures greater than about 110-120°C. For most applications in the laboratory this difference is not important since the boiling point of aqueous solutions used in PTC rarely, exceed 110°C. On an industrial scale however this difference may be significant, since conducting reactions under pressure, which invariably cause an increase in temperature, can increase reaction rates. It should be noted that again phosphonium cations are exceedingly sensitive to hydroxide ion[130,131] and they undergo a reaction of the type,

$$R_4P^+OH^- \longrightarrow R_3PO+RH$$

Since R_3PO is not reconvertable to $R_4P^+X^-$ under these conditions catalytic activity is irreversibly lost. So with strongly basic solution R_4N^+ catalysts are preferred over $R_4P^+X^-$ catalyst.

1.5. Significance of anions with a given alkyl cation

Quaternary salt selected for use as a PT catalyst may depend in their function on the anion originally present. The quaternary salts are useful as PT catalyst only if the anion accompanying the catalyst is distributed in the organic phase to a much lesser extent than the anion to be reacted. In general the large lipophilic Quaternary cation are soft in the HSAB[132] sense so that this cation tends to pair with the softest anion available in the solution and transfer it into the organic phase. For example many Quaternary salts are commercially available or easily prepared in the iodide form and is convenient to be used as PT catalyst. However, iodide ion associates much more strongly with quaternary cation in organic media than many other anions. This problem can be solved by renewing the aqueous phase periodically[15]. Various studies suggest that the nucleophilicity of the halide ion under PT condition are approximately equal[133] or slightly reversed[134] from the usually accepted order. ie F > Cl > Br > I. Thus the more commonly used catalysts have hydrogensulphate or chloride as the anionic moiety. Bromide is also good in many cases.

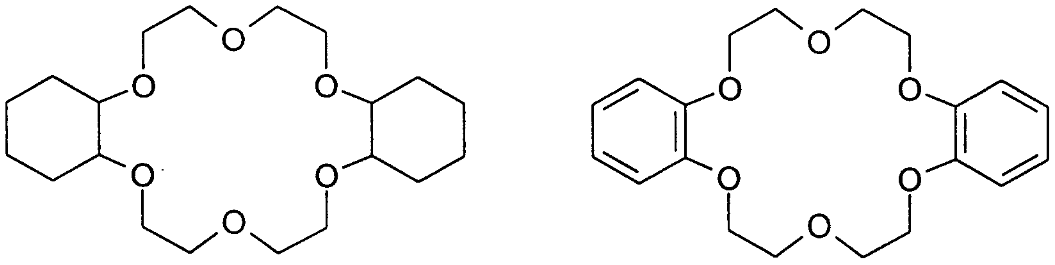
Taking into consideration the above factors the catalysts, which have been most commonly used, include benzyltriethylammonium chloride (BTEAC, 'Makoszas catalyst') trioctylmethylammonium chloride (TOMAC, 'Starks catalyst') and tetrabutylammonium hydrogensulphate (TBAHS, 'Brandstorms catalyst'). BTEAC is quite easy to prepare and can be recrystallised to purity and kept in a reasonably anhydrous state with little difficulty. TOMAC is readily available as an yellow oil from general mills and is quite inexpensive. It is more efficient than either TBAHS or BTEAC according to Herriott-Picker study[24].

Even though TBAHS is bit more expensive it has two important advantages. The hydrogensulphate anion is highly hydrophilic and readily partitioned into the aqueous phase where it plays no further role in the reaction. Moreover the crystalline hydrogensulphate can be treated with a variety of salts and it enables anion exchange reactions.

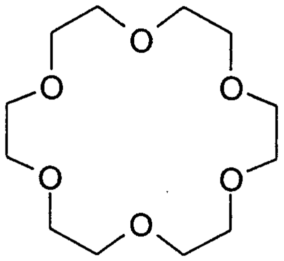
Brandstorm and co-workers have prepared numerous salts by this anion exchange reaction the details of which are given in his book on ion pair extraction[135].

1.6. The use of macrocyclic ethers in PTC

The macrocyclic polyethers were first discovered by Pedersen[105,106] and has shown to form a complex with a variety of cationic substrates like alkali metal cations, alkaline earth metal cations, or ammonium ions and can dissolve homogeneously in an organic solvent. The cavity in the crown ether can accommodate an alkali metal cation through the ion-dipole interaction to form an alkali cation -crown ether complex with a counter anion. In his study the ligand first prepared was dibenzo-18-crown-6 and because of the appearance of its molecular model and its ability on co-ordination to crown a metal ion the members of this series were referred to as crown compounds. The three crown ethers which have been most widely used are dibenzo-18-crown-6, dicyclohexyl-18-crown-6 and 18-crown-6 (Figure 1.1.a).



dicyclohexyl-18-crown-6 **dibenzo-18-crown-6**



18-crown-6

Fig 1.1a

Using the simple lock and key approach it is evident that these crowns have cavity dimensions (2.6 - 3.2 nm) of potassium ion (2.66 nm) and hence these crowns are more specific for potassium ion than sodium or lithium ion whose ionic diameters are 1.94nm and 1.36nm respectively.

The dibenzo crown (II) owes its popularity due to the fact that a straightforward and efficient preparation of this stable and readily handled substance was published early, and a detailed procedure is available in organic synthesis.[136] The difficulties with this compound are two-fold. First it is not one of the better cation complexing crown[137,138] and secondly its solubility in hydrocarbon media is marginal. More popular than (II) is dicyclohexyl-18-crown-6 (I) which is prepared from (II) by hydrogenation.[105] Compound (I) is quite soluble in variety of organic media, and is a strong cation complexer and is a stable white solid. But unfortunately it is a skin irritant[106] and is expensive. The most widely used crown catalysts have been 18-Crown-6. This compound is somewhat less lipophilic than (I), but much more than (II). Again 18-crown-6 can be prepared quite easily by several methods and can be obtained in pure form, and is found to be effective in a wide variety of PT processes.

A general comparison of quaternary salts with crown ether is given on table 1.1.a. The factors listed in the table 1.1.a. will enable the selection of either of these catalysts, according to the conditions and problems faced.

Table 1.1a

Comparison of quaternary salts and crown ethers as phase transfer catalysts

Effect	Quaternary salts used as PTC	Crown ethers
Catalytic activity	Depends upon the structure of the catalyst and is fairly high	Depends on the structure of the crown
Stability	Generally stable to 150°C but <70-80°C when strong alkalies are used	Reasonably stable
Ease of preparation and availability	Varieties of quaternary ammonium salts can be prepared, easily and commercially available	Certain crown ethers are easily prepared
Recovery of catalyst	Lower salts are easily recovered, but higher ones may be difficult	Easily recovered
Cost of catalyst	Relatively low	Relatively high
Addition of water for the dissolution of inorganic reagent	Reaction can be carried out with and without the addition of water	Added water may inhibit the reaction. Usually water is not required.
Inorganic cation	Not usually important.	Specific cation has to be used depending on the cavity size of the macrocyclic ether

1.7. The principle of phase transfer catalysis

Though quaternary salts and crown ethers bring about phase transfer catalysis they involve different mechanistic pathways. The phase transfer catalysis utilizing either a quaternary ammonium or phosphonium salt as catalyst works in the following way.

In the reaction vessel there are two immiscible phases. One of these phases (usually aqueous) contains a reservoir of the salt expected to function either as a base or a nucleophile. The second phase is organic and contains the substrate, which is expected to react with the salt. As the salt containing phase is insoluble in the substrate-containing phase, there will be no reaction observed in the absence of interfacial phenomena.[140] However if a small quantity of quaternary ammonium or phosphonium halide or bisulfate, which contains a lipophilic cation is added, then rapid reaction takes place. The lipophilic cation enjoys solubility in both aqueous and organic phases and when in contact with the aqueous reservoir of the salt, exchanges anions with the excess of anion in the salt solution. The quaternary ion is often given the cognomen "quat", and is frequently represented by the symbol "Q". The anion exchange is represented by the equilibrium shown in equation 1.(a).

$$Q^+X^-_{(aq)} + M^+Nu_{(aq)} \rightleftharpoons Q^+Nu_{(aq)} + M^+X^-_{(aq)} \quad \cdots\cdots\cdots\cdots 1(a)$$

Not only that the anion, which is functioning as the nucleophile be paired with Q^+, it should find its way into the organic solution also. A second equilibrium viz; the phase transfer equilibrium is therefore a requirement for PTC to be successful. This is shown in equation 1(b)

$$Q^+Nu_{(aq)} \rightleftharpoons Q^+Nu_{(org)} \ldots\ldots\ldots\ldots\ldots\ldots 1(b)$$

Once the nucleophile or base (represented by Nu) is in the non-polar (organic) media, then the displacement or deprotonation can take place resulting in the product formation. In the case of a nucleophilic displacement reaction Q^+ would ultimately be ion-paired with the nucleofuge. If the leaving group were X^-, the ion pair Q^+X^- would be generated and subjected to the equilibria formulated as shown above. Starks has offered a classic diagram of the phase transfer catalytic cycle[15] as given in fig. 1.1.b.

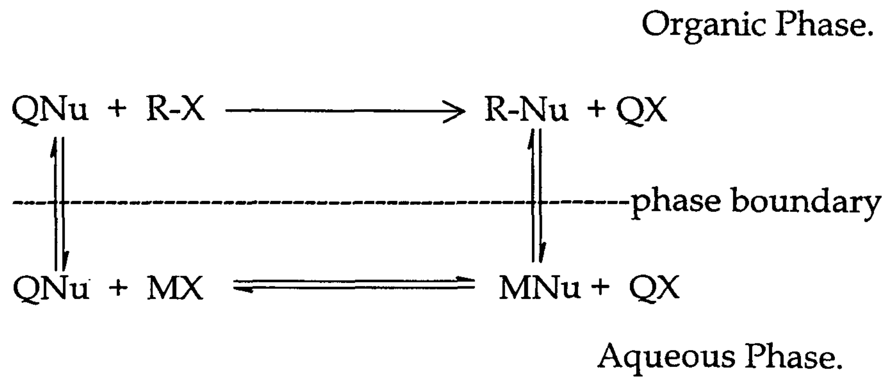
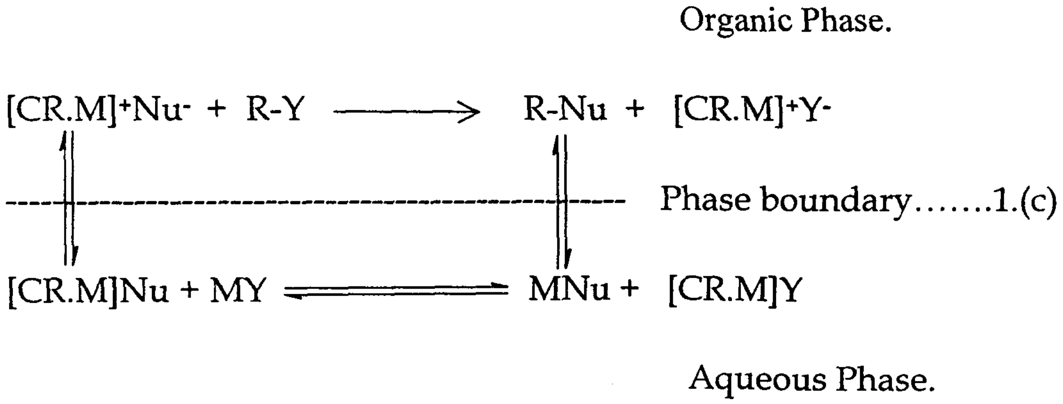


Fig.1.1.b. Starks phase transfer catalytic cycle

It is not necessary that the ion-pair QX generated in the organic phase be identical to the ion-pair originally added as the PT catalyst. It is only necessary that the lipophilic cation Q^+ or some equivalent cation solvator should be present in solution and whatever be the identity of X, it must be exchangeable with the Nu. Probably the most common choice of catalyst has been a quaternary ammonium or phosphonium chloride. The chloride ion readily exchanges with such diverse nucleophiles as hydroxide and cyanide and therefore allows the cycle to be completed.

Crown ethers function in a fashion similar to quaternary salts. They envelope the cation and make it larger, softer and more soluble in the organic phase. The phase transfer cycle using a crown can be represented as in equation 1(c), in which 'CR' represents the crown.



From the above it is clear that the onium cation replaces the cation added to the reaction mixture with the nucleophilic salt whereas the crown simply complexes with the cation. In either case a positively charged hydrophobic species is solvated by a non-polar solvent. This cation Q^+ or $[CR.M]^+$ provides the anion only weak stabilizing interactions and the anion is therefore more nucleophilic than it would be in water or alcohol. These anions are known as 'naked' anions or 'bare' anions.

1.8. Mechanism and rates in phase transfer catalyzed reactions

Recently, the PT catalyst has been widely used to improve the solubility of the inorganic and organic species in immiscible solutions. This has been established as a versatile and important synthetic technique in organic chemistry[129,141,142]. However, the mechanism and kinetics of the two-phase system in the presence of a PT catalyst are seldom reported[143-147].

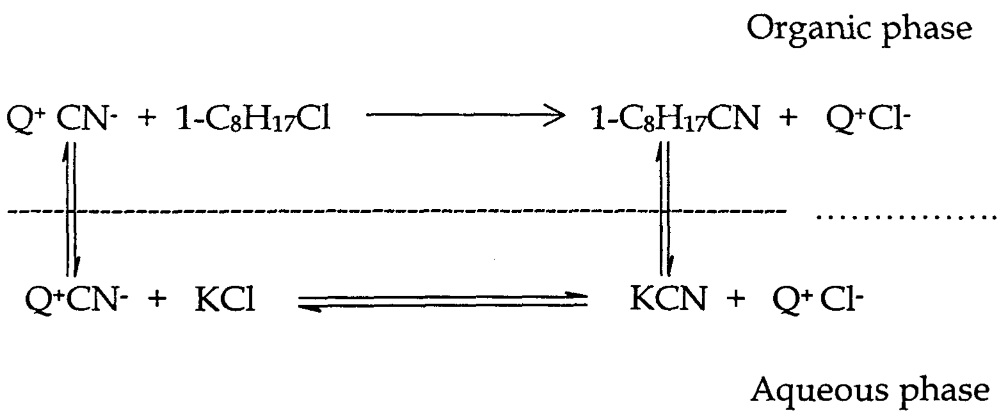
Since PTC involves a sequence of several steps, a detailed understanding of the factors, which influence each step, and a knowledge of the relationship between the various steps are desirable for enabling one for the application of the technique for useful synthetic or mechanistic study purposes. Much experimental work, especially with the displacement reactions has been done in understanding the mechanism and kinetics of PT catalysis and are given elsewhere[16,24,70].

The mechanism of PTC in anion-promoted reactions proposed by Starks[15,16] and supported by others[24,125,148] involve at least two steps:

(1) transfer of one reagent from its 'normal' phase into the second phase and

(2) reaction of the transferred reagent with the non-transferred reagent.

The most common example and the one for which a large number of data available is the cyanide displacement of an alkyl chloride 1(d).



1(d)

From the above equation it is clear that the anion transfer step involves all the three equilibria pictured above and the reaction of the transferred reagent CN^-, with alkyl chloride takes place in the non-aqueous phase. Therefore, an understanding of the system requires an understanding of the factors, which direct and influence each of the four steps. Alternatively it was formulated, the anion transfer step as a liquid ion exchange mechanism, wherein Q^+ resides exclusively in the organic phase and the ions are exchanged across the interface.

$$Q^+Cl^-_{(org)} + CN^-_{(aq)} \rightleftharpoons Q^+CN^-\,(org) + Cl^-_{(aq)} \quad \text{....1(e)}$$

Inorder to know more about this reaction one need to understand the factors which cause one anion to be preferentially taken into the organic phase by Q^+ than the second anion.

1.9. Transfer of anions from aqueous to organic phase

Most anions prefer to reside in an aqueous phase rather than in an organic phase. This is so even in the case of a highly polar one, because of the favorable thermodynamic effect afforded by the anion hydration in aqueous media. This effect results from spreading the electronic charge over the greater volume of the hydrated species, and is therefore dependent on the charge to volume ratio of the anion. This effect is more important when the anion is smaller and has a greater charge on it.

In order to transfer most of the anions into the organic phase, as in PTC, it is necessary to allow them to associate with a cation having much 'organic structure' so that the organic phase solvation of the cation is stronger than the aqueous phase solvation of the anion. To be highly effective in phase transfer for a two-phase displacement reaction, the catalyst cation-anion pair needs to be strongly partitioned into the organic phase. Therefore the factors affecting the partition of cations between the aqueous and organic phases must be taken into consideration.

1.10. Factors affecting the distribution of catalyst cation between aqueous and organic phases

The optimum distribution of catalyst cation in anion transfer catalysis is that the rate of the organic phase reaction must be equal to the rate of catalyst regeneration. For example in the cyanide displacement reaction sequence, Equation 1(f) & 1(g)

$RCl + Q^+CN^- \xrightarrow{K_0} RCN + Q^+ Cl^-$ **...1(f).**

Organic Phase Reaction

$Q^+Cl^- + NaCN \xrightarrow{K_r} Q^+CN^- + NaCl$...**1(g).**

Catalyst Regeneration.

The maximum rate is obtained when

$K_0 (RCl) (Q^+CN^-) = K_r (Q^+ Cl^-) (Na\ CN)$....................**1.(h).**

If we assume that the catalyst regeneration takes place only in the aqueous phase then a definite concentration of the catalyst cation in the aqueous phase would be required. Values of Kr typical for anion exchange reactions in aqueous media are 5-10 orders of magnitude greater than K_0, so that even if the catalyst regeneration occurred only in the aqueous phase only a few hundredths of a percentage of the catalyst be needed in the aqueous phase to satisfy or exceed the criteria represented by equation 1(h). Thus for most PT catalysed reactions involving anion transfer from aqueous to organic phase, we select a catalyst which is soluble in the organic phase.

The choice of a PT agent with only a small degree of organic structure, like $(CH_3)_4N^+$, is not likely to have enough oleophilic interaction with the organic phase to bring much of the desired anion into the organic phase. Such substances will act only in the interface as surfactants. At the other extreme, if we choose a highly organic catalyst cation like $(C_{16}H_{33})_4N^+$, which would be soluble even in the most non-polar media, it would be difficult to purify and handle it. Taking into consideration, the two aspects given above, quaternary salts having a total of 10-30 carbon atoms were found convenient for common use.

It was found that the distribution of catalyst cations between organic and aqueous phases depends not only on the organic structure of the cation, but also it depends on the nature of the associated anion, the polarity of the organic phase, the concentration of the inorganic salt in the aqueous phase and the presence of foreign salts.

1.11.The organic structure of the catalyst cation

The striking effect of even small changes in carbon structure is illustrated by Gibson[149] which shows a distribution ratio α, to

$$\alpha = \frac{\text{Qx in the organic phase}}{\text{Qx in the aqueous phase}}$$

increase by a factor of about 2 for each $-CH_2$ group added in a given homologous series. In general, distribution ratio of this type are correlated by equations of the form

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

where the constant is the value of 'log α' for the first member of a given homologous series with a particular organic phase-water mixture, and at a given temperature[150,151] and 'n' is the number of methylene groups in excess of that in the first member.

However, the number of carbon atoms present in the organic structure is not the only factor affecting catalysis by quaternary cations in PTC, as those salts having one long alkyl group and three methyl or ethyl groups or one pyridyl group at the quaternary centre are found to be poor PT catalysts. This arises from their tendency to form micelles and remain in the aqueous phase. Moreover, if salted out of the aqueous phase they may even form a third phase in a relatively non-polar organic medium. This effect is clearly demonstrated by the distribution ratios for several quaternaryammonium hydroxides between water and benzene[24].

The organic structure of the catalyst cations not only affects its ability to transport an anion from the aqueous to the organic phase, but also it strongly affects the rate of the organic phase reaction.

1.12. The anion associated with the catalyst cation

The kind of anion associated with the catalyst cation has enormous influence on the extend to which a given cation-anion pair is extracted from the aqueous to the organic phase[152-154], for example a catalyst cation which easily transfers iodide anions from the aqueous to the organic phase might be totally inadequate for the transfer of chloride ions.

Two principal characteristics of the anion, influence its tendency to increase or decrease the ability of a cation for transfer. First the anions are hydrated to different extends, depending mostly on the charge to volume ratio of the anion. The more the anion is hydrated the more strongly it will be attracted to the aqueous phase and the more difficult it will be to transfer. For most cases this water of hydration is found to accompany the anion when it is transferred into the organic phase[16,155]. Secondly, the organic structure of the anion will add to the total organic structure of the cation-anion pair, to increase partitioning of the pair into the organic phase.

A practical conclusion from the above facts is that, for medium-sized cations hydrogen sulfates are not only very good starting materials for the preparation of many onium salts but also are very useful PT catalysts. The addition of one molar equivalent sodium hydroxide will transform the hydrogen sulfate anion into neutral sulfate, which cannot interfere, because it is less easily extractable than almost any other inorganic or organic anion. Chloride is the second choice of anion, but iodides and to a lesser extent bromides should not be used as PT catalyst.

1.13. Polarity of the organic phase

Although one of the most useful aspects of PTC is the ability given by the catalyst to conduct many reactions without the use of an organic solvent, it is often advantageous to use an organic solvent to facilitate partition of the catalyst into the organic phase. It is known that the solubility and partitioning behaviour of quaternary salts are markedly affected by even slight changes in the organic phase.

A solvent useful for PTC work should be immiscible with water, otherwise highly hydrated and hence "shielded" ion-pairs of low reactivity will be present. In order to avoid hydrogen bonding to the ion-pair anion, the solvent should also be aprotic. The most commonly used solvents for PTC processes include the aromatic solvents (benzene, toluene, o-dichlorobenzene) and chlorocarbons (dichloroethane, 1,2-dichloroethane, chloroform) though the chlorocarbons are somewhat better solvents than the hydrocarbons. Not only do the chlorocarbons exhibit a high extraction capability for our standard salt, but they are also cheap and easily removable. One drawback of such solvents is that they give rise to side reactions but most of the PTC reactions are so fast that this is not a big danger. Brandstrom[156] has determined a large number of apparent extraction constants between water and various solvents for a standard quaternary ammonium salt viz., tetra-n-butylammonium bromide. This report serves as a helpful guide to verify the above facts.

1.14. Concentration of inorganic salt in the aqueous phase

Increasing the concentration of inorganic salt in the aqueous phase tends to salt out organic salts, pushing them into the organic phase. Increasing the inorganic salt concentration also ties up additional water of hydration, reducing the amount of water available for anion hydration, providing easier transfer of the anion into the organic phase. This effect illustrated by Herriott and Picker[24] for cetylpyridinium cation catalyzed reaction of sodium thiophenoxide with 1-bromooctane. Usually the best PTC conditions are realized when the aqueous phase is saturated with the inorganic reagent.

1.15. Salting-out effects

Extraction constants are not only influenced by solvent systems but also by many foreign salts. Brandstrom[156] examined the conditional extraction constants of NBu_4Cl and NBu_4Br between water and methylene chloride in the presence of potassium carbonate, and found a linear parallel dependence on the molality of K_2CO_3. Two moles of K_2CO_3 per litre increased the extraction constants about a thousand fold. This salting out effect is of great importance for PTC, especially with concentrated (50%) aqueous sodiumhydroxide. In this medium almost all quaternary ammonium salts are sparingly soluble and easily extracted.

1.16. Ionic reactions in the non-polar media

It is known that a phase transfer agent bring one reactant from its 'normal' phase into the phase of the second reactant, and makes the reagent available in a highly reactive form. Much evidence in the literature indicate, for example that even if sodium or potassium salts of many anions could be dissolved in most common organic solvents, reaction is extremely slow. On the other hand, anions associated with many quaternary cations and crown ether complexes of sodium or potassium ion exhibits remarkably high reactivity in relatively non-polar media, and it is this high reactivity, which allows these agents to be effective PT catalysts. Therefore it is necessary to examine the characteristics of these catalysts when they are in organic media and the factors which contribute to their higher activity.

Ugelstand and co-workers[71] have measured rates for the reaction of potassium and tetrabutyl ammonium phenoxide with 1-chlorobutane and 1-bromobutane in various solvents and mixtures. They concluded that the high reactivity of the quaternary salt resulted from its having a greater distance separating the anion and cation and therefore reduced cation-anion interaction energy as compared to the potassium salt.

Litvak and Shein[157] have shown that crown ether complexes of potassium phenoxide, like tetrabutylammonium phenoxide, also undergo rapid displacement reactions even in highly non-polar organic solvents.

1.17. Evidence for the mechanism of phase transfer catalysis

A difficult problem in kinetics of PT catalysed reactions is to sort out the rate effects due to

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

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

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

Most of the work published to date has dealt with the kinetics of anion transfer displacement reactions in which anion exchange and transfer is rapid, the step being the displacement reaction in the organic phase. Several groups have carried out detailed work and their conclusions are in substantial agreement.

Starks[15] examined the reaction of cyanide ion with n-octylbromide and found that

$$Q^+CN^- + C_8H_{17}Br \longrightarrow C_8H_{17}CN + Q^+Br^-$$

1. The reaction occurred in the organic phase and is the rate determining step.

2. The displacement was first order in alkyl halide and first order in catalyst (QX).

3. The rate of the reaction was shown to be directly proportional to the catalyst concentration and

4. Reaction rate was independent of stirring rate. Regarding the latter point, it was found that, at low stirring speed mass transfer was retarded. Beyond a minimal stirring rate, which ensured effective intermixing of the phases, there was no further variation in the reaction rate.

Herriott and Picker[22,24] examined the same question in a somewhat different way. They studied the two-phase reaction of secondary-octyl bromide with hydroxide ion. Based on Ingold's prediction, if the reaction occurred in the organic phase, elimination products would predominate, whereas reaction in the aqueous phase would favour substitution. It was inferred that the reaction occurred in the organic phase due to the predominance of elimination products. Beyond a minimum value stirring rate was found not to affect the reaction rate, a fact that allows one to exclude interfacial phenomena as an important factor.

Using liquid membrane, Landini *et al.* has found that in PTC the transport of anions from one phase into the other doesn't require the transfer of the organic cation[158]. The kinetic measurements indicate that the effectiveness of a PT catalyst depends mainly on its organophilicity.

1.18. Phase transfer assisted permanganate oxidation

The use of Potassium permanganate which is a very powerful oxidizing agent performs a dual function- as a selective oxidant and a scavenger to remove small amounts of organic materials present as contaminants in water or air.

The reactivity of permanganate as an oxidant is reflected in its ability to use different reaction paths, depending on the structure of the organic substrate and depending on the acidity and basicity of the solution[159,160]. Low enthalpies of activation, frequently in the range of 5 to 10 KCal/mole are further indications of the desire of permanganate to lower its chemical potential. The use of permanganate as a selective oxidant for a variety of reactions have been reviewed by Stewart[161], Arndt[162], Freeman[163], Waters[164] and

Lee[165]. But its full utility has sometimes eluded organic chemists because of its solubility problem.

The use of aqueous permanganate in synthesis is limited to the oxidation of organic compounds that are at least partially soluble in water. If the solubility is too low, there is not sufficient contact between the oxidant and reductant at the interface and the rate of the reaction is drastically reduced[166]. The classical way of overcoming the solubility problem has been by the use of polar organic solvents systems that will dissolve both reactants. Examples of solvents that have been used include ethanol, tert-butyl alcohol, pyridine, acetic acid, acetic anhydride and trifluoroacetic acid. Obviously, the use of organic solvent systems is limited to the oxidation of those compounds that react much more readily with permanganate than does the solvent itself.

Results obtained by PT catalysed permanganate oxidation are superior to those obtained using solvents to mediate the reaction. PT catalyzed permanganate oxidations are useful not only for preparative reactions but also for analytical purposes in titration of reducible substances. For permanganate oxidations in non-aqueous solvents, quaternary salts, crown ethers and polyethers (ethylene glycol) have been used as catalyst. Taking into account of the high cost of crown ethers, it has been reported to be more reasonable and advantageous to use quaternary ammonium salts as PT catalysts for $KMnO_4$ oxidation in liquid-liquid system as well as liquid-solid systems.

Gibson and Hosking were the first to report on phase transfer catalytic oxidation[126]. They found that it was possible to oxidize water-insoluble substrates in aprotic media by ion-pairing the anion with a lipophilic cation. Permanganate anion was extracted from an aqueous reservoir of $KMnO_4$ by exchange of chloride ion of methyltriphenylarsonium chloride. The methyltriphenylarsonium permanganate thus prepared in chloroform was found to oxidise olefins, alcohols, nitroalkanes, nitriles and 1,3,5-trimethylbenzene. But it did not oxidise t-butanol, benzene, toluene, ethyl acetate, diethyl ether, acetone or dipropylketone.

Another more recent approach involves the use of salts such as tetrabutylammonium permanganate[167], or benzyltriethylammonium permanganate[168], which because of the organophilicity of the quaternaryammonium cations are soluble in non-polar solvents. These salts may be prepared by adding a solution of the corresponding quaternaryammonium halide to a solution of potassium permanganate.

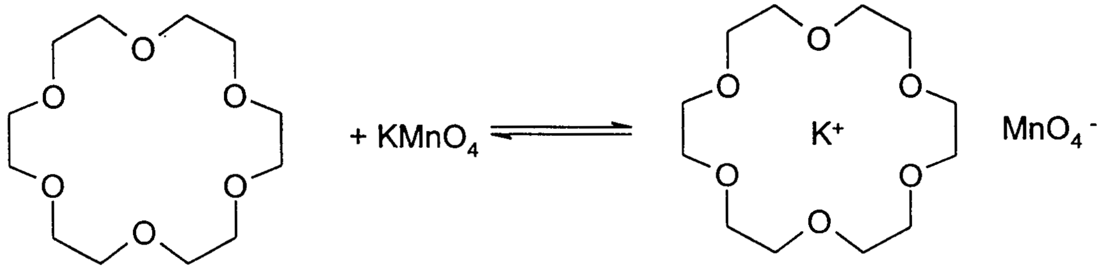
However, caution should be excercised because above a certain temperature most quaternaryammonium permanganate spontaneously ignite[169-171].

It is unnecessary, however to prepare and isolate the quaternary ammonium permanganates. They can be prepared in situ by reacting a quaternaryammonium halide (Q^+X^-) with potassium permanganate. Anion exchange (equation 1.i.) then produces a quaternary ammonium ion-pair that is soluble in non-polar solvents.

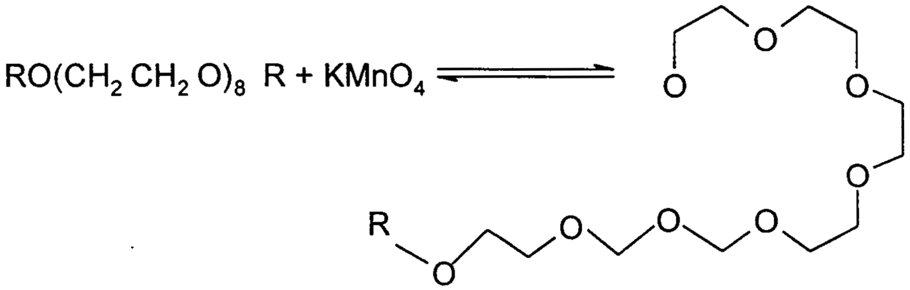
$$Q^+X^- + KMnO_4 \longrightarrow Q^+MnO_4^- + K^+X^- \text{......1.(i).}$$

This exchange usually takes place with a change of phase of permanganate ion. Typically the quaternaryammonium halide dissolved in an organic solvent such as methylene chloride is added either to solid $KMnO_4$ or an aqueous solution of potassium permanganate. During the exchange permanganate ion migrates to the organic phase and exists there as ion-pair. Quaternary phosphonium and arsonium salts can also be used as phase transfer catalysts.

Potassium permanganate can also be readily solubilized in non-polar media by using either cyclic or acyclic polyethers. The polyether complex envelops the potassium ion causing it to become organoplhilic and thereby producing an ion-pair that is soluble in organic solvents Equations(1.j&1.k).



.... 1(j)



.... 1(k)

Sam and Simmons[45] have found that dicyclohexyl-18-crown-6 could solubilize solid potassium permanganate in benzene to the extend of about 0.06 molar. The resulting "purple benzene" solution was used to oxidize a number of organic substrates in good to excellent yield.

Polyethylene glycol (PEG) [174] and bis-ethers[175,176] have been applied as PT catalysts in the oxidation using $KMnO_4$ though the complex formation and consequent solubilization by them is generally less efficient than by crown ethers. Polyethylene glycol is also able to form purple benzene by solubilizing solid $KMnO_4$ into benzene[177]. The electronic spectrum of PEG-purple benzene is identical with that reported by Sam and hence inferred that the features of the reaction in both cases are similar.

In general $Q^+MnO_4^-$ behaves like permanganate in neutral solution, being reduced in the presence of a suitable reductant to insoluble manganese dioxide.

1.19. Phase transfer from aqueous permanganate

The effectiveness of any particular PT system will be dependent on the ability of that system to bring the permanganate ion into the organic phase.

It is well known that $KMnO_4$ exists in an ionic form when dissolved in water. However, when quaternaryammonium permanganate dissolves in an organic solvent it exists predominantly as an ion-pair. This can be seen from the calculations described by

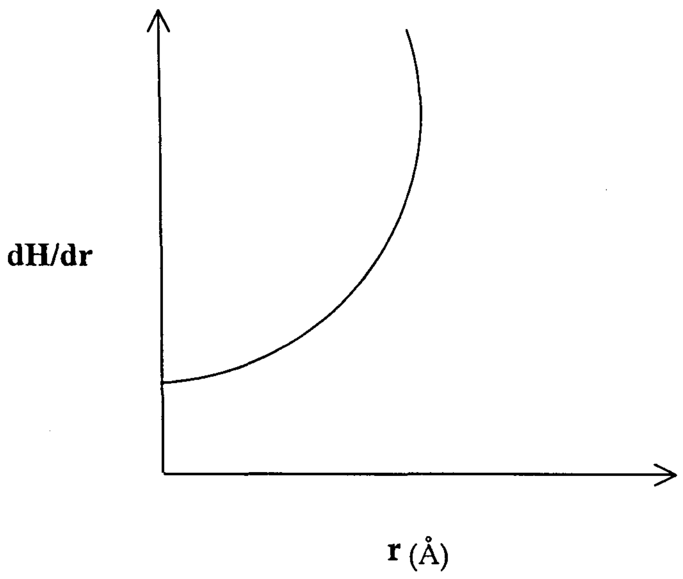
Brandstrom[156]. He has shown that for two spherical ions Q^+ and X^- situated in a large sphere of solvent with dielectric constant D the probability (P) of finding Q^+ and X^- separated by a distance between r and r+dr is given by the equation 1(.*l*) where R is the radius of the solvent sphere, k is the Boltzmann constant and T is the temperature[178].

$$dp = (3/4\pi R^3)4\pi r^2 \exp(-e^2/DkTr)dr \qquad ....1.(l)$$

Assuming that the sphere is large enough to give ideal behaviour even when the concentration of ions is increased, the total probability (dH) of finding the center of an ion X^- at a distance between r and r+dr from the centre of an ion Q^+ when more ions are present is given by the equation 1.(m)

$$dH = [Q^+][X^-](4\pi N/1000)^2(R^3/3)r^2 \exp(-e^2/DkTr)dr.....1.(m)$$

A plot of dH/dr against r passes through a minimum of $r = e^2/2DkT$ (Figure.1.1.c).



Plot of **dH/dr** against **r** (Figure 1.1.c)

The significance of the above figure can be understood in the following way: If the ions can approach each other sufficiently close so that the distance between their centers is less than $e^2/2DkT$, the attractive forces will be strong enough to cause ion-pair formation. If the ions cannot approach each other sufficiently close, the attractive forces will be smaller and the solvation (resulting in the formation of individual ions) will occur. 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 values of $e^2/2DkT$ for some solvents have been given below[156].

Solvent parameters

Solvent	Dielectric constant	$e^2/2DkT$ Å
Water	78.5	3.57
Methanol	32.5	6.8
Ethanol	24.3	11.5
Acetone	20.5	13.7
1,2-Dichloroethane	10.17	27.6
Methylene chloride	8.9	31.5
Chloroform	4.7	60
Diethyl ether	4.2	67
Benzene	2.27	123
Carbon tetrachloride	2.22	126

From this table one can determine if particular quaternary ammonium permanganate will exist in a particular solvent as ion-pair or as free ions. It can be seen that the value of 'r' for the ammonium permanganates will be substantially less than $e^2/2DkT$ in solvents with low dielectric constants, accepting the value of about 2.5 Å for the ionic radius of permanganate ion[179] and the value of about 3Å and 6Å for tetramethyl and tetraoctylammonium ions respectively[180].

Consequently it can be assumed that when permanganate ion is transferred into an organic solvent with the aid of a PT agent it exists for all practical purposes as an ion-pair.

Okimoto and Swern[181], Herriot and Picker[173] and Cram and coworkers[182] have studied the effectiveness of various PT agents with $KMnO_4$. The results arrived from all these studies indicate that the concentration of permanganate ion-pair that can be obtained in the non-aqueous phase will depend on three factors - **Structure of an organic cation, polarity of the organic phase and the nature of the anion involved.**

1.20. PTC catalysed hydrolysis of ester

Carboxylic acid esters are an important class of organic compounds and the kinetic investigations on the formation and hydrolysis of these have been subjects of great interest. Accordingly a large amount of research work carried out in this area has produced a very substantial literature. These studies aimed at unravelling the different aspects of the subject have been of great use both in theoretical and applied aspects. Ester hydrolysis reactions are subjected to acid as well as base catalysis. These reactions are also catalysed by enzymes. Besides different environmental factors such as the nature of the solvent, presence of ionic species and micelles, macromolecules, temperature, pressure, presence of finely divided solid materials such as silica alumina, etc. have profound influence on the rates and mechanisms of these reactions. In the present investigation studies have been made on the kinetics and mechanism of saponification of Benzyl Benzoate in different solvents with and without the use of phase transfer catalysts, under different conditions. The literature regarding the phase transfer assisted hydrolysis are scanty due to several reasons, which is included in the review of phase transfer assisted hydrolysis.

CHAPTER II

REVIEW OF THE PRESENT WORK

2.1. Oxidation of alcohols

A lot of literature is available on the oxidation of primary alcohols using different reagents like bromine, permanganate hypochlorite, dichromate, ruthenium tetrachloride, osmium tetroxide etc. in aqueous medium in the presence and absence of mineral acids[222]. The oxidation of alcohols involve hydride ion transfer from α-carbon of the carbinol to the oxidant. The primary alcohols are oxidised to aldehydes and the secondary ones to ketones. The hydride ion transfer has been established chiefly from the kinetic isotope effect during mechanistic studies[228].

Kinetic studies form the major part in the mechanistic investigations. A study shows that benzyl alcohol is oxidized by bromine at a rate four times faster than that of α-dideuterio benzyl alcohol at 25°C clearly confirms the hydride ion transfer mode in the mechanism[229].

Banerji *et al.*[230] studied the kinetics of the oxidation of benzyl alcohol to benzaldehyde by acid permanganate in the presence of fluoride ion. The rate constant 'ρ' for the oxidation of benzyl alcohol and nine substituted benzyl alcohol have values of -1.76 at 30°C. The activation enthalpies and entropies for the ten compounds are linearly related. The oxidation of α,α-dideuterio benzyl alcohol indicated a kinetic isotope effect K_H / K_D = 2.70 at 30°C. Moreover, the reaction did not show any solvent isotope effect. A mechanism involving the transfer of a hydride ion from the alcohol carbon to the oxidant has been established.

Sreenivas.N.S. *et al.*,[231] made kinetic studies on the oxidation of alcohols by N-chlorosuccinimide. They found that the rate is independent on the salt concentration, or the structure of alcohols. Fractional order dependence on the concentration of added H^+ and Cl^- were found. This has been interpreted by assuming that the reaction proceeds through the interaction of chlorine, generated in a steady state, in the slow rate-determining step. A rate expression for the observed kinetics has been suggested accordingly.

Labelled studies on the kinetics of the oxidation of primary aliphatic alcohols by acid permanganate has been found to proceed with a C–H bond rupture from the carbinol carbon as the rate-determining step as evidenced from the substantial kinetic isotope effect[232].

Kinetics and mechanism of the oxidation of primary alcohols by chloramines-T in acid medium has been studied[233] . The reaction is first order each with respect to the alcohol and the oxidant. The rate is reported to be proportional to the square of the acidity. The kinetic isotope effect $K_H/K_D = 4.31$ at 30°C. The enthalpies and entropies of activation are linearly related. A mechanism involving the transfer of a hydride ion from the alcohol carbon to the oxidant is suggested. Stevan R.V, *et al.*,[234] have reported the oxidation of secondary alcohols to ketones with sodium hypochlorite in acetic acid in the absence of catalyst. Primary alcohols showed sluggish reactivity with sodium hypochlorite and formed dimeric esters via hemiacetal intermediates.

The kinetics and mechanism of the oxidation of ten ortho substituted benzyl alcohols by acid permanganate have been studied by Mathur *et al*[235]. The reaction is first order each with respect to the concentration of alcohol, the oxidant and H^+ ions respectively. Chartons extended Hammet equation involving inductive, resonance and steric parameters gave excellent correlations with the specific rates. The polar reaction is subjected to steric acceleration by the ortho substituents.

Kinetics of the oxidation of the substituted benzyl alcohols by quinolinium dichromate in dimethylformamide in the presence of added acid were reported[236]. The reaction showed first order dependence on each of the alcohol, the quinolinium dichromate and the acid concentration. Electron releasing substituents accelerate the reaction whereas electron withdrawing groups retard the reaction rate which is in accordance with hydride ion transfer and the rate data obeyed Hammet relationship. The kinetic isotope effect $K_H/K_D = 5.89$ at 313 K was also obtained. A mechanism involving the transfer of a hyride ion from the alcohol carbon to the oxidant is suggested. The above study has special relevance to the studies on oxidation under PTC.

The kinetics and mechanism of the oxidation of primary aliphatic alcohols by bis(2,2-bipyridyl)copper(II) permanganate was reported[237]. The oxidation leads to the formation of the corresponding aldehydes. The reaction is first order with respect to bis(2,2-bipyridyl) copper(II) permanganate. Michaelis-Menton type kinetic was found to be followed. The formation constant for the alcohol - bis(2,2-bipyridyl) copper(II) permanganate complex and the rates of decomposition have been evaluated. The reaction rate increases with increase in concentration of hydrogen ion. With an amount of acetic acid in the solvent mixture of acetic acid and water, the rate increases. Kinetic studies on the oxidation of 1,1-dideuterio ethanol also exhibited a substantial kinetic isotope effect.

The oxidation of benzyl alcohol, its para methoxy, para chloro and para nitro derivatives by permanganate have been studied in aqueous acetic acid medium in the presence of perchloric acid[238]. The reaction is first order in $[MnO_4^-]$ and $[x\text{-}C_6H_4CH_2OH]$, but the order was complex with respect to $[H^+]$. The reaction involves the protonation of the alcohol in a fast pre-equilibrium step followed by a rate-determining oxidation step. A two electron transfer oxidation has been suggested for benzyl alcohol and its para chloro and nitro substituted alcohols while the oxidation of methoxy compounds involves a one electron transfer via free radical mechanism.

Anjali *et al.*[239] have reported the oxidation of secondary alcohols by bis(2,2-bipyridyl)copper(II) permanganate in aqueous acetic acid medium leading to the formation of the corresponding ketones. The reaction is first order with respect to bis(2,2-bipyridyl)copper(II) permanganate and alcohol. The reaction rate increases with increase in the concentration of H+ ions. A suitable mechanism has been suggested. The oxidation of substituted benzyl alcohol by bis(2,2-bipyridyl)copper (II) permanganate[240] to the corresponding aldehydes has been reported. Michaelis-Menton type kinetics was found to be followed with respect to alcohol. The rates of oxidation of meta and para substituted benzyl alcohols were correlated in terms of chartons triparametric LDR equation where as ortho substituted benzyl alcohols were correlated with a four parametric LDR equation. The results of the correlation analysis point to an electron deficient reaction center in the transition state.

The oxidation of the benzyl alcohol and some of its ortho, meta and para substituted derivatives by benzyltrimethylammonium chlorobromate in aqueous acetic acid medium was reported[241]. The corresponding benzaldehydes were formed as the product in the reaction. The reaction conformed to first order kinetics with respect to benzyltrimethylammonium chlorobromate and the alcohol concentrations. The reaction rate increased with increase in the polarity of the medium.

The oxidation of primary aliphatic alcohols by tetrabutyl ammonium tribromide in acetic acid medium were reported[242]. The oxidation reaction leads to the formation of the corresponding aldehydes and the reaction is susceptible to both polar and steric effect. Michaelis-Menton type kinetics was found to be followed with respect to alcohols. A Hydride ion transfer mechanism is involved.

2.2. Phase transfer catalysis in the oxidation reactions

Phase transfer catalysis has been found to be a very effective synthetic method in many organic reactions especially when the organic substrates are water insoluble. The technique is employed usually for solid-liquid, liquid-liquid or gas-liquid heterogeneous systems. Many inorganic reactants including oxidants that are insoluble in organic media can be transferred into the organic phase using PTC[129,141,142]. Oxidizing agents like hypochlorite, chromate, dichromate, peroxide, permanganate, etc. have been reported to be used for the oxidation of organic substrates employing PT catalysts such as the quaternary onium salts, the crown ethers, etc. The synthetic processes involving these reactants are usually made to take place in a heterogeneous aqueous-organic liquid system.

2.3. Oxidation with hypochlorite

Hypochlorite ion is an effective oxidizing agent for a variety of organic substrates when the reaction are to be conducted under PT conditions. Lee and Freedman have demonstrated that hypochlorite ion can be transferred into an organic phase using quaternary ammonium salts for the oxidation of alcohols and amines and no reaction occurs in the absence of the catalyst.

Oxidation of benzyl alcohol was conducted using triethylbenzyl ammonium chloride as PT catalyst in a two phase system[183]. The results obtained provide evidence for the initial chlorination at the benzyl carbon. Since no reaction takes place in the absence of a PT Catalyst it clearly shows the involvement of an ionic species in the organic phase.

A systematic study on both the extraction of hypochlorite ion from the aqueous phase to the organic phase and the kinetics of the oxidation of benzyl alcohol by hypochlorite ion in the presence of tetrabutylammonium chloride as PT catalyst was studied[184]. The results show that the oxidation of benzyl alcohol by hypochlorite ion in two immiscible aqueous dichloromethane systems was reaction controlled and occurred in the organic phase when the stirring rate was larger than 500rpm. The experimental results also revealed that the reaction order of both tetrabutylammonium ion pair and benzyl alcohol in the organic phase are both equal to one.

Oxidation of benzyl alcohol using hypochlorite ion via PT catalysis was investigated in a heterogeneous liquid-liquid system[185]. Cetyltrimethylammonium bromide and toluene were chosen as the best catalyst and solvent respectively. The observed reaction rates were proportional to the organic phase interfacial concentration of cetyltrimethylammonium hypochlorite which is formed by the ion exchange between bromide and hypochlorite ions.

The kinetics of the anodic oxidation of benzyl alcohol in a two phase system involving both the redox mediator, OCl^- / Cl^- and a PT catalyst were investigated[186]. The reaction order of anodic oxidation of chloride ion in aqueous phase was unity. The charge transfer parameters α, K_2 and exchange current density i_o of the chloride ion oxidized on graphite are obtained in the temperature range from 5 to 45°C. The model calculation of the anodic oxidation of benzyl alcohol by the theoretical analysis correlates well with the experimental results.

The synergetic action of the electron transfer catalyst, meso-tetra phenylporphyrin Mn(III) chloride complex with a common PT catalyst, trioctylmethylammonium chloride to promote the oxidation of alcohols has been reported[187,188].

Do and Do have carried out indirect anodic oxidation of benzyl alcohol[189,190] in the presence of a PT catalyst in a continuous stirred tank electrolysis reactor (CSTER). Effect of current density, organic to aqueous volume ratio, concentration of PT catalyst, flow rate and temperature on current efficiency of producing benzaldehyde were systematically studied in this work. In the conversion of benzyl alcohol the yield of benzaldehyde increased and selectivity of benzaldehyde decrease at a high organic flow rate, when both the current density and concentration of PT catalyst were increased.

Rapid spectroscopic assessment of reaction rates in PTC has been carried out by Trifanov and Kuzmanova[191]. The reactions examined include hypochlorite oxidation of benzyl alcohol and plot of E (Optical Density) Vs. $t^{1/2}$ (time) was found to be linear. The PT catalyst used were aliquat 336, $Bu_4N^+HSO_4^-$ and Bu_4PBr.

Amsterdamsky[192] has proposed a procedure for the oxidation of benzhydrol to benzophenone using bleach as the oxidant, ethyl acetate as the organic phase and tetrabutylammonium hydrogen sulphate as PT catalyst. The oxidation is essentially completed in 30 min and the yields range from 70% to 85% after recrystallisation.

Alkyl and aryl substituted hydroquinones are rapidly oxidized to p-benzoquinones by stirring the solution in an organic solvent with sodium hypochlorite in the presence of catalytic amounts of tetrabutyl ammonium hydrogensulphate[193]. In the oxidation of monosubstituted hydroquinines, dichloromethane and chloroform are more suitable solvents than ethyl acetate or benzene. In the case of di, tri and tetra substituted hydro quinines comparable results were obtained in dichloro methane, chloroform, ethyl acetate or benzene.

Using a PT catalyst the kinetics of the oxidation of benzaldehyde with hypochlorite was carried out in a batch reactor[194]. The reaction orders were unity with respect to benzaldehyde as well as tetra butyl ammonium hypochlorite in the organic phase.

Aromatic aldehydes were oxidized to carboxylic acids in high yields and the selectivity using aqueous sodium hypochlorite as oxidant in a PT system[195]. The reaction was strongly influenced by the pH of the aqueous phase with maximum reaction rates at pH 9 - 11. The extraction of hypochlorite was also maximum in this pH range. The maxima are attributed to the co-extraction of hypochlorus acids together with the hypochlorite anion into the organic phase, the former significantly increasing the reaction rates.

2.4. Oxidation with chromate

Hutchins *et al*[196]. showed that a facile solubilisation of potassium dichromate was effected in several organic solvents using a 2:1 ratio of Andogen- 464 to dichromate. The resulting orange solution was fairly stable at ambient temperature but slowly darkened after several days. These solutions were used for the neutral oxidation of the activated alcohols.

Pletcher[197] and Tait have studied the oxidation of alcohols with stoichiometric quantity of dichromate in 3 M aqueous sulphuric acid using tetrabutylammonium bisulphate as the PT catalyst. They suggested that the reaction proceeded via disproportionation of chromate ester in which the proton catalysed deproportionation of Cr(V) or Cr(IV) to Cr(VI) are important.

The kinetics of the oxidation of benzyl alcohol in two phase system by chromic acid and in aqueous solutions were determined[198]. The use of a two phase system allowed obtaining clean kinetic results by preventing further oxidation of benzaldehyde to carboxylic acid. The results confirm the order 1 with respect to both the reactants and an order, approximately 2 with respect to the acid concentration. The reaction rates are found to be of the same magnitude when the reaction are localized in aqueous phase or in the organic phase in the presence of a PT reagent although the reactivity seems to be much higher in organic phase.

Gelbard *et al*[199] have demonstrated the use of onium salts as PT catalyst to get complex chromate salts which is soluble in aprotic organic solvents such as dichloromethane. This complex chromate was used for the oxidation of several alcohols.

Considering the low cost and availability of tricaprylmethyl ammonium chloride[200], it was used with chromium trioxide as oxidant in dichloromethane medium for the conversion of alcohols to the corresponding carbonyl compounds in excellent yields under mild conditions.

The kinetics of the oxidation of substituted benzyl alcohols by quinolinium dichromate in the presence of an acid was studied by Dey and Mahanti[201]. They found that further oxidation of benzaldehyde did not occur under their experimental conditions.

A systematic kinetic analysis of the mechanism of the oxidation of benzyl chloride by dichromate in liquid-liquid phase transfer catalysis has been carried out to throw light on the course of reaction[202]. The rate of the reaction depends on the pH of the aqueous phase and presence of mineral acids in the aqueous phase are needed to generate the oxidising species in organic phase. It was observed that $QHCrO_4$ was the active species for oxidation. The reaction proceeds via the formation of benzyl alcohol which is oxidized to benzaldehyde. Kinetic studies on oxidation of organic substrates with dichromate are quite scanty.

2.5. Oxidation with hydrogen peroxide

Quaternary ammonium salts assists the extraction of both hydrogen peroxide and metal salts like ruthenium or palladium chloride from the aqueous to the non aqueous component of a two phase system. This system has been used for the oxidation of styrene[203] with hydrogen peroxide in water - Dichloromethane containing both ruthenium chloride and a PT catalyst gave mainly benzaldehyde. Similar oxidation of styrene in the presence of palladium chloride gave acetophenone.

A phase transfer procedure for the oxidation of terminal alkynes were described[204]. The catalytic system involve dilute hydrogen peroxide and Na_2MO_4 [M= Mo, W and $Hg(OAc)_2$]. In the absence of mercuric derivative no oxidation of the substrate takes place. By changing the pH of the aqueous phase and the nature of the PT agent either cationic or neutral as well as metal (Mo, W) carboxylic acid or α-keto aldehydes may be selectively obtained in good yields. Selectivity in reactions is typical of reactions carried out under PTC.

The selective oxidation of the primary aliphatic alcohols to carboxylic acids (60-70% selectivity), secondary alcohols to ketones (100% selectivity) and primary benzylic alcohols (95-100% selectivity) to carboxylic acids as well as selective oxidation of allylic alcohols to ketones (80% selectivity) were performed in a H_2O_2-$RuCl_3.3H_2O$ PT catalyst system at a high Substrate : $RuCl_3$ (625:1) ratio[205]. It was found that the PT catalyst also protects the metallic catalyst against reduction. In the presence of quaternary ammonium PT agent the selective oxidation of dehydrogenation of alcohols are catalysed by copper salts and hydroxyacids by tert-butyl hydroperoxide in an aqueous-organic two phase system[206].

2.6. Oxidation with potassium permanganate

Potassium permanganate is a powerful oxidant in aqueous medium. It is even more powerful when phase transferred to organic media. Starks[207] have reported that terminal olefins can be oxidized by potassium permanganate using PT catalyst to the one carbon shorter carboxylic acid. Sam and Simmons[208] found that dicyclohexyl-18-crown-6 ether complex of potassium permanganate is effective in quantitatively oxidizing internal olefins to diacids. Weber and Shepherd[209] had reported the controlled oxidation of olefins to the corresponding cis-glycols in moderate yields by potassium permanganate in dichloroethane using benzyltriethylammonium chloride as catalyst.

Herriot and Picker[210] had carried out the oxidation of several organic substrates(phenylacetonitrile, benzyl alcohol, trans-stilbene, 1-octanol, 2-octene) by potassium permanganate under PTC condition using tricarprylmethyl ammonium chloride with very good yields. In the presence of 15-crown-5, 18-crown-6, tetrabutylammonium bromide and triaurylmethylammonium bromide as PT catalyst ,the instability of the solutions of potassium permanganate solubilised in benzene, toluene and chloroform has been reported[211].

Styrene and acrolein diethyl acetal were oxidized with potassium permanganate under PT conditions[212] using chiral ammonium salts like benzyl-1-methyl-dimethylammonium bromide, 1-methyl-trimethylammonium iodide and benzyldimethyl[(+)-1-phenylethyl]ammonium bromide as well as benzyltriethyl ammonium chloride with pure water and methylene chloride as non polar organic solvent.

The oxidation rates of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone with potassium permanganate in both the liquid-liquid and solid-liquid systems were found to increase by the addition of crown ether which functions as a PT catalyst[213]. The rate of liquid-liquid phase oxidation was larger in a non polar organic solvent whereas a polar organic solvent was more effective for the solid-liquid phase oxidation. The crown ether with a cavity that is the best suited for potassium ion was found to function as the most effective PT catalyst regardless of the reaction system used. The addition of an inorganic or an organic acid was found to increase the rate of liquid-liquid phase oxidation using crown ether as PT catalyst .

Kinetics of the cyclohexene oxidation with potassium permanganate in mono or biphasic systems using the initial rate method have been investigated spectrophotometrically[214]. Kinetic parameters in the presence of the PT agent and of small quantities of acetic acid have been determined.

PT assisted potassium permanganate oxidation of primary aromatic amines to their corresponding azocompounds in good yields[215] has been reported. Permanganate solubilised in methylene chloride with the aid of a PT agent oxidizes benzyl alcohol to benzaldehyde and benzyl ethers to benzoate esters[216]. Although the rate of oxidation of ether is about an order of magnitude slower than alcohol oxidation, both respond in the identical way to the unique effect caused by the introduction of substituents into the ring. In addition primary kinetic isotope effect are observed for both reactions. Because of these similarities it is proposed that benzyl alcohol and benzyl ether are oxidized by similar mechanism and the difference in rates has been ascribed to steric effects.

Oxidation of benzaldehyde and para X (where X = nitro, chloro and methyl) substituted benzaldehydes and benzyl cyanide by potassium permanganate under PTC condition using different catalysts and solvents were reported[217]. A correlation of structure and activity relationship of the catalysts is made and a comparison of the efficiencies of the solvents used was also made. It was found that TBAB and TCMAC functioned as better catalyst and benzene acted as the best medium in a group of solvents like benzene, CCl_4, CH_2Cl_2, etc. The oxidation of propylene with the help of tetrabutylammonium permanganate and characterized by IR and X-ray photoelectron spectroscopic studies is an example of gas-solid PTC reaction[218]. Scanning Electro Microscopy (SEM) was utilised to examine the surface topography and peel strength measurements were employed to examine the bond strength.

2.7. Review of phase transfer assisted ester hydrolysis

Hydrolysis of esters by aqueous NaOH is sometimes facilitated by the use of PT catalysts although such reactions have not been carefully studied. For example C.M. Starks[248] have shown that no hydrolysis of dimethyl adipate takes place by aqueous 50% NaOH at room temperature. However if a small amount of tricaprylmethyl ammonium chloride is added hydrolysis begans immediately with sufficient heat evolution to cause the mixture to reflux and the reaction is completed in 0.5 hour. However as the size of the carboxylate group increases its tendency to associate with the quaternary cation becomes greater and greater such that the catalyst loses its effectiveness for the transference of OH^- ions. For example[249] the catalysed hydrolysis of methyltetradecanoate with 50% aqueous NaOH begins rapidly but as the reaction proceeds hydrolysis slows and eventually stops after about 35% reaction. Hydrolysis of poly(methylacrylate) behaves similarly.

C.L. Arcus, C.G. Gonzalez and D.F.C. Linnecar[250] have shown that poly(vinyl benzyl trimethyl ammonium) hydroxide were tested as catalyst for the hydrolysis of a number of esters with aqueous NaOH. No catalysis was observed in the hydrolysis of simple esters such as ethyl, propyl and butyl acetates, propionates and butyrates, but two to five fold rate increases were measured with potassium ethyl oxylate, malonate, succinate, glutarate and adipate. Increased rates with monoesters of dicarboxylic acids were attributed to the migration of the ester anions into hydrolytic counter ion layer of the polymeric alkali.

San Filippo[251] and coworkers have reported the reaction of carboxylic esters with approximately a three fold excess potassium superoxide solubilized in benzene with 18-Crown-6 to produce after acidic aqueous work up the corresponding carboxylic acid and alcohol in moderate excellent yields. Esters of primary, secondary, tertiary alcohols, phenols and thiols were also investigated. Phosphate esters of phenol were also cleaved by superoxide but corresponding esters of alkyl alcohols showed no appreciable reactivity. The use of DMSO as the solvent produced shorter reaction times but the yields were much reduced. Reaction of superoxides with acetate esters of (-)-R-2-octanol gave only (-)-R-2-octanol indicating that the reaction proceeded by means of an acyl-oxygen cleavage. This mechanism was also in agreement with the influence which the structure of the alcohol portion of the ester has on the relative rates of reaction (Ph > 1°, > 2°, > 3°). The authors also report that simple amides and nitriles did not react with superoxide under the conditions of ester cleavage.

Sam and Simmons[252] have subsequently reported that using the procedure described by Pedersen for the formation of KOH-dicyclohexyl-18-crown-6 only 11% of the anions in toluene were hydroxide. The major species was methoxide ion.

Hydroxide[253] ion displacement of alkyl halides under liquid-liquid PTC conditions is complicated by several factors. Firstly the hydroxide ion is highly hydrated relative to chloride or bromide ions and tends to be poorly transferred into the organic phase.

$$Q^+ Cl^-_{(org)} + OH^-_{(aq)} \rightleftharpoons Q^+ OH^-_{(org)} + Cl^-_{(aq)}$$

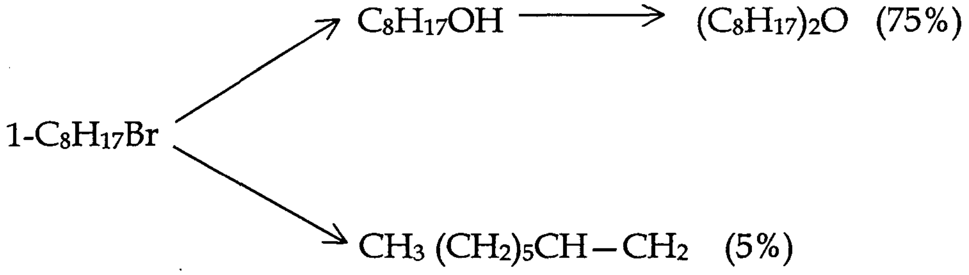
Thus the aqueous phase OH^- concentration must be very high to maintain a high proportion of the catalyst in the active Q^+OH^- form. Secondly the quaternary ammonium hydroxides are thermally unstable.

$$(R\text{-}CH_2\text{-}CH_2)_4 N^+OH^- \longrightarrow R\text{-}CH{=}CH_2 + (R\text{-}CH_2\text{-}CH_3)_3N + H_2O$$

At 70°C the half life of a typical tetraalkyl ammonium salt in contact with strong NaOH solution (50 wt %) is in the order of 30 minutes to 1 hour. Use of dilute (eg. 2M) NaOH solution allows higher temperatures (80°C) and a longer catalyst life. This problem limits the practical upper temperature limit for $R_4N^+X^-$ catalysts to about 50-60°C.

The third complication is that once alcohol is formed by primary displacement, it is readily converted to an alkoxide. Since alkoxide ions are more organic like they associate much more strongly with the quaternary cation than does the OH^- resulting in the formation of ethers as the main product.

A.W. Herriot[254] and D. Picker have shown that in OH^- reactions with alkyl halides often results in the formation of elimination products. For eg:



With 2-bromooctane elimination is the major reaction path (86% to a mixture of 28% octane and 72% cis and trans octene), with only 14% displacement products. The predominance of olefin product is not affected by changes in concentration, added organic solvents or the use of different tetraalkylammonium catalysts. In a homogeneous solution of reformed tetrabutylammonium hydroxide in benzene the elimination was 97%.

Gorden[255] have shown that treatment of allyl chloride with excess of aqueous 50% NaOH in the presence of $(C_8H_{17})_3CH_3N^+Cl^-$ gave diallyl ether in 100% selectivity at 23% conversion.

A highly interesting type of PT catalyst for use in OH^- displacement of alkyl halide is the 'betaine' quaternary salts $R_3N^+CH_2CO_2^-$. These exhibits activities 10 to 50 fold greater than ordinary tetraalkyl ammonium salts as catalysts, for the reaction of 1-halo alkanes with aqueous NaOH. The enhanced activity of betaines is likely due to rapid carboxylate displacement followed by anion exchange and hydrolysis.

Pederson[256] and coworkers have reported that sterically hindered esters of 2,4,6 trimethyl benzoic acid were saponified with KOH- crown complexes in aromatic hydrocarbons. The same reaction carried out in hydrolytic solvents gave essentially no product. That this reaction occurred by an acyl-oxygen cleavage mechanism is clear from the fact that the 1-methanol isolated from the hydrolysis of 2,4,6 trimethyl benzoate ester with KOH-crown was completely optically pure, whereas the KOH- crown complex in toluene produced a 58% yield of hydrolysis products from methyl 2,4,6-trimethyl benzoate in 31 hour at 73.8°C.

Dietrich and Lehn[257] have shown that in the above case by replacing the crown by cryptate VIIIC a 70% yield was achieved in 12 hours at 35°C.

W.E. McEwen and co-workers have shown that tetraalkyl phosphonium salts mixed with strong sodium hydroxide are less stable decomposing at room temperature.

$$R_4P^+X^- + OH^- \longrightarrow R_3PO + RH$$

Hence phsphonium salts are found to be poor in transferring OH^- ions into the organic phase from the aqueous phase. In addition of these certain miscellaneous hydrolysis reactions under PT conditions have been reported. Michihiro[258] and coworkers have reported that propylene oxide gave propan-1,2-diol almost free of polyglycols when heated with water and methyl tributyl phosphonium iodide in an autoclove under CO_2.

CHAPTER III
EXPERIMENTAL

I. Oxidation of alcohols using PTC

In this chapter the details regarding the materials used and methods employed for investigation of the work is presented. The main objectives of the present investigation are the

(1) Kinetic studies on the oxidation of some aliphatic and aromatic carbinols using phase transferred permanganate and

(2) Ester bond cleavage of difficultly hydrolysable and water insoluble esters in non polar solvents using phase transferred hydroxide.

The PT catalysts employed are:

- Tetrabutylammonium bromide (TBAB)
- Tetrabutylphosphonium bromide (TBPB) and
- Tetrabutylammonium hydrogen sulphate (TBAHS)

These are commercially available and are of SISCO quality. They were used as such. The 2-phenyl ethanol used was E. Merck quality and further purified by distillation under vacuum. Butanol and hexanol chosen were also purified before use. The non-polar solvents employed such as benzene, toluene, carbon tetrachloride etc. were purified by standard methods before use.[233,234]

The stoichiometries in the oxidation reactions were determined under heterogeneous conditions by dissolving the carbinol in benzene and equilibrating it with aqueous potassium permanganate solution in the presence of the PT catalyst (TBAB). It was found that one mole of permanganate reacts with one mole of carbinol to give phenyl acetic acid.

$$C_6H_5\,CH_2\text{-}CH_2\text{-}OH + MnO^{-}_4 \longrightarrow C_6H_5\text{-}CH_2COOH + MnO_2 + H_2O$$

The extraction of permanganate to study the following was also made.

1. Effect of concentration of $KMnO_4$
2. Effect of concentration of PT catalysts
3. Effect of structure of the catalyst
4. Effect of polarity of solvent and
5. Effect of added salt.

Stability of the extracted permanganate ions in various organic solvents at different time intervals were analysed spectrophotometrically by measuring the absorption of MnO_4^- ion at λ_{max} = 528 nm. The phase transferred permanganate remained stable over a period of time for making kinetic analysis conveniently.

Analar grade potassium permanganate (FLUKA) was used for the preparation of $KMnO_4$ solution in double distilled water. In order to have a comparative idea of the parameters of the oxidation without the use of PTC, kinetic studies of oxidation of 2-phenyl ethanol were carried out in aqueous acetic acid media also.

Acetic acid (E Merck) was purified by refluxing with potassium dichromate and the fraction boiling between 117°-118°C were collected and used.

3.1. Kinetic investigations

The kinetic experiments were carried out at various desired temperatures in suitable thermostats to maintain the temperature of the system within a variation of $\pm$ 0.05°C. A known volume of 0.005 mol dm^{-3} aqueous $KMnO_4$ is equilibrated with equal volume of benzene containing 0.02 mol dm^{-3} PT catalyst ($Q^+ X^-$ where Q^+ is the Quaternary ammonium cation and X^- is either Br^- or HSO^-_4). The $Q^+MnO^-_4$ formed in benzene was separated and made anhydrous over 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 a calibrated pipette. The reaction mixture was shaken well and kept undisturbed in the thermostat. Aliquots were withdrawn at regular intervals of time (5 minutes) from the reaction mixture and the progress of the reaction was monitored spectrophotometrically in a Shimadzu 1601 UV-VIS. spectrophotometer by measuring the absorption of MnO_4^- ions at λ_{max} of 528 nm. Pseudo first order condition was maintained by keeping [carbinol] >> [$QMnO_4$].

The experiments were carried out by varying the concentration of oxidant and carbinol at different temperatures in different solvents. The influence of the catalyst structure on the rate of oxidation of alcohols were studied using three different catalysts viz TBAB, TBPB and TBAHS.

The kinetics of the oxidation of 2-phenyl ethanol were studied in aqueous acetic acid (10% v/v). The effect of oxidant concentration, the effect of substrate concentration, the effect of temperature, 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. The activation parameters were also computed. Kinetics were studied under the condition [carbinol] >> [MnO_4^-] and the concentration of the 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 formed is ascertained.

3.2. Computation of kinetic data and evaluation of rate constants[224,225,235]

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 or three kinetic runs.

3.3. Thermodynamic parameters[235-237]

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

Energy of activation (Ea) was calculated using the Arrhenius equation

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

where A = frequency factor; R = universal gas constant and T is the absolute temperature and k is the Specific Rate. Ea values were calculated from the slopes of log k Vs. 1/T.

3.4. Enthalpy of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$

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

$$k = k_bT/h \ \ \exp[(T\Delta S^{\#} - \Delta H^{\#})/RT]$$

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

where k_b = Boltazmann constant; h = Plancks constant.

A plot of log k/T vs 1/T should therefore be linear with a slope equal to $-\Delta H^{\#}/2.303R$ from which $\Delta H^{\#}$ can be determined.

Substituting the values of k_b, h, R and $\Delta H^\#$ into the above equation, $\Delta S^\#$ values can be evaluated.

3.5. Free energy of activation $\Delta G^\#$

The free energy of activation was computed from the equation $\Delta G^\# = \Delta H^\# - T\Delta S^\#$.

3.6. Extraction of permanganate ions from aqueous to organic media for kinetic study

For the kinetic studies of the oxidation of alcohols in organic medium the permanganate ions from the aqueous media should be first extracted into the 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 catalyst
3. Structure of the catalyst
4. Nature of the solvents.

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

The extraction was studied by equilibrating a definite volume of a 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.

$$\% \text{ of } MnO_4^- \text{ extracted into the organic phase} = \frac{[QMnO_4]_{org}}{[MnO_4^-]_{aq}} \times 100$$

3.7. Effect of catalyst concentration on extraction of MnO_4

The amount of extraction of permanganate ion from aqueous to the organic phase in a given solvent increased with the increase in the concentration of the PT catalysts. The extraction is almost complete and attained a steady state with the catalytic concentration twice that of aqueous permanganate concentration. Further it was found that in a given solvent the extractive power was highest for TBAHS, followed by TBAB and TBPB respectively.

Table 3.1

Effect of catalytic concentration of the extraction of MnO_4 ions

Time: 30 mts
Temp: 303 K.

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

[PT catalyst] (mol dm^{-3})	% of MnO_4^- extracted into organic phase		
	TBPB	TBAB	TBAHS
0.010	76	78	80
0.150	86	90	92
0.020	91	94	97
0.025	91	94	97

It is found that with the use of moderate excess of aliphatic quaternary salt it is possible to extract MnO_4^- almost quantitatively into the organic phase [218,220].

3.8. Effect of solvent polarity in the extraction of MnO_4^-

The effect of solvent polarity on the extraction of permanganate ions from the aqueous to the organic phase was investigated with respect to solvents like benzene, toluene and chloroform. The results were 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}

Temp : 303 K
Time : 30 mts

Organic solvent used		C_6H_6	$C_6H_5CH_3$	$CHCl_3$
Dielectric constant		2.27	2.40	4.70
% extraction of MnO_4^-	TBPB	76	77	83
	TBAB	78	80	89
	TBAHS	80	85	92

Chloroform has been found to be the best solvent for the extraction of MnO_4^- ions using quaternary salts as PT catalyst. This has been already reported by various workers[221, 227, 236] .The extraction was found to increase with the increase in the dielectric constant of the solvent.

3.9. Effect of the 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

Effect of initial concentration of $KMnO_4$ on extraction

Time : 30 mts.
Solvent: Benzene

[PT catalyst] : 0.01 mol dm^{-3}
Temp : 303 K

$[MnO_4^-]$ mol dm^{-3}	% extraction of MnO_4^- into the organic phase		
	TBPB	TBAB	TBAHS
0.005	49	53	60
0.010	76	78	80
0.015	80	86	91
0.120	86	91	97
0.025	89	93	97

The increase in the amount of extraction with increase in the initial concentration of anions may be due to the fact that the increasing concentration of inorganic anions tie up additional water of hydration reducing the amount of water available for anion hydration providing easier transfer of the anions into the organic phase[222,226].

3.10. 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 $Q^+MnO_4^-$. The results are represented in Table 3.4.

Table 3.4

Effect of added NaCl

Time : 30 mts.
Solvent : Benzene

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

[NaCl]x10^2 mol dm^{-3}	% extraction of MnO_4^- into the organic phase		
	TBPB	TBAB	TBAHS
0	76	78	80
0.5	79	83	85
1.0	83	88	91
2.0	88	92	96

3.11. Stability of permanganate ion in the organic medium

The stability of MnO_4^- extracted into various organic solvents was studied by measuring its absorbance of λ_{max} 528 for a period of one to two hours. It was found that the absorption remained almost unchanged for about one hour and decreased slightly, 2 to 3% within a time of one and a half hours. It was found that Tetrabutylammonium permanganate obtained from TBAHS was slightly more stable than the one from TBAB and TBPB.

3.12. Stoichiometry of the reaction

A reaction mixture containing known concentration of 2-phenyl ethanol and $QMnO_4$ in benzene was kept for nearly 4 to 5 hours in a thermostat at 35°C until the reaction was completed under the condition $[QMnO_4] > [\text{Carbinol}]$. The concentration of the unreacted MnO^-_4 ions was determined spectrophotometrically by measures of its absorbance at λ_{max} of 528 nm. (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 alcohol, the stoichiometry of the reaction was calculated.

3.13. Product analysis

A reaction mixture containing excess of $QMnO_4$ over 2-phenyl ethanol in benzene was allowed to react completely by keeping it at 40°C for 4 hours. The unreacted permanganate ions were destroyed by the addition of sodium sulphite and 50% HCl. The resulting solution was extracted three times with ether and all the ether layers were combined. The ether layer was then extracted with 5% Na_2CO_3 three times and then all these layers were combined and acidified with

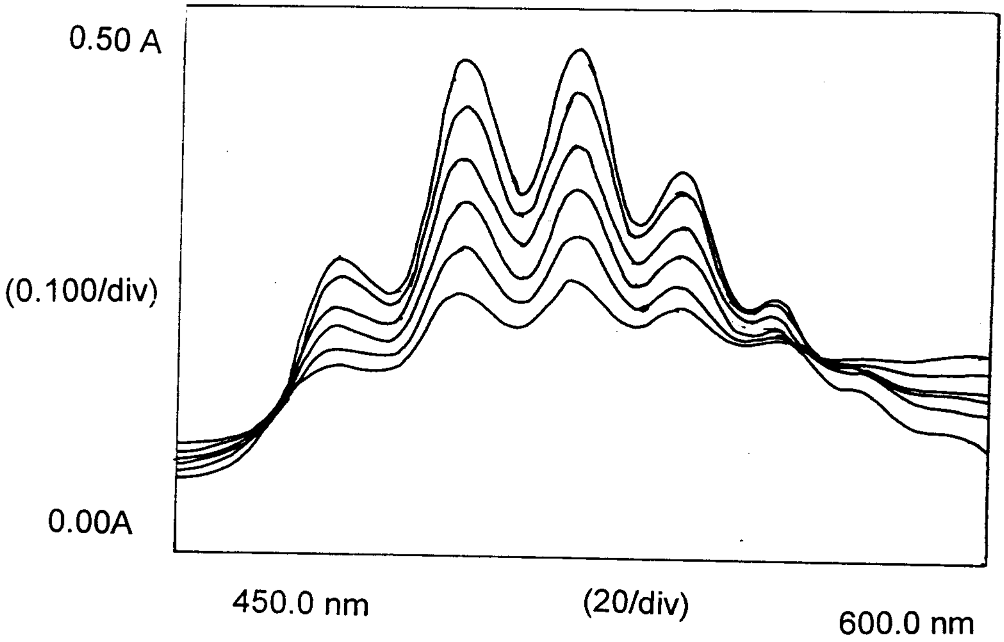
HCl. The product obtained was Phenyl acetic acid. It was filtered, dried and purified and the melting point was determined.

Again a TLC was conducted with the reaction mixture and the product formed was confirmed to be phenylacetic acid.

3.14. Oxidation of 2-Phenyl ethanol by phase transferred permanganate in benzene-tetrabutylphosphonium bromide as PT catalyst

Oxidation of 2-phenyl ethanol by phase transferred permanganate in benzene–tetrabutylphosphonium bromide as PT catalyst has been carried out in the following way. 10 ml of 0.005 mol dm^{-3} aqueous $KMnO_4$ was equilibrated with 10 ml of benzene containing 0.02 mol dm^{-3} TBPB. The organic layer was separated and dried over sodium sulfate. The tetrabutylphosphonium permanganate (TBPP) obtained in benzene was determined spectrophotometrically.

Fig. 3.1. U.V spectrum of the oxidation of 2-phenyl ethanol using tetra butylphosphonium bromide



3.15. Kinetic studies

The oxidation of 2-phenyl ethanol by phase transferred permanganate was studied at different conditions such as varying the oxidant concentration, varying the substrate concentration at different temperatures in various organic solvents under the condition that, [Carbinol] >> [$QMnO_4$].

3.16. Effect of oxidant (TBPP) concentration on the rate of oxidation of 2-phenyl ethanol

The kinetics of the oxidation of 2-phenyl ethanol with phase transferred MnO^-_4 (TBPP) obtained with the assistance of TBPB in benzene were studied by taking a fixed concentration of the substrate (1.202 x 10^{-2} mol dm^{-3} and varying the concentration of the oxidant from 4.77 x10^{-4} mol dm^{-3} to 7.30 x 10^{-4} mol dm^{-3}. The concentration of the substrate was always taken to be at least 10 times greater than the concentration of the oxidant so as to maintain pseudo-first order condition. The reaction was followed spectrophotometrically by measuring the absorbance of MnO_4^- ions of a λ_{max} of 528 nm. The pseudo-first order rate constants $K_{(obs)}$ were computed from the linear plot of log (absorbance) of $QMnO_4$ versus time Fig. 3.2.

Fig. 3.2. Effect of [QMnO₄] on the oxdn. of 2-phol using TBPB

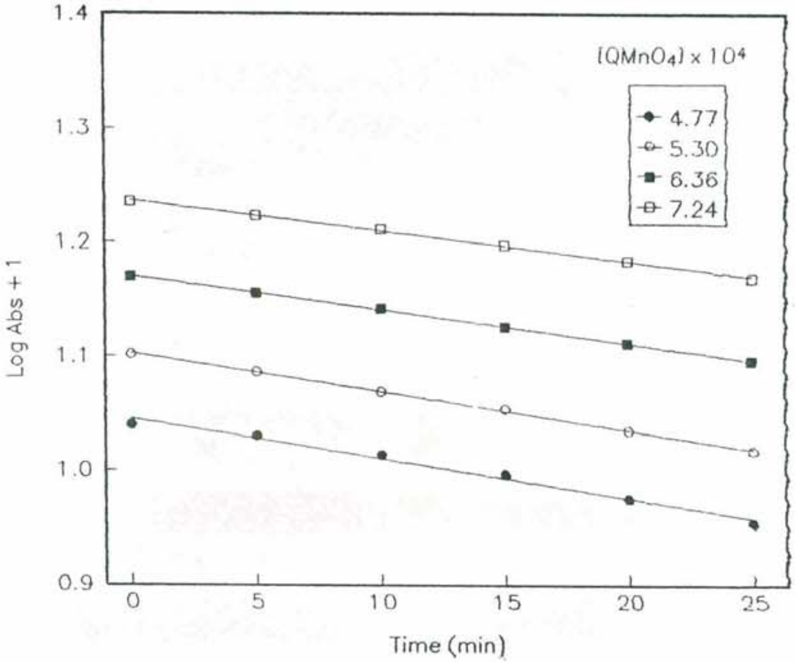


Table 3.5

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

[PhCH$_2$-CH$_2$-OH] = 1.202 x 10^{-2} mol dm^{-3} PT catalyst: TBPB
Solvent : Benzene Temp : 308 K

10^4 x [TBPP] (mol dm^{-3})	10^2x[carbinol] (mol dm^{-3})	10^4 k$_{obs}$ (s^{-1})	k$_2$ x 10^2 = k$_{obs}$/[substrate] (dm^3 mol^{-1}s^{-1})	Corr:
4.77	1.202	1.33	1.11	0.9931
5.30	1.202	1.30	1.08	0.9994
6.36	1.202	1.14	0.95	0.9997
7.24	1.202	1.01	0.85	0.9990

Duplicate kinetic runs showed that the rate constants were reproducible within ± 5%. The pseudo first order rate constants (k_{obs}) were determined by the method of least squares is represented in Table 3.5.

3.17. Effect of varying the concentration of the substrate on the rate of oxidation of 2-phenyl ethanol

The effect of varying the concentration of 2-phenyl ethanol on the rate of oxidation was studied for a concentration range of 2-phenyl ethanol from 1.202×10^{-2} mol dm^{-3} to 4.007×10^{-2}, mol dm^{-3} keeping the concentration of the oxidant in all the cases to be 5.30×10^{-4}, mol dm^{-3} which maintained the pseudo-first order condition. All the other kinetic conditions were kept the same. Hence the order obtained will be that with respect to the oxidant. From the observed pseudo-first order rate constant (Fig. 3.3). The order with respect to carbinol was obtained by dividing k_{obs} with the concentration of alcohol and a constant k_2 values were observed (Table 3.6).

Fig. 3.3. Effect of substrate on the oxdn. of 2-phol using TBPB

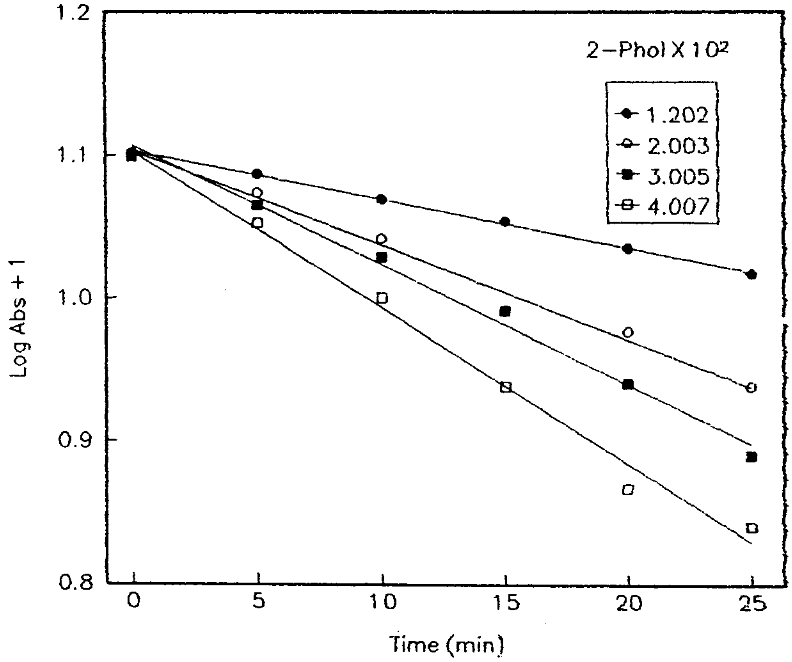


Table 3.6

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

[TBPP] = 5.30 x 10^{-4} mol dm^{-3}
Solvent : Benzene

PT Catalyst : TBPB
Temp : 308 K

10^4 x (TBPP) (mol dm^{-3})	10^2 x [carbinol] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	k_2 x 10^2 = k_{obs}/[substrate] (dm^3 mol^{-1}s^{-1})	Correlation
5.30	1.202	1.30	1.08	0.9997
5.30	2.003	2.53	1.26	0.9942
5.30	3.005	3.20	1.06	0.9963
5.30	4.007	4.18	1.04	0.9954

3.18. Effect of temperature on the rate of oxidation of 2-phenyl ethanol

The effect of temperature on the rate of oxidation of 2-phenyl ethanol was studied at a temperature range from 303 to 318K under condition such that the substrate concentration of 1.202 x 10^{-2} mol dm^{-3} and oxidant concentration of 5.30 x 10^{-4} mol dm^{-3} were maintained. All other conditions being the same. The results are shown in table 3.7. From the kinetic data various thermodynamic parameters like $\Delta H^{\neq}$, E_a, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were calculated.

Fig. 3.4. Effect of temp. on the oxdn. of 2-phol using TBPB

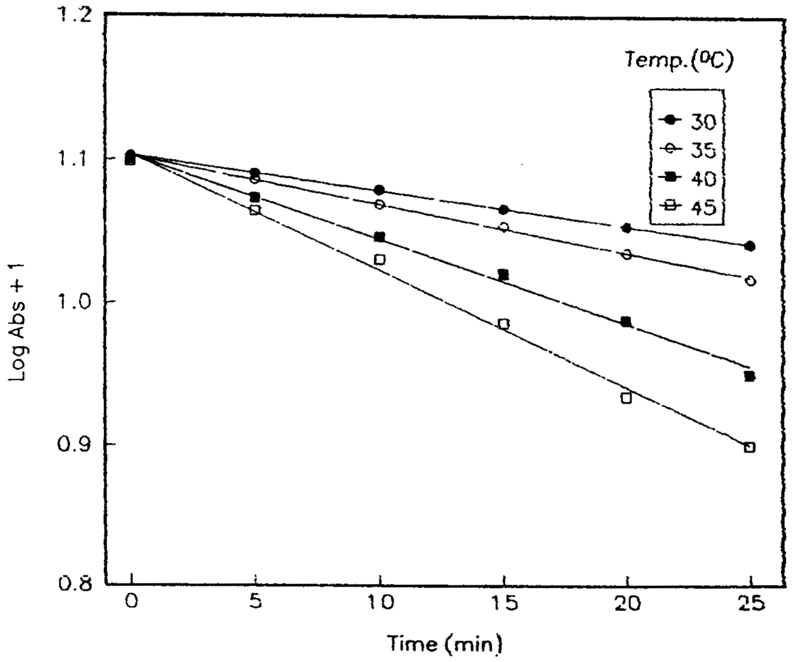


Table 3.7

Effect of temperature on the rate of oxidation of 2-phenyl ethanol using tetraburyl phosphonium permanganate

[Ph CH_2CH_2OH] : 1.202 x 10^{-2} mol dm^{-3} [TBPP] : 5.30 x 10^{-4} mol dm^{-3}
Solvent : Benzene Pt Catalyst : TBPB

Temp	10^4 x k_{obs} (s^{-1})	10^2 x k_2 = k_{obs}/ [Substrate] (dm^3 mol^{-1} s^{-1})	Correlation
303	0.9480	0.7887	0.9998
308	1.30	1.08	0.9994
313	2.26	1.88	0.9974
318	3.13	2.60	0.9975

3.19. Effect of polarity of the medium on the rate of oxidation of 2-phenyl ethanol

The reaction was carried out in organic solvents like benzene, toluene and chloroform at 308K by keeping the substrate concentration at 1.202 x 10^{-2} mol dm^{-3} and the oxidant concentration of 5.30 x 10^{-4} mol dm^{-3} All the other conditions were kept the same. The reactions were carried out inorder to get the type of interaction in the rate-determining slow step of the reaction. The results are presented in Table 3.8.

Fig. 3.5. Effect of solvent on the oxdn. of 2-phol using TBPB

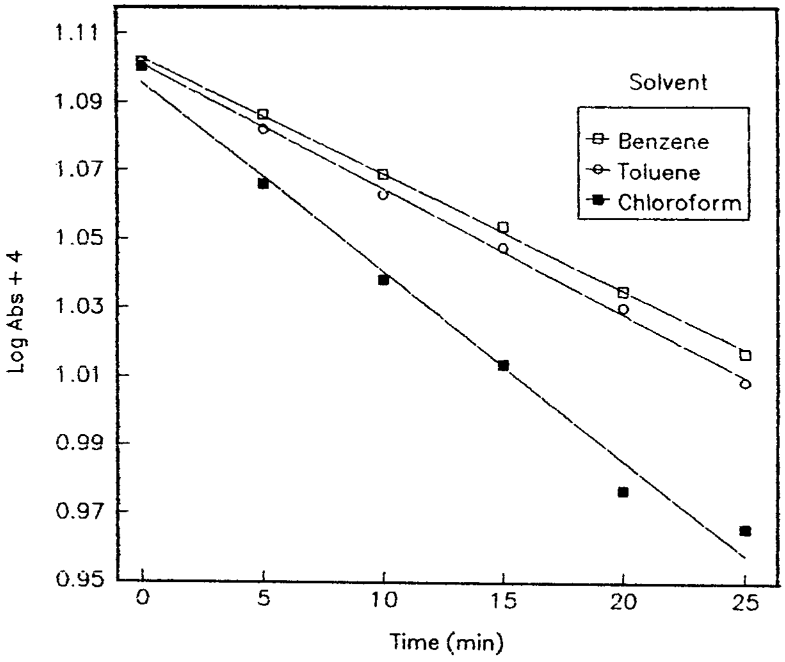


Table 3.8

Effect of solvent polarity on the rate of oxidation of 2-phenyl ethanol, using TBPP

[Ph CH_2CH_2OH] : 1.202×10^{-2} mol dm^{-3} [TBPP] : 5.30×10^{-4} mol dm^{-3}
PT catalyst : TBPB Temp : 308 K

Solvent	Dielectric constant	$10^4 \times k_{obs}\ s^{-1}$	$k_2 \times 10^2$ $dm^3\ mol^{-1}s^{-1}$	Correlation
Benzene	2.27	1.30	1.08	0.9994
Toluene	2.40	1.39	1.16	0.9990
Chloroform	4.70	2.11	1.75	0.9938

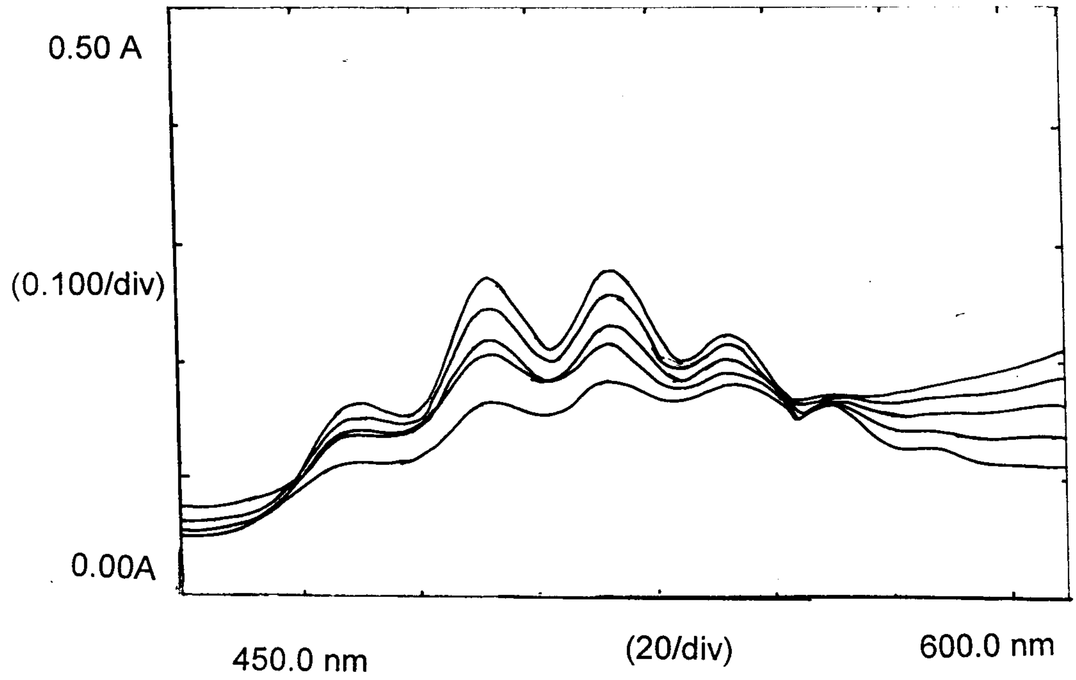
3.20. Effect of addition of acrylonitrile

To the reaction mixture containing 1.202 x 10^{-2} mol dm^{-3} of 2-phenyl ethanol and 5.30 x 10^{-4} mol dm^{-3} of Tetrabutyl phosphonium permanganate in benzene medium 5 ml of acrylonitrile was added and kept for more than 6 hours. No polymerization was observed indicating the absence of any free radicals formed during the course of the reaction.

3.21. Oxidation of 2-phenyl ethanol by phase transferred permanganate in benzene-tetra butyl ammonium bromide as PT catalyst

10 ml of 0.005 mol dm^{-3} aqueous $KMnO_4$ was equilibrated with 10 ml of benzene containing 0.02 mol dm^{-3} TBAB. The tetrabutylammonium permanganate obtained (TBAP) in benzene was made anhydrous and its concentration was determined spectrophotometrically.

3.6. Spectrum of the oxidation of 2-phenyl ethanol using tetra butylammonium Bromide



3.22. Kinetic studies

The oxidation of 2-phenyl ethanol by phase transferred permanganate was studied at different conditions such as varying the oxidant concentration, varying the substrate concentration at different temperatures in various organic solvents, under the condition that [Carbinol] >> [$QMnO_4$].

3.23. Effect of oxidant (TBAP) concentration on the rate of oxidation of 2-phenyl ethanol

The kinetics of the oxidation of 2-phenyl ethanol with phase transferred MnO_4^- (TBAP) obtained with the assistance of TBAHS in benzene were studied by taking a fixed concentration of the substrate (1.202×10^{-2} mol dm^{-3}) and varying the concentration of the oxidant from 4.77×10^{-4} mol dm^{-3} to 7.30×10^{-4} mol dm^{-3} The concentration of the substrate was always taken to be at least 10 times greater than the concentration of the oxidant so as to maintain pseudo-first order condition. The reaction was followed spectrophotometrically by measuring the absorbance of MnO_4^- ions of a λ_{max} of 528 nm. The pseudo-first order rate constants k_{obs} were computed from the linear plot of log(absorbance) of $QMnO_4$ versus time Fig. 3.7.

Fig. 3.7. Effect of [$QMnO_4$] on the oxdn. of 2-phol using TBAB

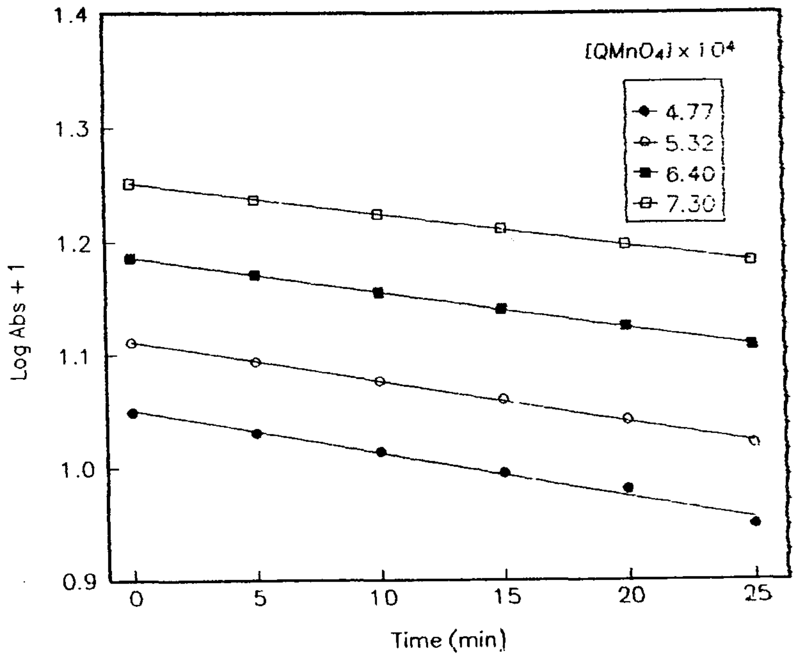


Table 3.9

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

[Ph CH_2CH_2OH : 1.202 x 10^{-2} mol dm^{-3} PT catalyst : TBAB
Solvent : Benzene Temp : 308 K

10^4 [TBAP] (mol dm^{-3})	10^2 x [Carbinol] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	$k_2 \times 10^2$ = k_{obs}/ [substrate] dm^3 mol^{-1} s^{-1}	Correlation
4.77	1.202	1.47	1.22	0.9930
5.32	1.202	1.37	1.14	0.9992
6.40	1.202	1.18	0.986	0.9997
7.30	1.202	1.04	0.865	0.9997

3.24. Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

The effect of varying the concentration of 2-phenyl ethanol on the rate of oxidation was studied for a concentration range of 2-phenyl ethanol from 1.202 x 10^{-2} mol dm^{-3} keeping the concentration of the oxidant in all the cases to be 5.30 x 10^{-4} mol dm^{-3}, which maintained the pseudo-first order condition. All the other kinetic conditions were kept the same. Hence the order obtained will be that with respect to the oxidant. From the observed pseudo-first order rate constant (Fig. 3.8) the order with respect to the carbinol was obtained by dividing k_{obs} with the concentration of the alcohol when constant k_2 values were observed.

Fig. 3.8. Effect of substrate on the oxdn. of 2-phol using TBAB

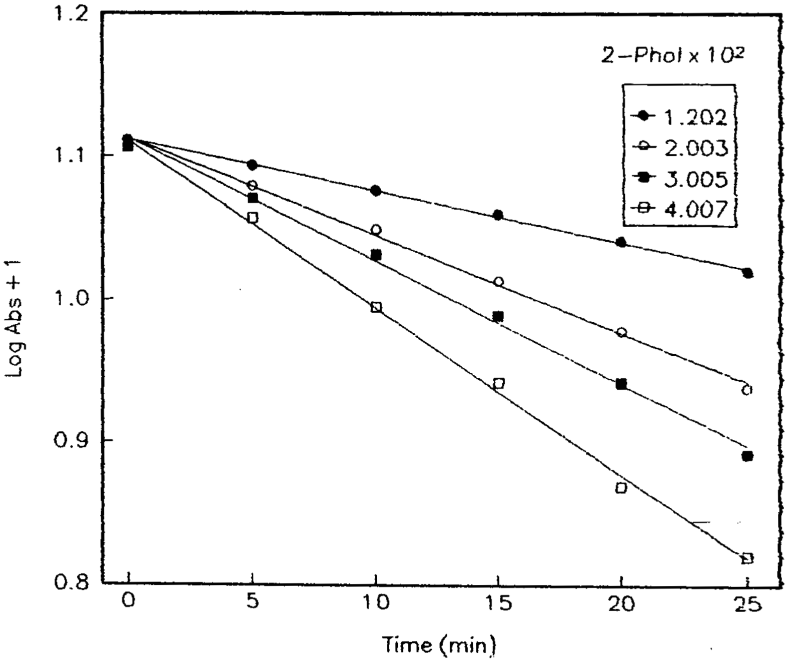


Table 3.10

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

[TBAP] : 5.32 X 10^{-4} mol dm^{-3} PT Catalyst : TBAB
Solvent : Benzene Temp : 308 K

10^4 x [TBAP] (mol dm^{-3})	10^2 x [Carbinol] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	$k_2 \times 10^2 = k_{obs}$/[substrate] $dm^3\ mol^{-1}\ s^{-1}$	Correlation
5.32	1.202	1.37	1.14	0.9992
5.32	2.003	2.60	1.29	0.9983
5.32	3.005	3.29	1.09	0.9981
5.32	4.007	4.48	1.11	0.9987

3.25. Effect of temperature on the rate of oxidation of 2-phenyl ethanol

The effect of temperature on the rate of oxidation of 2-phenyl ethanol were studied of a temperature range from 303 to 318 K, under conditions such that the substrate concentration is 1.202×10^{-2} mol dm^{-3} and the oxidant concentration 5.30 x 10 mol dm^{-3} other conditions were kept the same. The results are shown in Table 3.11. From the kinetic data, various thermodynamic parameters like Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were calculated.

Fig. 3.9. Effect of temp. on the oxdn. of 2-phol using TBAB

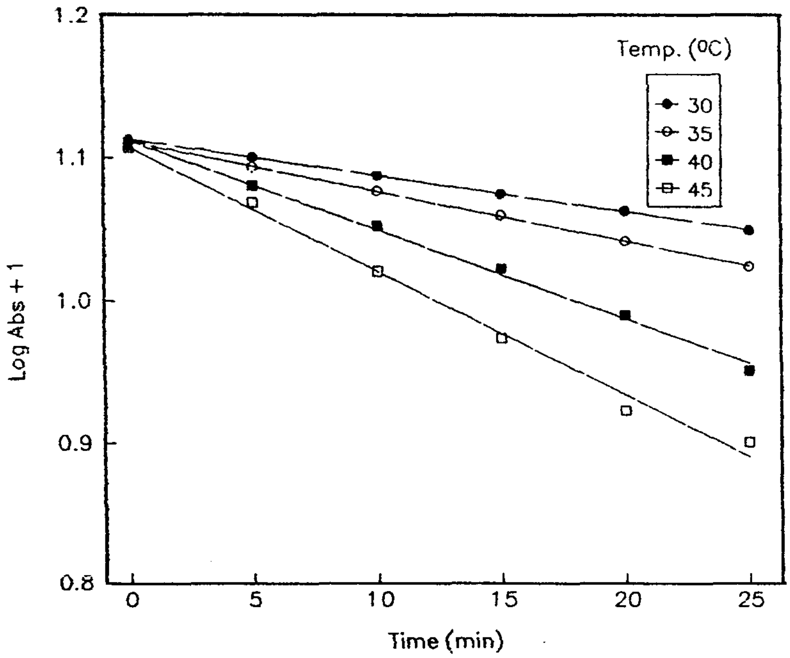


Table 3.11

Effect of temperature on the rate of oxidation of 2-phenyl ethanol using tetrabutylammonium permanganate

[Ph CH_2OH] : 1.202 x 10-2- mol dm^{-3} [TBAP] : 5.32 x 10^{-4} mol dm^{-3}
Solvent : Benzene PT catalyst : TBAB

Temp.	10^4 x k_{obs} (s^{-1})	10^2 x k_2 = k_{obs}/[Substrate] (dm^3 mol^{-1} s^{-1})	Correlation
303	0.9710	0.8079	0.9998
308	1.37	1.14	0.9992
313	2.40	1.99	0.9980
318	3.33	2.77	0.9960

3.26. Effect of polarity of the medium on the rate of oxidation of 2-phenyl ethanol

The reaction was carried out in organic solvents like benzene, toluene and chloroform of 308K by keeping the substrate concentration of 1.202 x 10^{-2} mol dm^{-3} and the oxidant concentration of 5.30 x 10^{-4} mol $dm^{-3.}$ All the other conditions were kept the same. The reactions were carried out in order to get the type of interaction in the rate-determining slow step of the reaction. The results are presented in Table 3.12.

Fig. 3.10. Effect of solvent on the oxdn. of 2-phol using TBAB

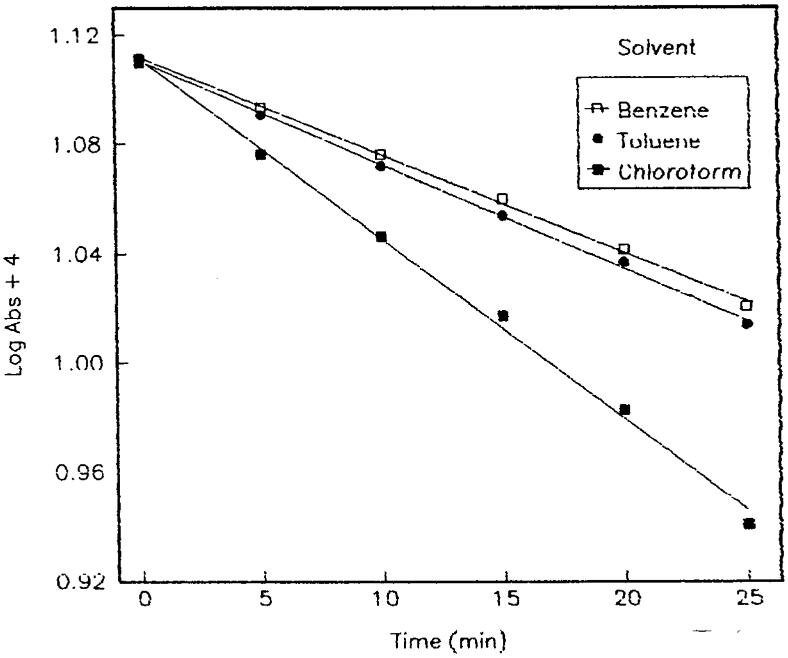


Table 3.12

Effect of solvent polarity on the rate of oxidation of 2-phenyl ethanol using TBAP

[Ph CH_2CH_2OH] : 1.202×10^{-2} mol dm^{-3}
PT catalyst : TBAB

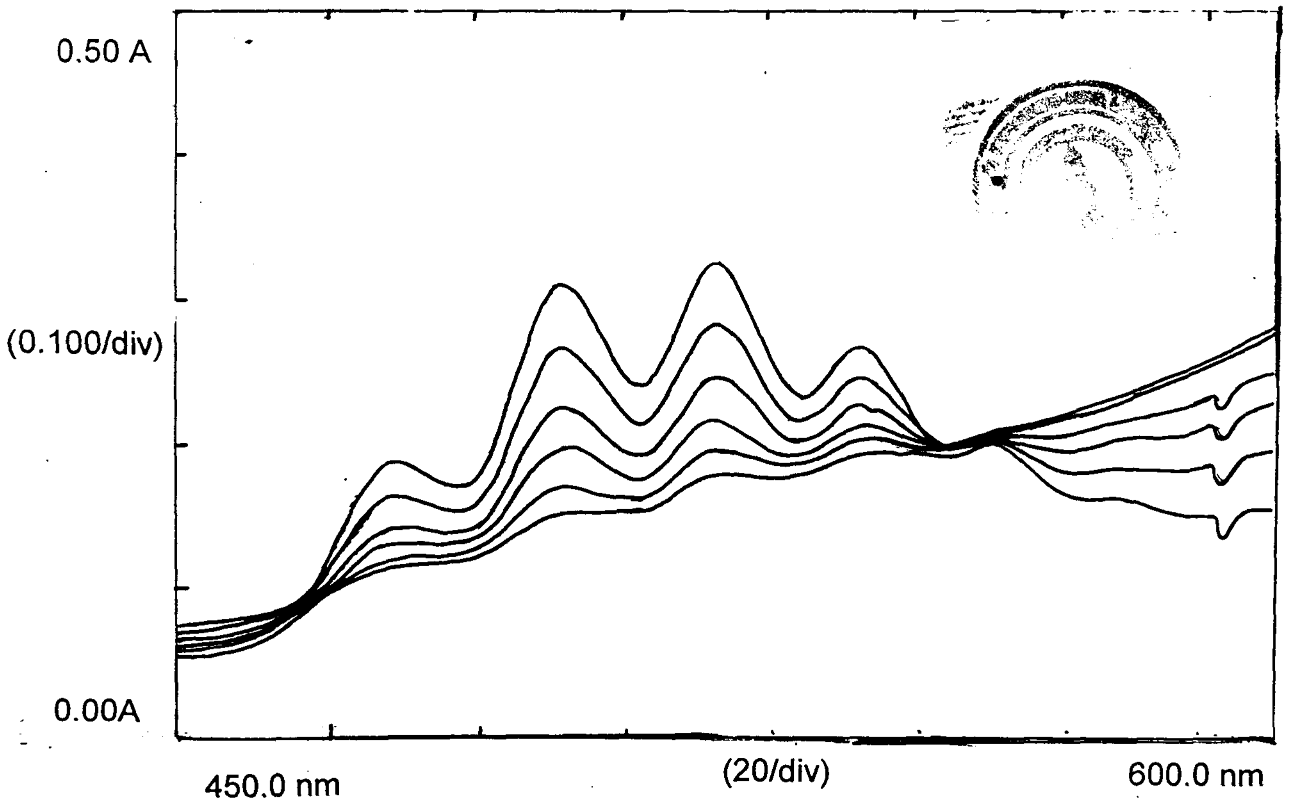
[TBAP] : 5.32×10^{-4} mol dm^{-3}
Temp : 308 K

Solvent	Dielectric constant	$10^4 \times k_{obs}$ s^{-1}	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}	Correlation
Benzene	2.27	1.37	1.14	0.9992
Toluene	2.40	1.46	1.21	0.9992
Chloroform	4.70	2.53	2.11	0.9982

3.27. Oxidation of 2-phenyl ethanol by phase transferred permanganate in benzene tetra butyl ammonium hydrogen sulfate

10 ml of 0.005 mol dm^{-3} aqueous $KMnO_4$ was equilibrated with 10 ml of benzene containing 0.02 mol dm^{-3} TBAHS. The tetra butyl ammonium permanganate (TBAP) in benzene was determined spectrophotometrically.

Fig. 3.11. UV-spectrum of the oxidation of 2-phenyl ethanol using tetrabutylammonium hydrogen sulfate



3.28. Kinetic studies

The oxidation of 2-phenyl ethanol by phase transferred permanganate was studied at different conditions such as varying the oxidant concentration, varying the substrate concentration, at different temperature in various organic solvents etc. under the condition that [carbinol] >> [$QMnO_4$].

3.29. Effect of oxidant (TBAP) concentration on the rate of oxidation of 2-phenyl ethanol

The kinetics of the oxidation of 2-phenyl ethanol with phase transferred MnO_4^- (TBAP) obtained with the assistance of TBAHS in benzene were studied by taking a fixed concentration of substrate (1.202×10^{-2} mol dm^{-3} of 2-phenyl ethanol) and varying the concentration of oxidant (TBAP). The concentration of the substrate was always kept greater than at least 10 times than the oxidant concentration. So that the reaction was carried out under pseudo-first order condition. The reaction was followed spectrophotometrically by measuring the absorbance of MnO_4^- ions at λ_{max} 528nm. The pseudo-order rate constants (k_{obs}) were computed from the linear plot of log (absorbance) of $QMnO_4$ versus time Fig. 3.12.

Fig. 3.12. Effect of $[QMnO_4]$ on the oxdn. of 2-phol using TBAHS

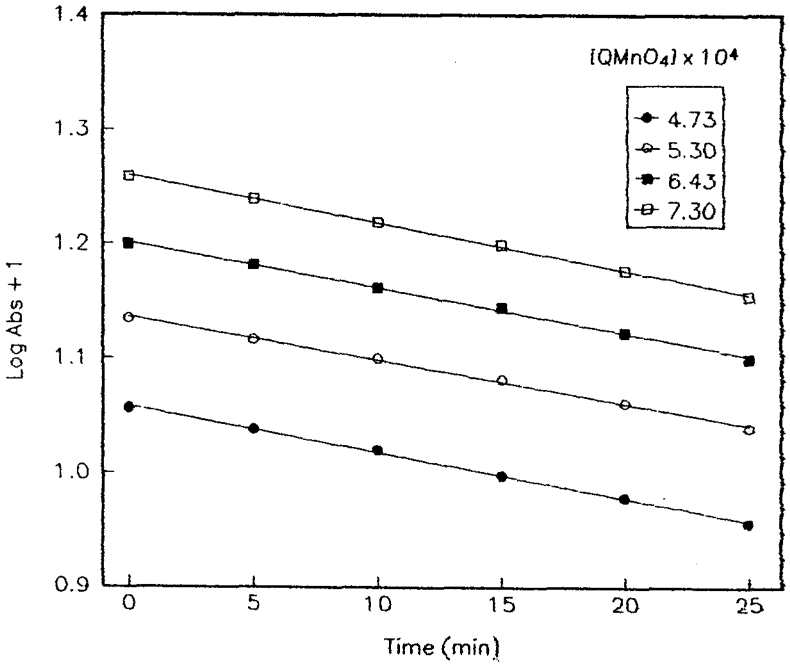


Table 3.13

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

$Ph[CH_2OH]$: 1.202 x 10^{-2} mol dm^{-3} PT Catalyst : TBAHS
Solvent : Benzene Temp : 308 K

10^4 [TBAP] (mol dm^{-3})	10^2 x [Carbinol] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	$k_2 \times 10^2 = k_{obs}/[substrate]$ $dm^3\ mol^{-1}\ s^{-1}$	Correlation
4.73	1.202	1.54	1.28	0.9993
5.30	1.202	1.44	1.20	0.9987
6.43	1.202	1.51	1.25	0.9988
7.30	1.202	1.59	1.32	0.9995

3.30. Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

The effect of varying the concentration of 2-phenyl ethanol on the rate of oxidation was studied for a concentration range of 2-phenyl ethanol from 1.202 x 10^{-2} mol dm^{-3} to 4.007 x 10^{-2} mol dm^{-3}. Keeping the oxidant concentration in all the cases to be 5.30 x 10^{-4} mol dm^{-3}. Substrate concentration is large excess than the concentration of oxidant so that the pseudo-first order condition was maintained. All other kinetic conditions were kept the same. Hence the order obtained will be that with respect to the oxidant. From the observed pseudo-first order rate constant, Table 3.14 the order with respect to the carbinol was obtained by dividing k_{obs} with the concentration of the alcohol, when a constant k_2 values are obtained.

Fig. 3.13. Effect of Substrate on the oxdn. of 2-phol using TBAHS

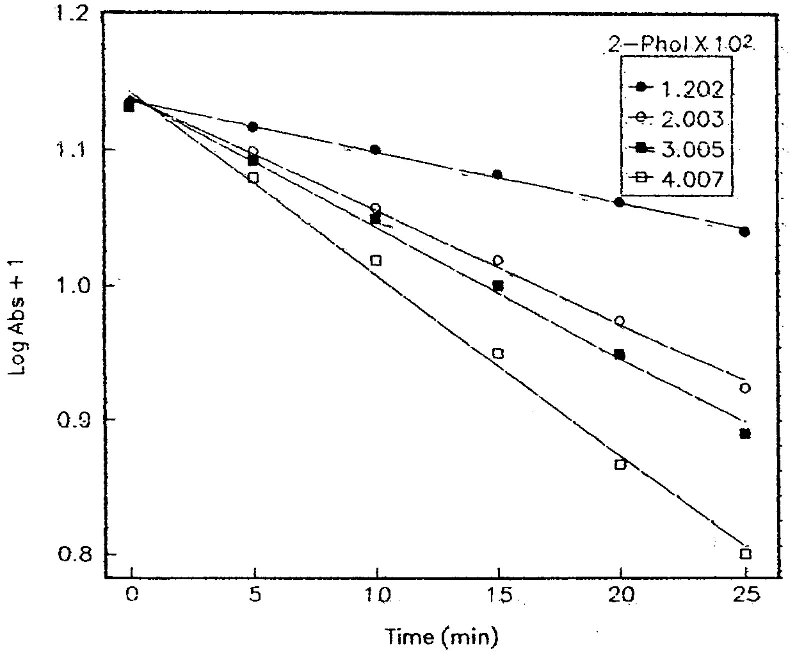


Table 3.14

Effect of Varying the Concentration of Substrate on the Rate of Oxidation of 2-Phenyl Ethanol

[TBAP] : 5.30 X 10^{-4} mol dm^{-3} PT Catalyst : TBAHS
Solvent : Benzene Temp : 308 K

10^4 [TBAP] (mol dm^{-3})	10^2 x [Carbinol] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	k_2 x 10^2 = k_{obs}/ [substrate] dm^3 mol^{-1} s^{-1}	Correlation
5.30	1.202	1.44	1.20	0.9987
5.30	2.003	3.19	1.59	0.9983
5.30	3.005	3.69	1.23	0.9975
5.30	4.007	5.17	1.29	0.9973

3.31. Effect of temperature on the rate of oxidation of 2-phenyl ethanol

The effect of temperature on the rate of oxidation of 2-phenyl ethanol was studied at a temperature range from 303 to 318 K under identical condition. The results are shown in Table 3.15. From the kinetic data the various thermodynamic parameters like energy of activation (Ea), entropy of activation $\Delta S^{\neq}$, enthalpy of activation $\Delta H^{\neq}$ and free energy of activation $\Delta G^{\neq}$ were evaluated.

Fig 3.14 Effect of temp. on the oxdn. of 2-phol using TBAHS

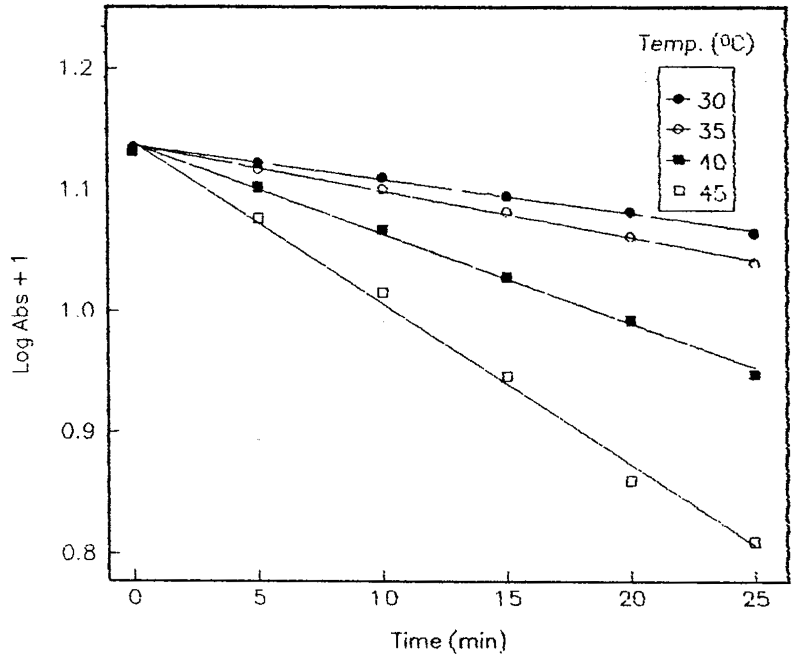


Table 3.15

Effect of temperature on the rate of oxidation of 2-phenyl ethanol using tetrabutylammonium permanganate

[Ph CH_2CH_2OH] : 1.202×10^{-2} mol dm^{-3} [TBAP] : 5.30×10^{-4} mol dm^{-3}
Solvent : Benzene PT catalyst : TBAHS

Temp. (K)	$10^4 \times k_{obs}$ (s^{-1})	$10^2 \times k_2 = k_{obs}$/[Substrate] ($dm^3$ mol^{-1} s^{-1})	Correlation
303	1.06	0.8877	0.9983
308	1.44	1.20	0.9987
313	2.81	2.34	0.9984
318	5.09	4.24	0.9974

3.32. Effect of polarity of the medium on the rate of oxidation of 2-phenyl ethanol

Keeping the substrate concentration at.1.202 x 10^{-2} mol dm^{-3} and the oxidant concentration at 5.30 X 10^{-4} mol dm^{-3} carried out the reaction in organic solvents like benzene, toluene and chloroform. All other conditions were kept the same. The reactions were carried out inorder to get the type of interaction in the rate-determining slow step of the reaction. The results are presented in Table 3.16.

Fig. 3.15. Effect of solvent on the oxdn. of 2-phol using TBAHS

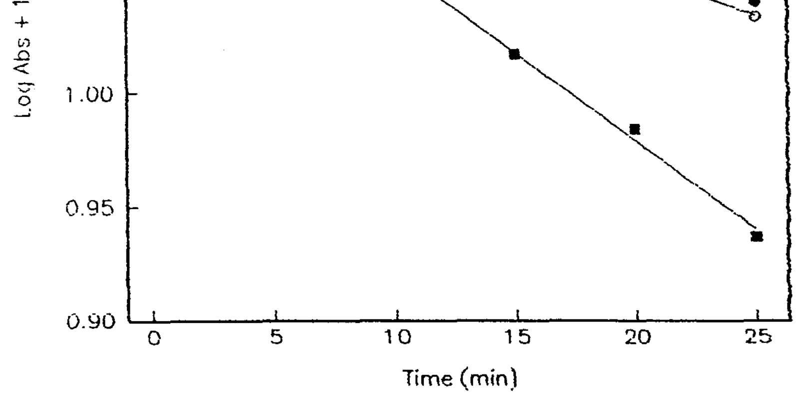


Table 3.16

Effect of solvent polarity on the rate of oxidation of 2-phenyl ethanol using TBAP

[Ph CH_2CH_2OH] : 1.202 x 10^{-2} mol dm^{-3}
[TBPP] : 5.30 x 10^{-4}- mol dm^{-3}
PT catalyst : TBAHS
Temp : 308K

Solvent	Dielectric constant	10^4 x k_{obs} s^{-1}	k_2 x 10^2 dm^3 mol^{-1} s^{-1}	Correlation
Benzene	2.27	1.44	1.20	0.9987
Toluene	2.40	1.51	1.25	0.9987
Chloroform	4.70	2.96	2.46	0.9992

3.33. Kinetics of the oxidation of aliphatic primary alcohols using phase transferred TBAP

10 ml of 0.005 mol dm^{-3} aqueous $KMnO_4$ was equilibrated with 10ml benzene containing 0.02 mol dm^{-3} TBAB. The tetrabutylammonium permanganate (TBAP) obtained in benzene was determined spectrophotometrically. The kinetics of the oxidation of aliphatic primary alcohols like butanol and hexanol with phase transferred MnO_4^- (TBAP) in benzene were studied by taking a fixed concentration of the substrate 1.202 x 10^{-2} mol dm^{-3} and the concentration of the oxidant to be 5.30 x 10^{-4} ,mol dm^{-3} so that pseudo first order condition were maintained. The reaction was carried out at 308K. The reaction was followed spectrophotometrically by

measuring of the absorbance of MnO_4^- ions at a λ_{max} of 528 nm. The pseudo-first order rate constants k_{obs} were computed from the linear plot of log (absorbance) of $QMnO_4$ versus time.

Table 3.17

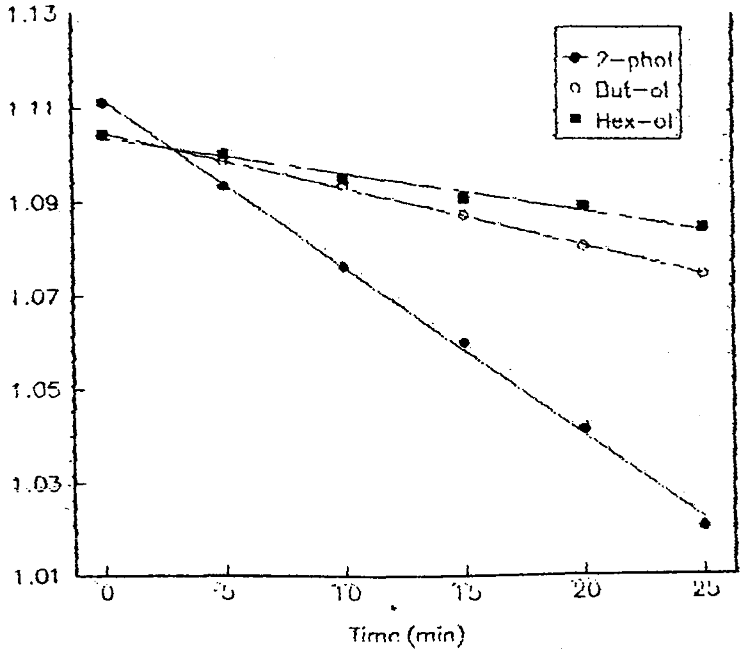
Kinetics of the oxidation of aliphatic primary alcohols using phase transferred TBAP

[Carbinol] : 1×10^{-2} mol dm^{-3}
Solvent : Benzene
PT catalyst : TBAB

[TBAP] = 5.32×10^{-4} mol dm^{-3}
Temp: 308 K

Carbinol	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ dm^3 mol^{-1} s^{-1}	Correlation
Butanol	4.606	3.8319	0.9991
Hexanol	2.9939	2.4907	0.9990
2-Phenyl ethanol	13.7	11.4	0.9992

Fig. 3.16. Oxidation of aliphatic and aromatic primary alcohols using phase transferred TBAP



3.34. Oxidation of 2-phenyl ethanol by $KMnO_4$ in aqueous acetic acid medium

The kinetics of the oxidation of 2-phenyl ethanol were studied in 10% aqueous acetic acid medium with a view to compare the investigation with that of the PTC oxidation in benzene.

3.35. Stoichiometry of the reaction

A reaction mixture containing a known concentration of 2-phenyl ethanol and a known concentration of $KMnO_4$ in 10% aqueous acetic acid was kept at room temperature for 6 hours (for the completion of the reaction). 2ml aliquot of the reaction mixture was pipetted out and the concentration of unreacted MnO_4^- ions were estimated iodometrically. The estimation was repeated at regular intervals of time to get concordant sulphate titre value; corresponding to a constant concentration of $KMnO_4$, the stoiochiometry of the reaction was determined.

3.36. Isolation of product of oxidation

The product of the reaction was determined as follows. A reaction mixture containing excess of $KMnO_4$ over 2-phenyl ethanol in 20% aqueous acetic acid was kept for 6 hours for the completion of the reaction. The unreacted $KMnO_4$ was decolorized by added sodium bisulphate followed by 50% HCl. The Manganese dioxide particles in the mixture were removed by filtration. The solution was extracted three or four times with ether. The ether layers were combined and to this aqueous sodium hydroxide solution was added. The sodium hydroxide layer was then separated and acidified with HCl. The product obtained is benzoic acid. The formation of benzoic acid as the product was confirmed by noting the melting point. Again a TLC was also conducted which again confirmed the formation of phenyl acetic acid.

3.37. Kinetic studies

The kinetics of the oxidation of 2-phenyl ethanol by $KMnO_4$ in 10% aqueous acetic acid was studied at different conditions of oxidant concentration, substrate concentration, at different temperatures. The effects of addition of salt, mineral acid and change of polarity of the medium on the rate of oxidation were also analyzed.

3.38. Effect of oxidant concentration on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid

The kinetics of the oxidation of 2-phenyl ethanol using $KMnO_4$ in 10% aqueous acetic acid were followed by taking a fixed amount of the substrate (1.002×10^{-2} mol dm^{-3} and varying the amount of oxidant ($KMnO_4$) from 3.27×10^{-4} mol dm^{-3} to 7.570×10^{-4} mol dm^{-3}. The pseudo- first order condition was maintained by keeping [carbinol] >> [$KMnO_4$]. The concentration of the unreacted $KMnO_4$ was determined iodometrically at regular intervals of time. The pseudo-first order rate constant were computed by the method of least squares from the linear plot of log [$KMnO_4$] versus time Fig. 3.17. The results are tabulated in Table.3.18

Fig. 3.17. Effect of [MnO_4^-] on oxdn. of 2-phol in 10% aq. acetic acid

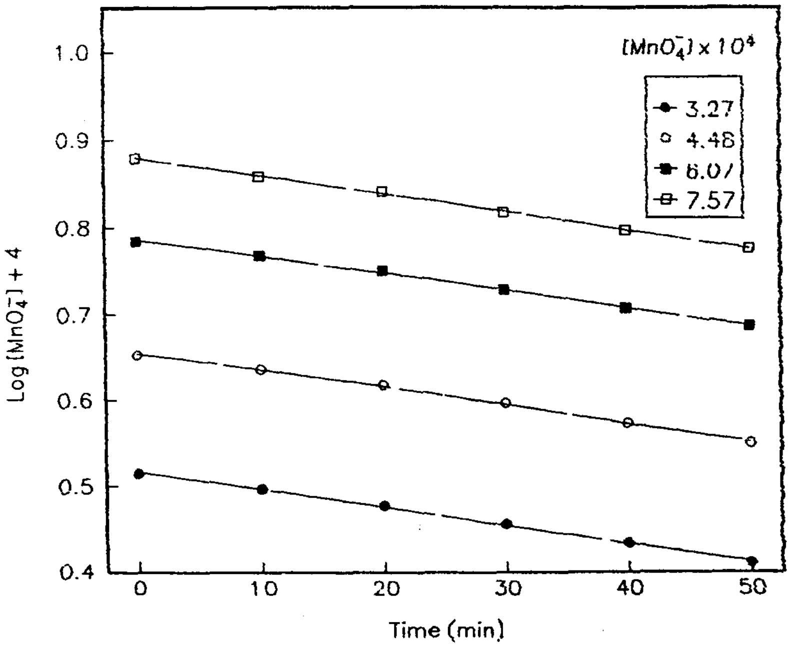


Table 3.18

Effect of oxidant concentration on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid

Medium : 10% aq. acetic acid (v/v) Temp: 308 K

$[KMnO_4] \times 10^4$ (mol dm^{-3})	[carbinol]x 10^2 mol dm^{-3}	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ $dm^3\ mol^{-1}\ s^{-1}$	Correlation
3.27	1.002	8.02	8.006	0.9994
4.48	1.002	7.83	7.81	0.9993
6.07	1.002	7.52	7.50	0.9992
7.57	1.002	7.86	7.85	0.9994

3.39. Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid

The effect of varying the concentration of 2-phenyl ethanol on the rate of oxidation was studied at a concentration range of 1×10^{-2} mol dm^{-3} to 3×10^{-2} mol dm^{-3}, of alcohol. The oxidant concentration was kept at 7.57×10^{-4} mol dm^{-3}, so that pseudo-first order condition were maintained. All other kinetic conditions were kept the same. From the pseudo-first order rate constant, the second order rate constant was calculated by dividing k_{obs} by [carbinol]. The results are presented in Table 3.19.

Fig. 3.18. Effect of 2-Phol on the oxdn. of 2-phol 10% in aq. acetic acid

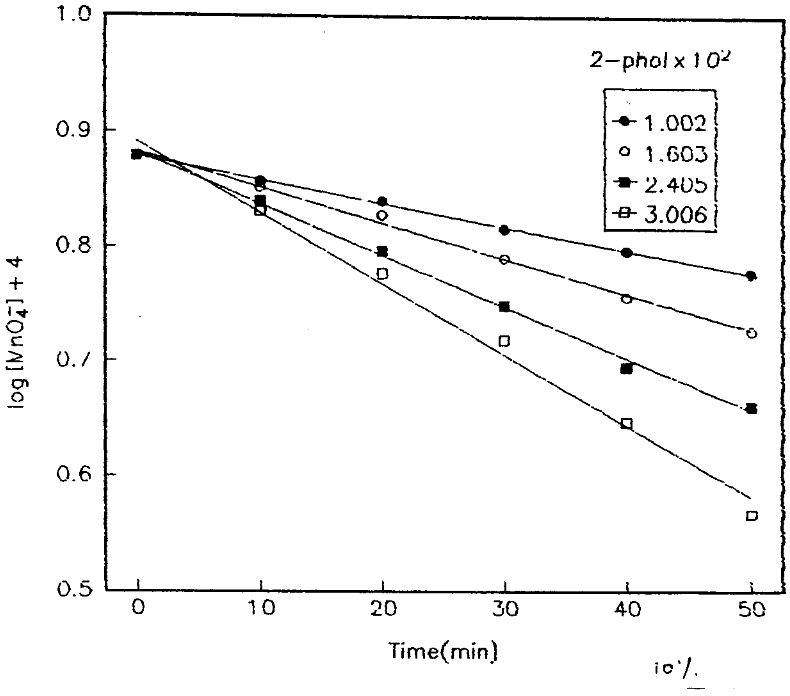


Table 3.19

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid

medium.10% aq. acetic acid　　　　Temp. 308 K

[KMnO$_4$]x10^4 (mol dm^{-3})	[carbinol]x 10^2 mol dm^{-3}	k$_{obs}$ x 10^5 s^{-1}	k$_2$ x 10^3 dm^3 mol^{-1} s^{-1}	Correlation
7.57	1.002	7.86	7.85	0.9994
7.57	1.6032	11.93	7.44	0.9978
7.57	2.4048	17.27	7.18	0.9985
7.57	3.006	23.75	7.90	0.9953

3.40. Influence of added salt on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

The effect of ionic strength was studied using NaCl in 10% aqueous acetic acid medium under pseudo first order condition. The concentration of the salt was varied from 1 x 10^{-2} mol dm^{-3} to 4 x 10^{-2} mol dm^{-3}. The concentration of the substrate was kept at 1.002 x 10^{-2} mol dm^{-3} and that of the oxidant of 7.57 x 10^{-4} mol dm^{-3}. All other conditions were kept the same.

Fig. 3.19. Effect of [NaCl] on the oxdn. of 2-phol in 10% aq. acetic acid

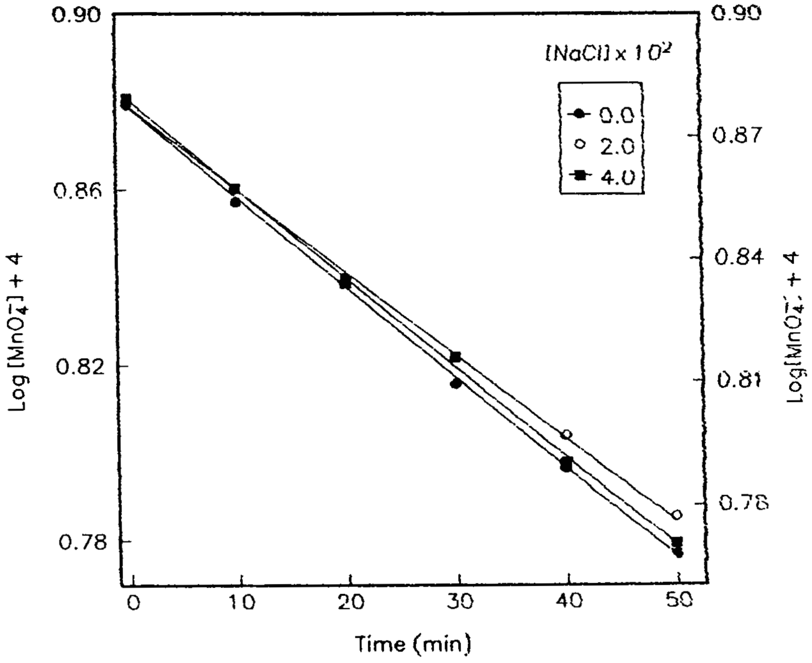


Table 3.20

Influence of added salt on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3}
[Carbinol] : 1.002×10^{-2} mol dm^{-3}

Medium : 10% aq. acetic acid (v/v)
Temp : 308 K

10^2 [NaCl] mol dm^{-3}	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ dm^3 mol^{-1} s^{-1}	Correlation
0.00	7.86	7.85	0.9994
0.01	7.79	7.77	0.9991
0.04	8.36	8.35	0.9995

3.41. Effect of added mineral acid (effect of H^+ ion) on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

The effect of H^+ ions on the rate of oxidation of 2-phenyl ethanol was studied by varying the concentration of H_2SO_4 from 2×10^{-2} mol dm^{-3} to 15×10^{-2} mol dm^{-3}, under pseudo-first order condition fig 3.20 The observed rate constants are tabulated in Table 3.21.

Fig. 3.20. Effect of $[H_2SO_4]$ on the oxdn. of 2-phol in 10% aq. acetic acid

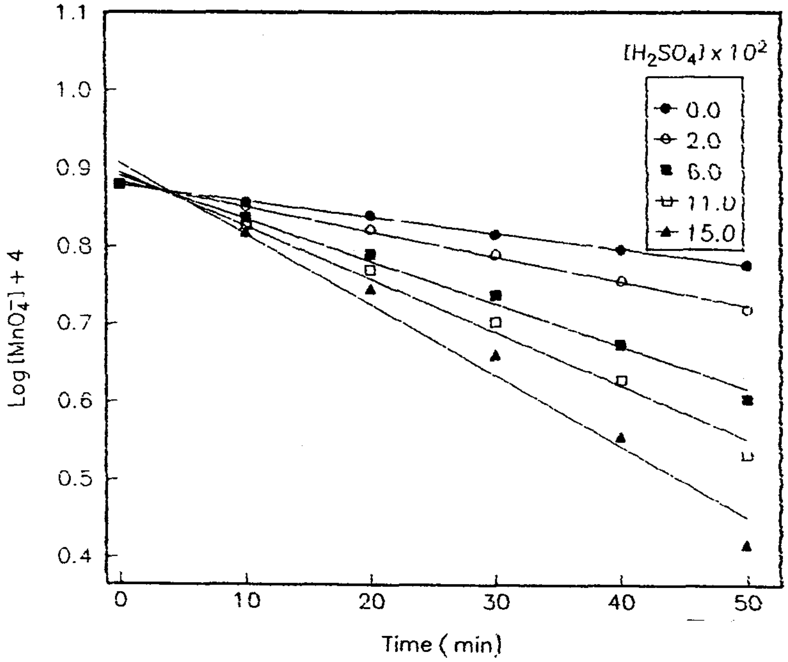


Table 3.21

Effect of added mineral acid (effect of H^+ ion) on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

$[KMnO_4]$: 7.57 x 10^{-4} mol dm^{-3} [2.phenyl ethanol] : 1.002 x 10^{-2} mol dm^{-3}
Medium : 10% aq. acetic acid (v/v) Temp. : 308 K

$[H_2SO_4] \times 10^2$ mol dm^{-3}	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ dm^3 mol^{-1} s^{-1}	Correlation
0.00	7.86	7.85	0.9994
2.00	12.28	12.22	0.9985
6.00	20.99	20.95	0.9951
11	26.25	26.20	0.9938
15	34.8	34.78	0.9889

3.42. Effect of polarity of the medium on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

The reaction was carried at different percentage of acetic acid composition in water (from 10-50%) at 303 K under pseudo-first 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 3.22 and Fig. 3.21.

Fig. 3.21. Effect of % composition of Acetic acid on the oxdn of 2-phol in aq. acetic acid

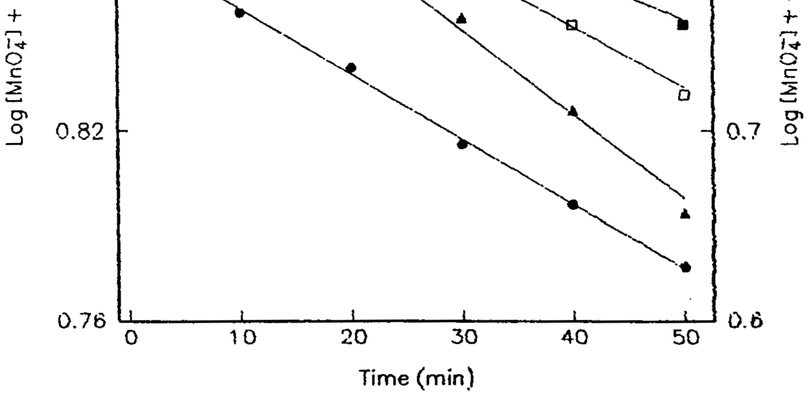


Table 3.22

Effect of polarity of the medium on the rate of oxidation of 2-phenyl ethanol in aq acetic acid using $KMnO_4$

[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3}
[2-phenyl ethanol] : 1.002×10^{-2} mol dm^{-3} Temp : 308 K

% of Acetic Acid (v/v)	10	20	30	40	50
Dielectric constant	67.85	61.0	53.02	47.0	39.8
$k_{obs} \times 10^5$ s^{-1}	7.86	8.09	9.44	12.28	17.04
$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}	7.85	8.08	9.42	12.25	17.008
Correlation	0.9994	0.9993	0.9991	0.9985	0.9972

3.43. Effect of temperature on the rate of oxidation of 2-phenyl ethanol in aq. acetic acid using $KMnO_4$

The effect of temperature on the kinetics of the oxidation of 2-phenyl ethanol in 10% acetic acid was studied by varying the temperature from 303 to 318 K under identical conditions. In all the cases pseudo-first order condition was maintained by keeping the [alcohol] >> [$KMnO_4$]. Fig : 3.22. The results are tabulated in Table 3.23.

Fig. 3.22. Effect of temp. on the rate of oxdn. of 2-phol in 10% aq. acetic acid using $KMnO_4$

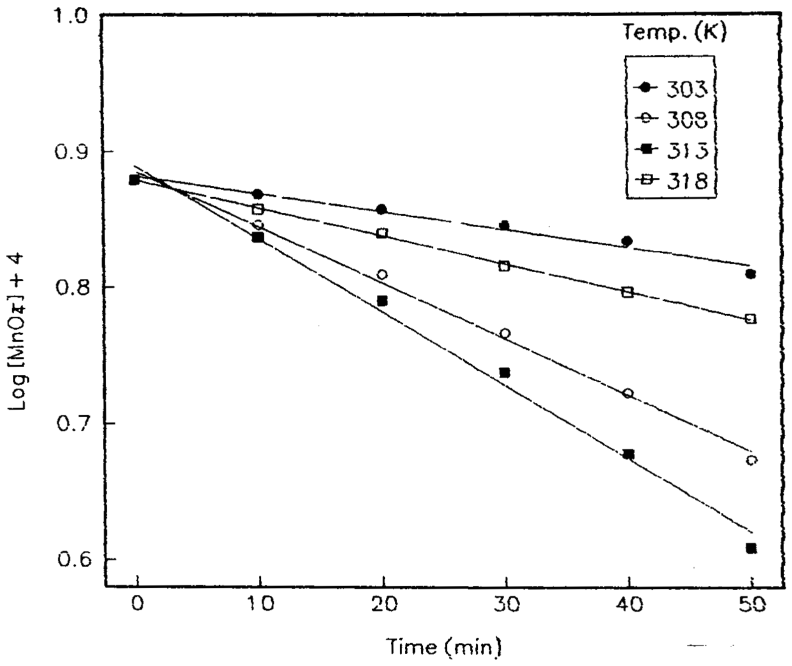


Table 3.23

Effect of temp. on the rate of oxdn. of 2-phol in 10% aq. acetic acid using $KMnO_4$

[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3} [2-phenyl ethanol] : 1.002×10^{-2} mol dm^{-3}
Medium : 10% aq. acetic acid (v/v)

Temp.	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ dm^3 mol^{-1} s^{-1}	Correlation
303	5.06	5.05	0.9967
308	7.86	7.85	0.9976
313	15.77	15.74	0.9959
318	20.61	20.57	0.9994

II. Saponification of benzyl benzoate in aqueous organic solvents in the presence of quaternary ammonium salts as phase transfer catalyst (homogeneous condition)

A known volume of the ester was dissolved in a known volume of organic solvent taken in the reaction vessel which was kept in the thermostat. Required quantity of NaOH was transferred to the ester solution to start the reaction so that the concentrations were 0.04 M with respect to ester and 0.05 M with respect of NaOH. 5 ml samples of ester solutions were pipetted out at known intervals of time into 10 ml 0.03 M HCl and the excess acid titrated against 0.1 M NaOH using phenolphthalein as the indicator. The experiment was conducted at four different temperatures, with and without the use of PTC.

The reaction followed second order kinetics and the rate constants were calculated using the equation:

$$k = \frac{2.303}{t\,(a - b)} \log \frac{b\,(a - x)}{a\,(b - x)}$$

TABLE 3.1.a

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.4	--
1800	8.1	2.6663
2400	8.3	2.7017
3000	8.45	2.6301
3600	8.6	2.6269
4200	8.75	2.6747
α	9.65	

k= 5.1944 x 10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 3.1.b.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.4	
1800	8.35	3.8541
2400	8.55	3.7142
3000	8.75	3.7445
3600	8.9	3.7000
4200	9.05	3.7584
α	9.65	

k = 7.3284×10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 3.1.c

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3 mol^{-1} sec^{-1}$
0	7.4	
1800	8.5	4.6626
2400	8.75	4.6807
3000	8.95	4.6909
3600	9.1	4.6512
4200	9.2	4.5089
α	9.65	

k = 9.0552×10^{-7} lit. $mol^{-1} sec^{-1}$

TABLE 3.1.d

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.4	
1800	8.8	6.6029
2400	9.05	6.5773
3000	9.2	6.3125
3600	9.35	6.4743
4200	9.45	6.5763
α	9.65	

$k = 1.2705 \times 10^{-6}$ lit. $mol^{-1}sec^{-1}$

TABLE 3.1.e

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M
[NaOH] = 0.0525 M
[TBAB] = 0.0601M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.5	
1200	8.1	3.4909
1800	8.3	3.2632
2400	8.5	3.2426
3000	8.7	3.3345
3600	8.85	3.3227
4200	8.95	3.2053
α	9.65	

k = 6.3902 x 10^{-7} lit. mol^{-1}sec^{-1}

TABLE 3.1.f

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester]	= 0.0408 M	Solvent	= 60% Acetonitrile
[NaOH]	= 0.0525 M	[HCl]	= 0.0976 M
[TBAB]	= 0.0601M	Temp.	= 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.5	
1200	8.3	4.8948
1800	8.5	4.3235
2400	8.7	4.1681
3000	8.9	4.2297
3600	9.05	4.2153
4200	9.15	4.0902
α	9.65	

k = 8.2090 x 10^{-7} lit. mol^{-1}sec^{-1}

TABLE 3.1.g

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M	Solvent = 60% Acetonitrile
[NaOH] = 0.0525 M	[HCl] = 0.0976 M
[TBAB] = 0.0601M	Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} $dm^3\ mol^{-1}\ sec^{-1}$
0	7.5	
1800	8.65	5.2290
2400	8.9	5.2872
3000	9.05	5.0584
3600	9.2	5.0909
4200	9.3	5.0105
α	9.65	

k = 1.0024 x 10^{-6} lit. $mol^{-1}sec^{-1}$

TABLE 3.1.h.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M
[NaOH] = 0.0525 M
[TBAB] = 0.0601M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.5	
1800	8.9	7.0496
2400	9.15	7.1578
3000	9.3	7.0147
3600	9.4	7.5028
4200	9.5	7.1539
α	9.65	

$k = 1.4007 \times 10^{-6}$ lit. $mol^{-1}sec^{-1}$

TABLE 3.1.i

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	
1200	8.45	4.5364
1800	8.7	4.2500
2400	8.9	4.0507
3000	9.1	4.0668
3600	9.25	4.0176
α	9.9	

$k = 7.8946 \times 10^{-7}$ lit. $mol^{-1} sec^{-1}$

TABLE 3.1.j.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ dm^3 mol^{-1} sec^{-1}
0	7.65	
1800	8.8	4.8025
2400	9.0	4.5412
3000	9.2	4.5533
3600	9.35	4.5166
α	9.9	

$k = 8.8721 \times 10^{-7}$ lit. $mol^{-1} sec^{-1}$

TABLE 3.1.k

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	
1800	8.95	5.7202
2400	9.2	5.6916
3000	9.4	5.7588
3600	9.5	5.4549
α	9.9	

$k = 1.0901 \times 10^{-6}$ lit. $mol^{-1} sec^{-1}$

TABLE 3.1.1.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	
1800	9.1	6.7781
2400	9.3	6.3861
3000	9.5	6.5459
3600	9.6	6.2917
α	9.9	

$k = 1.2528 \times 10^{-6}$ lit. $mol^{-1} sec^{-1}$

TABLE 3.1.m.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M
[NaOH] = 0.0510 M
[TBAB] = 0.0620 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.8	—
1800	8.85	4.5992
2400	9.05	4.4330
3000	9.25	4.5234
3600	9.4	4.5509
α	9.9	

k = 8.7241 x 10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 3.1.n.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M
[NaOH] = 0.0510 M
[TBAB] = 0.0620 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.8	–
1800	8.9	4.9047
2400	9.1	4.7114
3000	9.3	4.811
3600	9.45	4.8615
α	9.9	

k = 9.2936 x 10^{-7} lit. mol^{-1}sec^{-1}

TABLE 3.1.o.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M
[NaOH] = 0.0510 M
[TBAB] = 0.0620 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.8	
1200	8.85	6.8988
1800	9.1	6.2818
2400	9.3	6.0139
3000	9.5	6.2842
3600	9.6	6.0435
α	9.9	

k = 1.1846 x 10^{-6} lit. mol^{-1}sec^{-1}

TABLE 3.1.p.

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M	Solvent = 60% 1,4-dioxane
[NaOH] = 0.0510 M	[HCl] = 0.096 M
[TBAB] = 0.0620 M	Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.8	
1800	9.25	7.5390
2400	9.45	7.2922
3000	9.6	7.2523
3600	9.7	7.2105
α	9.9	

$k = 1.4114 \times 10^{-6}$ lit. $mol^{-1}sec^{-1}$

III. Yield Study

Saponification of benzyl benzoate in benzene using PTC (heterogeneous condition)

The yield study was carried out by preparing a 50 ml system which contained 5 ml benzyl benzoate, 20 ml benzene, 25 ml NaOH and TBAB. The contents were taken in a flat bottomed flask fitted with a reflux condenser and stirred using a magnetic stirrer.

When the prefixed time has reached the stirring was stopped and the reaction was arrested using HCl. The contents were then poured into a separating funnel and shaken with ether. The ether layer was separated and then shaken with NaOH. The NaOH layer was then collected, acidified with HCl and the precipitated benzoic acid was filtered, dried and weighed.

The experiment was repeated with different concentrations of NaOH, TBAB, and at different stirring time.

Saponification of benzyl benzoate in benzene using PTC (heterogeneous condition)

Time Hours	Amount of Ester taken	Amount of NaOH taken	Amount of TBAB taken	Amount of Benzene taken	Weight of Benzoic acid obtained
6	5 ml (1.0223 M)	25 ml (5 M)	2 g (0.2481 M)	20 ml	1.9278 g (61.83%)
"	"	"	1.5 g (0.18612 M)	"	1.7995 g (57.71%)
"	"	"	1 g (0.12408 M)	"	1.6545 g (53.06%)
"	"	"	0.5 g (0.06204 M)	"	0.9322 g (29.90%)

Saponification of benzyl benzoate in benzene using PTC (heterogeneous condition)

Time Hours	Amount of Ester taken	Amount of NaOH taken	Amount of TBAB taken	Amount of Benzene taken	Weight of Benzoic acid obtained
12	5 ml (1.0223 M)	25 ml (5 M)	2 g (0.2481 M)	20 ml	2.2088 g (70.84%)
"	"	"	1.5 g (0.18612 M)	"	20.2040 g (70.69%)
"	"	"	1 g (0.12408 M)	"	1.4516 g (46.55%)
"	"	"	0.5 g (0.06204 M)	"	0.80 g (25.65%)

CHAPTER IV

RESULTS AND DISCUSSION

In this Chapter the experimental results on the kinetic investigation on the rate of oxidation of 2-phenyl ethanol in benzene and various other organic solvents using different phase transfer catalysts are presented and discussed. The studies on the oxidation of 2-phenyl ethanol using permanganate in aqueous acetic medium have been carried out and is given separately. A comparison of the rate data and the data of the activation parameters of the reaction taking place in the presence of the catalyst and the one taking place in aqueous acetic acid without the use of catalyst reveals the effect of phase transfer catalytic activity.

4.1. Oxidation of 2-phenyl ethanol using phase transferred permanganate using TBPB, TBAB and TBAHS in benzene

The experimental results on the kinetic studies on the oxidation of 2-phenyl ethanol in benzene using phase transferred permanganate with tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogensulphate

(TBAHS) as phase transfer catalysts are presented in this section. The oxidation of 2-phenyl ethanol can also be carried out in heterogeneous conditions, using a benzene solution of 2-phenyl ethanol mixed with aqueous permanganate and appropriate amount of phase transfer catalyst . Here the oxidant was first phase transferred into an organic solvent and to this a known concentration of 2-phenyl ethanol was added. Hence here the rate measurements were done in a homogeneous condition, which enabled the measurements to be carried out more conveniently. Organic solvents, like benzene, toluene and chloroform were used for the studies of the oxidation of 2-phenyl ethanol using phase transferred permanganate. The solvent effects in relation to the properties of the solvent like dielectric constant are presented and discussed in this chapter.

4.2. Stoichiometry and product of oxidation

The stoichiometry for the reaction was carried out under the condition that the concentration of the oxidant was taken in excess of the concentration of the alcohol, using TBPB, TBAB and TBAHS as the catalysts. The ratio of [2-phenyl ethanol] : [$QMnO_4$] was found to be (1:2).

The product of the reaction was found to be phenyl acetic acid from the melting point values and TLC analysis, with respect to all the three catalysts(TBPB,TBAB and TBAHS) used.

4.3. Kinetic studies

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

The oxidation of 2-phenyl ethanol were carried out with different initial concentration of the oxidant using TBPB, TBAB and TBAHS as PT catalyst and in all the cases the rates were measured under the condition [2-phenyl ethanol] $\geq$ [$QMnO_4$]. The plot of log(absorbance) of $QMnO_4$ versus time gave a 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 studies are given in Table 4.1.

Table 4.1

Effect of oxidant concentration on the rate of oxidation of 2-phenyl ethanol using TBPB, TBAB and TBAHS as phase transfer catalyst

$[PhCH_2\text{-}CH_2OH] = 1.202\times10^{-2}$ mol dm^{-3} Solvent = Benzene
Temp. = 308K

Oxidant($QMnO_4$)			$k_{obs}\times 10^4$ s^{-1}	$k_2\times 10^2$ dm^3 mol^{-1} s^{-1}	Corr:
TBPB$\times10^4$ (mol dm^{-3})	TBAB $\times10^4$ (mol dm^{-3})	TBAHS$\times10^4$ (mol dm^{-3})			
4.77			1.33	1.11	0.9931
5.30			1.30	1.08	0.9994
6.36			1.14	0.95	0.9997
7.24			1.01	0.85	0.9990
	4.77		1.47	1.22	0.9930
	5.32		1.37	1.14	0.9992
	6.40		1.18	0.986	0.9997
	7.30		1.04	0.865	0.9997
		4.73	1.54	1.28	0.9993
		5.30	1.44	1.20	0.9987
		6.43	1.51	1.25	0.9998
		7.30	1.59	1.32	0.9995

4.4. Effect of substrate concentration on the rate of oxidation of 2-phenyl ethanol using TBPB,TBAB and TBAHS as catalyst

The measurements of the rate of the oxidation of 2-phenyl ethanol were carried out with different initial concentration of 2-

phenyl ethanol. The observed rate constant k_{obs} increased linearly with the increase in the concentration of alcohol with all the three catalysts used to phase transfer the oxidant. Again the second order rate constants k_2 obtained by dividing k_{obs} by the concentration of the alcohol was almost constant indicating first order behaviour with respect to the concentration of the alcohol.

Table 4.2

Effect of substrate concentration on the rate of oxidation of 2-phenyl ethanol using TBPB,TBAB and TBAHS as phase transfer catalyst

Solvent = Benzene Temperature = 308 K

Oxidant ($QMnO_4$) mol dm^{-3}			[2-Phol] x 10^2 mol dm^{-3}	$\bar{k}_{Obs}$x10^4 s^{-1}	k_2 x 10^2 dm^3 mol^{-1} s^{-1}	Corr:
[TBPP]x 10^4	[TBAP] x 10^4	[TBAP]x 10^4				
4.77			1.202	1.30	1.08	0.9997
5.30			2.003	2.53	1.26	0.9942
6.36			3.005	3.20	1.06	0.9963
7.24			4.007	4.18	1.04	0.9954
	4.77		1.202	1.37	1.14	0.9992
	5.32		2.003	2.60	1.29	0.9983
	6.40		3.005	3.29	1.09	0.9981
	7:30		4.007	4.48	1.11	0.9987
		4.73	1.202	1.44	1.20	0.9987
		5.30	2.003	3.19	1.59	0.9983
		6.43	3.005	3.69	1.23	0.9975
		7.30	4.007	5.17	1.29	0.9973

The first order dependence of the alcohol concentration is further confirmed by the double logarithmic plot of log(k_{obs}) vs log[alcohol], which is linear with a slope almost equal to unity(figure 4.1, 4.2, 4.3). The above table indicates that TBAHS is a better catalyst than TBPB and TBAB for these type of oxidations.

Fig. 4.1. Order with respect to 2-phol using TBPB

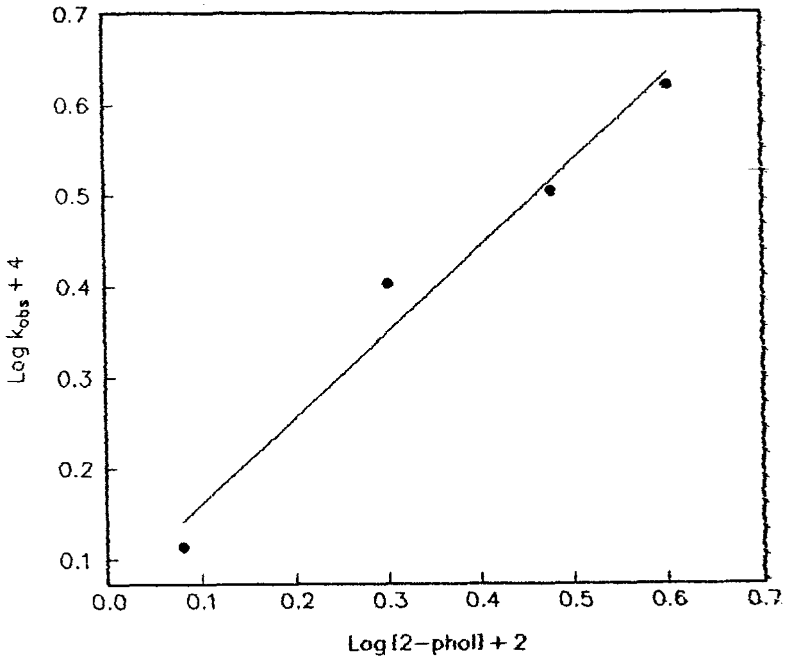


Fig. 4.2. Order with respect to 2-phol using TBAB

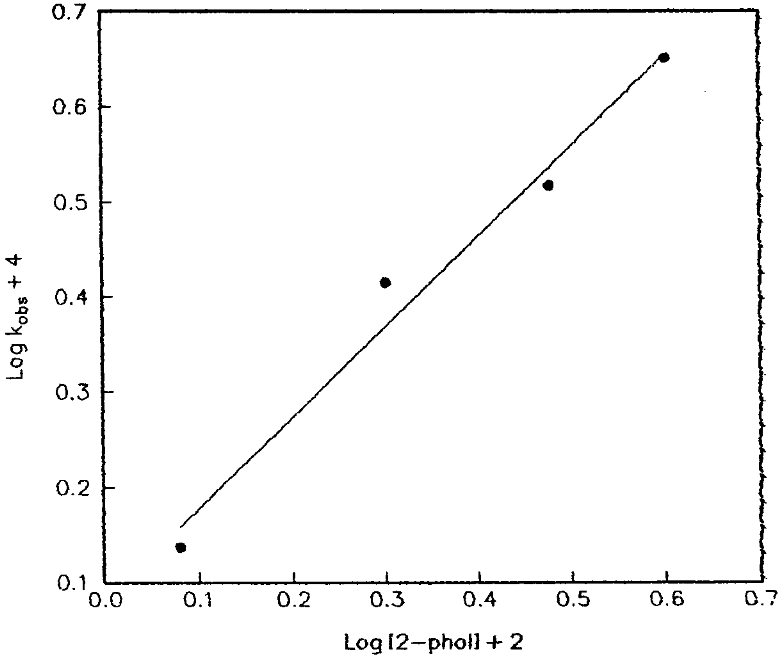
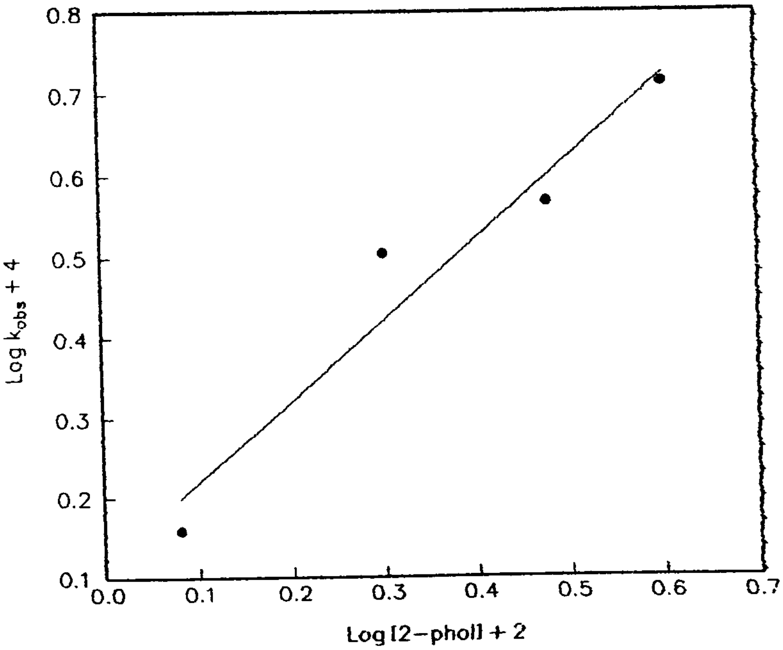


Fig. 4.3. Order with respect to 2-phol using TBAHS



The double reciprocal plots (Lineweaver-Burke-Plot) of $1/k_{obs}$ vs. 1/[2-phenyl ethanol], fig. 4.4, 4.5, 4.6 are found to be linear passing through the origin in all the cases, where TBPB, TBAB and TBAHS were used as the catalyst. This rules 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.

Fig. 4.4. Lineweaver-Burke Plot of $1/k_{obs}$ vs 1/[2-phol] using TBPB

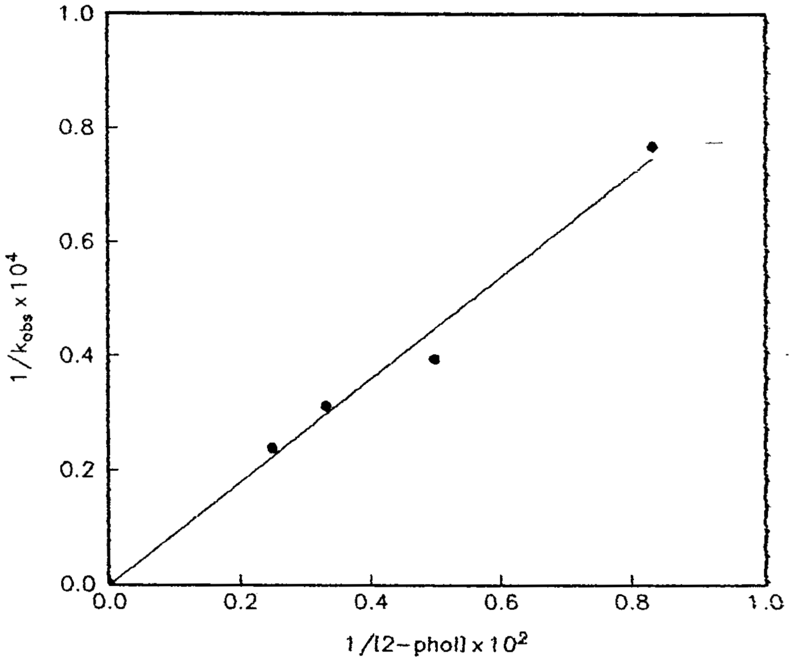


Fig. 4.5. Lineweaver-Burke Plot of 1/k$_{obs}$ vs 1/[2-phol] using TBAB

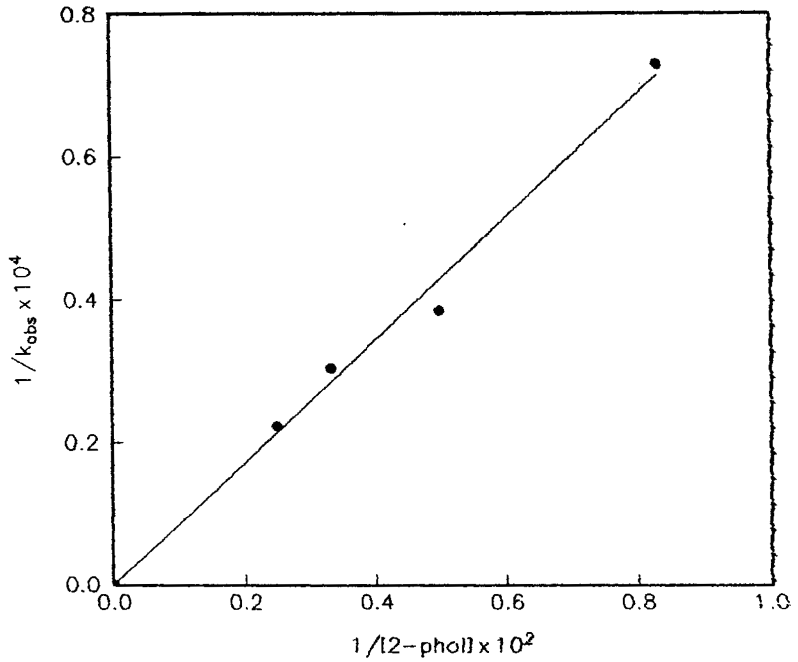
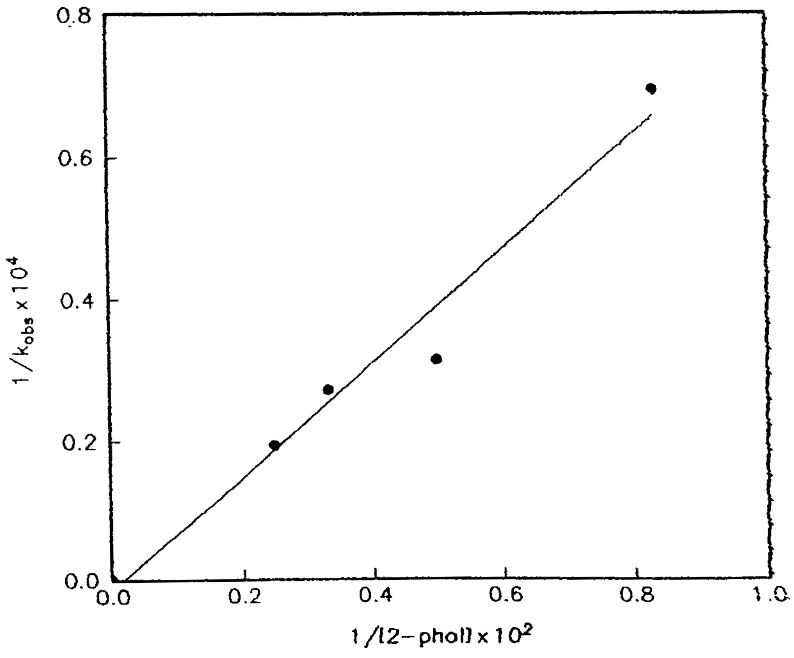


Fig. 4.6. Lineweaver-Burke Plot of 1/k$_{obs}$ vs 1/[2-phol] using TBAHS



4.5. Effect of dielectric constant of the solvent on the rate of oxidation of 2-phenyl ethanol.

The influence of various solvents with different dielectric constants on the rate of oxidation of 2-phenyl ethanol is given in Table 4.3.

Table 4.3

Effect of solvent on the rate of oxidation of 2-phenyl ethanol

$QMnO_4$	: 5.30×10^{-4} mol dm^{-3}
[2-phenyl ethanol]	: 1.202×10^{-2} mol dm^{-3}
Temperature	: 308 K

Solvent	Dielectric Constant	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1} Catalyst TBPB	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1} Catalyst TBAB	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1} Catalyst TBAHS
Benzene	2.27	1.08	1.14	1.20
Toluene	2.40	1.16	1.21	1.25
Chloroform	4.70	1.75	2.11	2.46

Fig. 4.7. Plot of log(k2) vs 1/D using TBPB

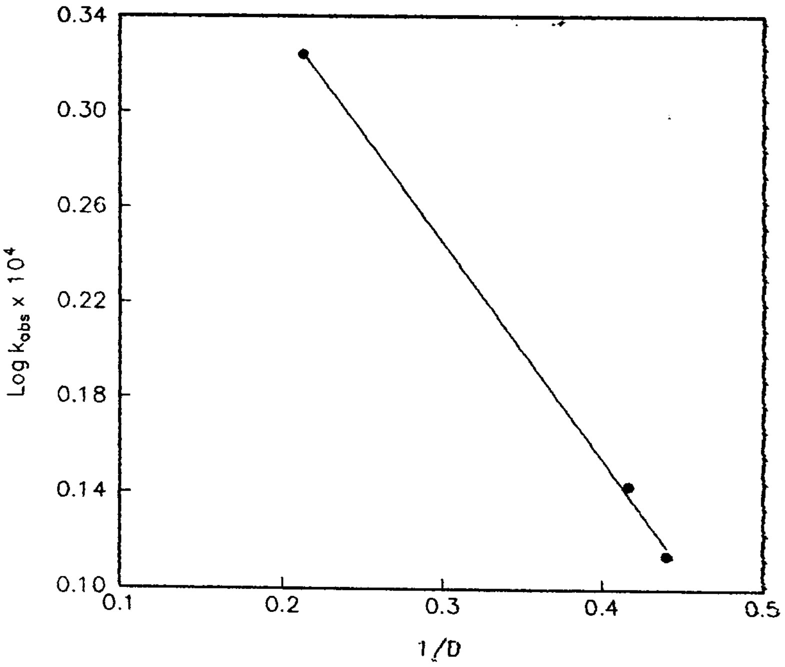


Fig. 4.8. Plot of log(k2) vs 1/D using TBAB

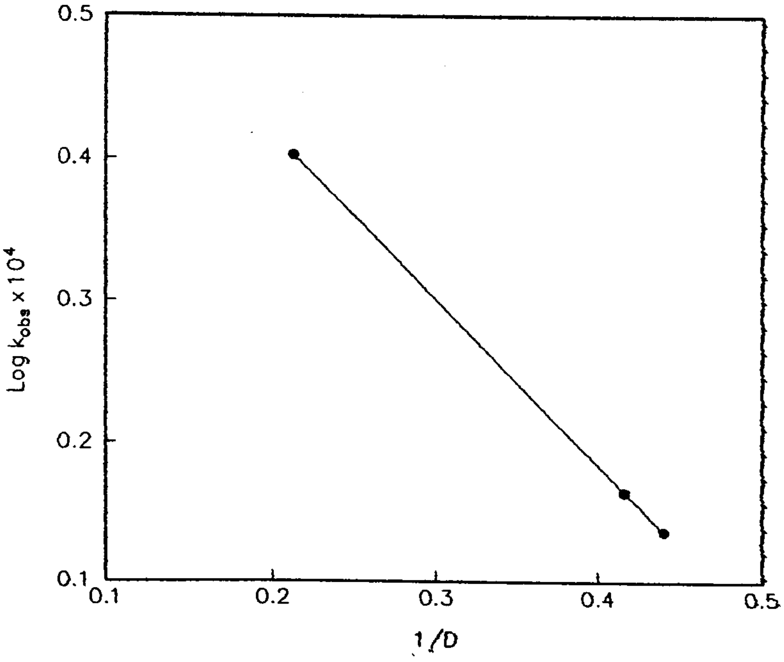
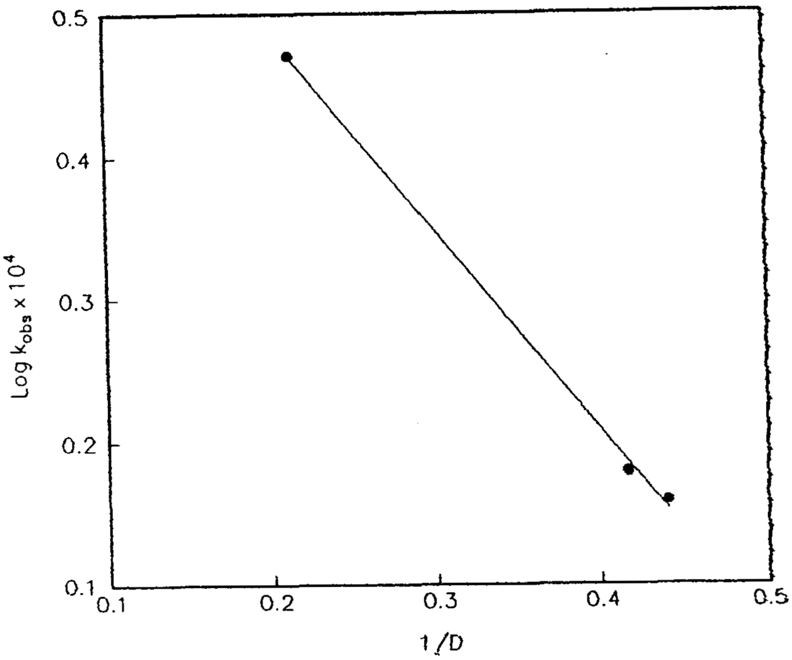


Fig. 4.9. Plot of log(k_2) vs 1/D using TBAHS



The results represented in the table show that the rate of oxidation increases with increase in the dielectric constant of the organic solvent used. The order of reactivity of the oxidation of 2-phenyl ethanol in various organic solvents are as follows $CHCl_3$ > $C_6H_5CH_3$ >C_6H_6. The plot of log k_2 Vs 1/D of the solvent fig.4.7,4.8,4.9 was linear with a negative slope. This indicates that there is an interaction between an anion and a dipole according to the Amis equation[168,169]. The possibility of greater charge separation in the transition state compared to the ground state is also evident.

4.6. Effect of temperature on the rate of oxidation of 2-phenyl ethanol

The effect of temperature on the rate of oxidation of 2-phenyl ethanol in benzene using TBPB, TBAB and TBAHS as PT catalyst were studied at different temperatures ranging from 303 to 318K. The activation parameters for the oxidation of 2-phenyl ethanol were determined using the Arrhenius equation $k=Ae^{-Ea/RT}$. The Plot of log k_2 Vs. 1/T and log k_2/T Vs 1/T were used for this purpose Fig.4.10 4.11, 4.12; 4.13, 4.14, 4.15 In all the cases good linear fits were obtained. The effect of temperature on the rate of oxidation 2-phenyl ethanol using TBPB, TBAB and TBAHS as phase transfer catalysts are given in Table: 4.4. The results show that the rate of oxidation increases with an increase in temperature.

Fig. 4.10. Plot of log k_2 vs 1/T using TBPB

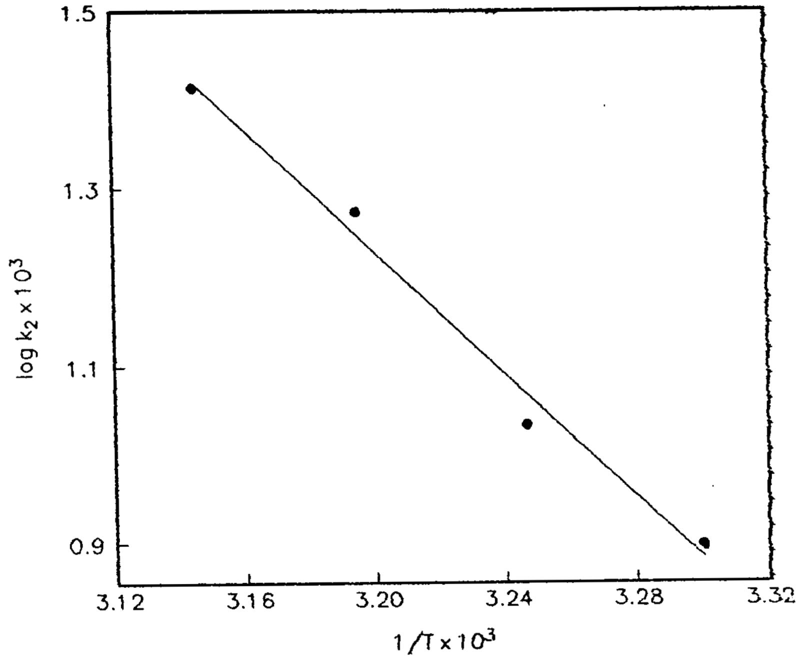


Fig. 4.11. Plot of log k_2 vs. 1/T using TBAB

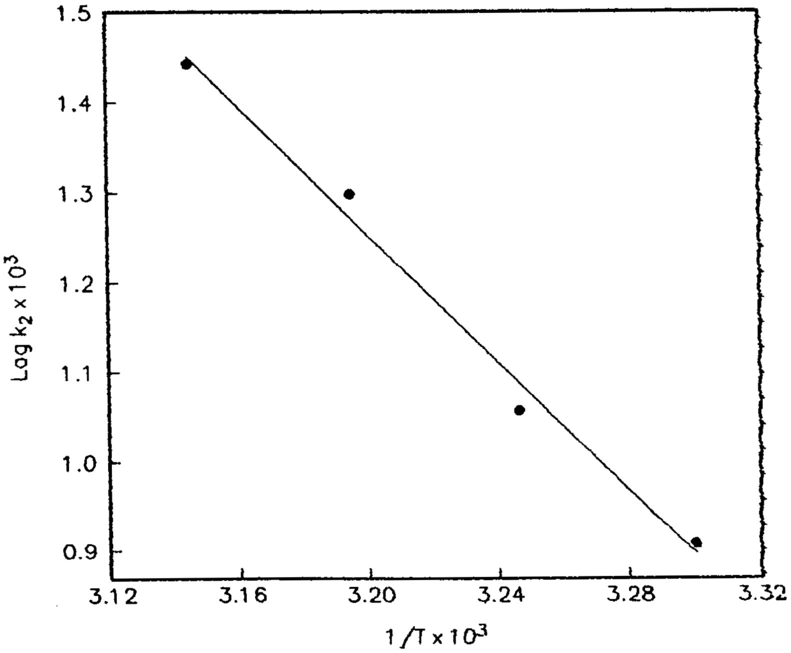


Fig. 4.12. Plot of log k_2 vs. 1/T using TBAHS

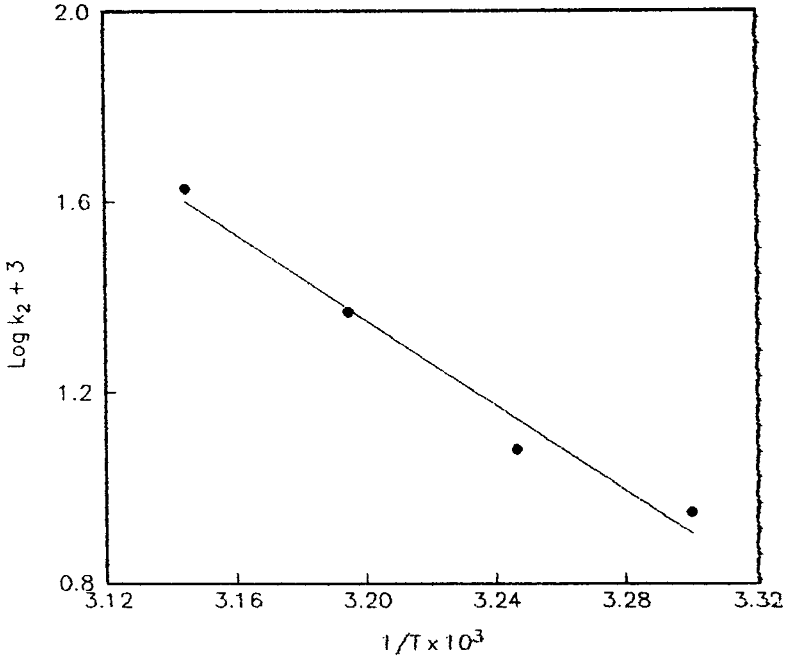


Fig. 4.13. Plot of log (k_2/T) vs. 1/T using TBPB

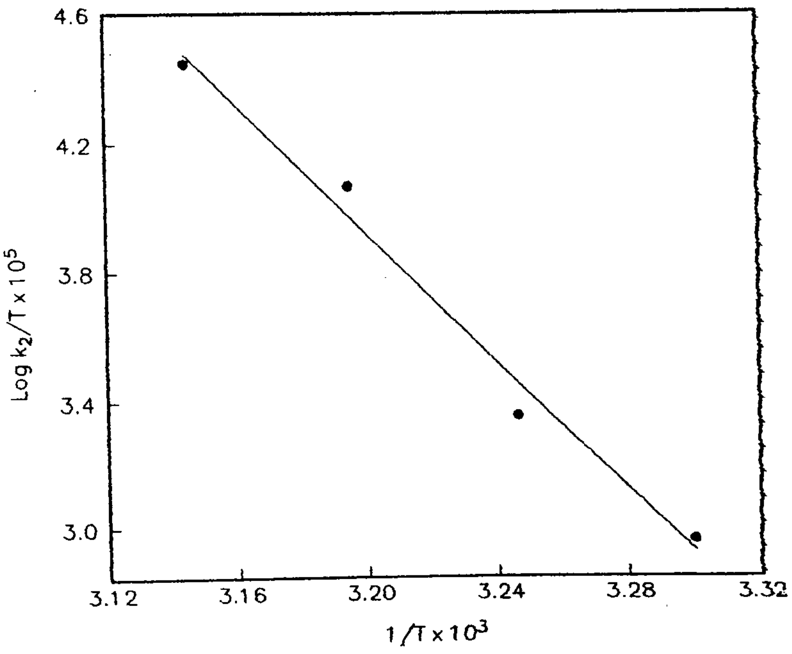


Fig. 4.14. Plot of log (k_2/T) vs. 1/T using TBAB

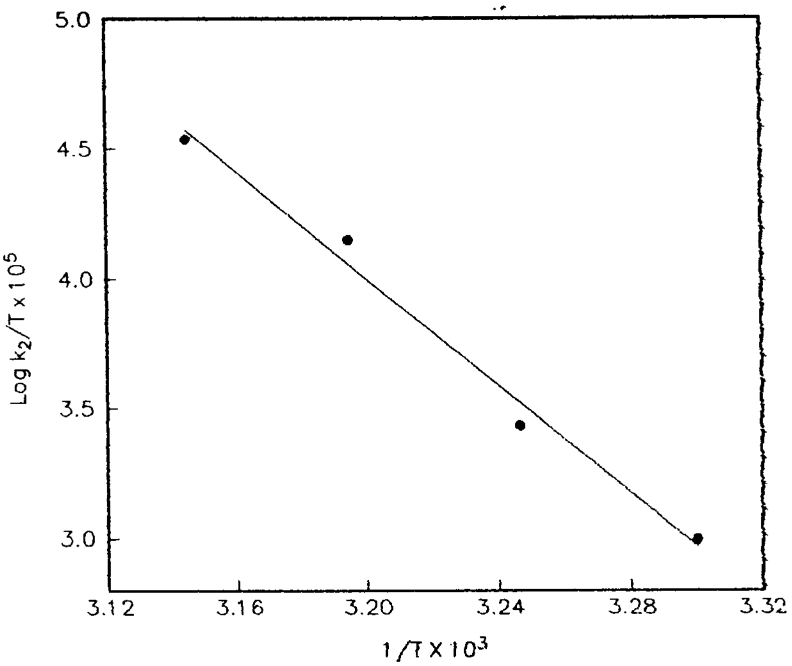


Fig. 4.15. Plot of log (k_2/T) vs. 1/T using TBAHS

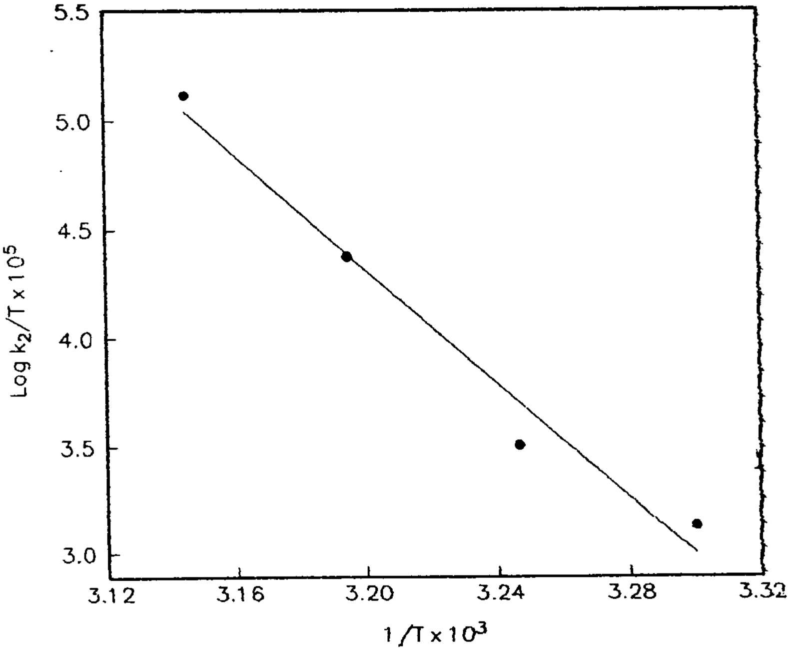


Table: 4.4.

Effect of Temperature on the Oxidation of 2-Phenyl Ethanol

Temp:	TBPB				TBAB				TBAHS			
	303	308	313	318	303	308	313	318	303	308	313	318
$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}	0.7887	1.08	1.88	2.60	0.8079	1.14	1.99	2.77	0.8877	1.20	2.34	4.24
Corr:	.9998	.9994	.9974	.9975	.9988	.9992	.9980	.9960	.9983	.9987	.9984	.9974

Table 4.5

Activation parameters for the oxidation of 2-phenyl ethanol in organic solvents using PTC

PT Catalyst	$k_2 \times 10^2$ $dm^3\ mol^{-1}\ s^{-1}$	Ea kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ K^{-1}Jmol^{-1}	$\Delta G^{\#}$ kJmol^{-1}
TBPB	0.7887	66.3142	63.7427	75.01794	86.4731
TBAB	0.8079	68.2653	65.6823	68.4160	86.4123
TBAHS	0.8877	85.8615	83.2690	9.7950	86.2368

In the case of 2-penyl ethanol k_2 increases from 0.7887x10^{-2}mol dm^{-3} to 2.60x10^{-2} mol dm^{-3} when the temp. changes from 303 to 318K, when TBPB was used as the phase transfer catalyst. Similarly the values of k_2 increases from 0.8079x10^{-2} mol dm^{-3} to 2.77 x10^{-2} mol dm^{-3} and 0.8877x 10^{-2} to 4.24 x10^{-2} mol dm^{-3} when TBAB and TBAHS were used as the phase transfer catalyst.

The activation parameters computed for 2-phenyl ethanol with TBPB, TBAB and TBAHS as phase transfer catalyst are given in Table: 4.5.

4.7. Kinetics of the oxidation of 2-phenyl ethanol in aqueous acetic acid medium

The results obtained on the kinetics of the oxidation of 2-phenyl ethanol 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.

4.8. Stoichiometry and the product of the reaction

The oxidation of 2-phenyl ethanol in 20%aqueous acetic acid using $KMnO_4$ was carried out. The ratio of [alcohol] : [$KMnO_4$] = 1:2 was obtained.

The product of the oxidation was ascertained to be benzoic acid. This was confirmed by noting the melting point. The TLC analysis further confirmed the product of oxidation to be benzoic acid.

4.9. Kinetic study

The rate constants for the oxidation of 2-phenylethanol in aqueous acetic acid with $KMnO_4$ were determined under different experimental conditions by varying the oxidant concentration, the substrate concentration, ionic strength, different solvent composition, temperature and the effect of added mineral acid are presented in this section.

4.10. Effect of oxidant concentration on the rate of oxidation of 2-phenyl ethanol

The plots of log [$KMnO_4$] vs time are linear showing first order dependence on the oxidant concentration. Further the pseudo-first order rate constant k_{obs} is independent for the initial concentration of $KMnO_4$. The results are represented in Table 4.6

Table 4.6

Effect of oxidant concentration on the rate of oxidation of 2-phenyl ethanol

Medium 10% aq .acetic acid (v/v) : Temp 308K

10^4 x $KMnO_4$ mol dm^{-3}	[2-phol]x10^2 mol dm^{-3}	k_{obs} x10^5 s^{-1}	k_2 x 10^3 dm^3 mol^{-1} s^{-1}	Corr:
3.27	1.002	8.02	8.006	0.9994
4.48	1.002	7.83	7.81	0.9993
6.07	1.002	7.52	7.50	0.9992
7.57	1.002	7.86	7.85	0.9994

4.11. Effect of substrate concentration on the rate of oxidation of 2-phenyl ethanol in 10%aq.acetic acid(v/v)

The rate constants determined under the experimental conditions were directly proportional to the concentration of the alcohol. The second order rate constants (k_2) obtained by dividing k_{obs} with [alcohol] are almost constant. The first order dependence of the alcohol concentration is further confirmed by the plot of the log kobs vs log[alcohol], which is linear and passing through the origin, Fig.39. The results are represented in Table 4.6.

The Plot of the $1/k_{obs}$ vs. 1/[alcohol] is also linear passing through the origin which rules out the formation of long-lived intermediate fig.40. 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 alcohol with oxidant.

Table 4.7

Effect of substrate concentration on the rate of oxidation of 2-phenyl ethanol in 10%aq.acetic acid(v/v)

Medium 10% aq .acetic acid (v/v) Temp : 308K

$KMnO_4 x10^4$ mol dm^{-3}	[2-phol]x 10^2 mol dm^{-3}	$k_{obs}x10^5$ s^{-1}	k_2 x10^3 dm^3mol^{-1} s^{-1}	Corr:
7.57	1.002	7.86	7.85	0.9994
7.57	1.6032	11.93	7.44	0.9978
7.57	2.4048	17.27	7.18	0.9989
7.57	3.006	23.75	7.90	0.9953

Fig. 4.17. Order w.r.t. 2-phol in 10% aq. acetic acid

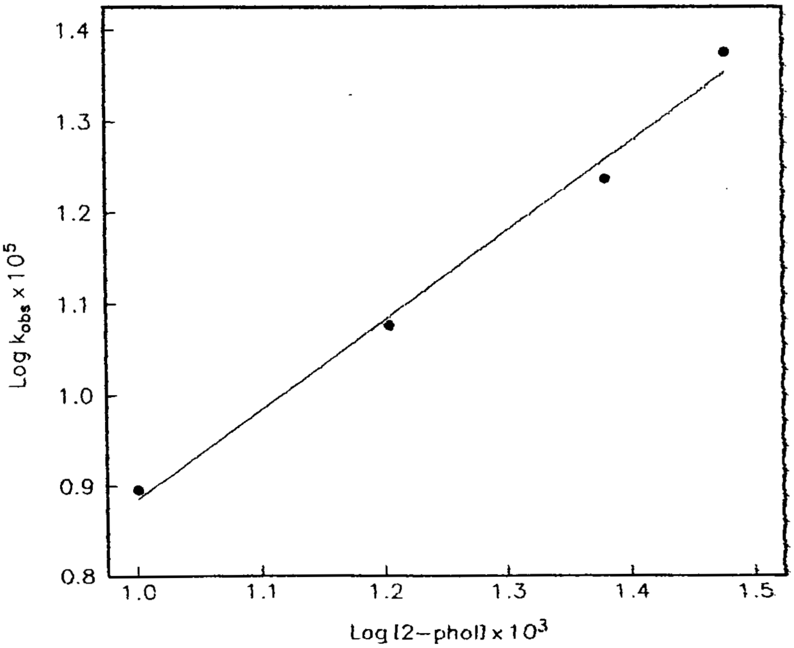
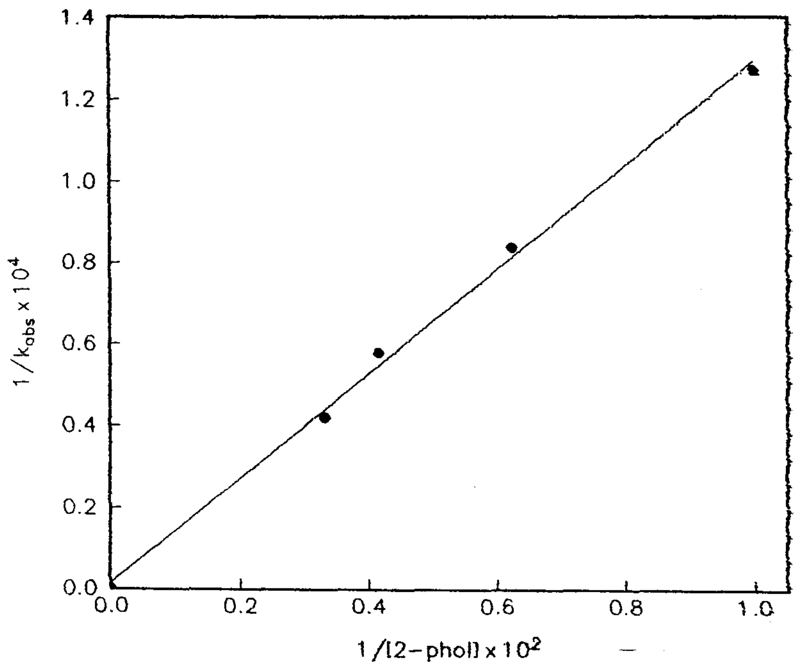


Fig. 4.18. **Lineweaver-Burke plot of $1/k_{obs}$ vs. 1/[2-phol] in 10% aq. acetic acid**



4.12. Influence of ionic strength on the rate of oxidation of 2-phenyl ethanol - influence of added salt

The table given below shows that the addition of salt did not produce any primary kinetic salt effect. The rate constant remained practically constant with different concentrations of NaCl added. It suggests the absence of an ion-ion type interaction and hence the possibility could be that of an ion and a dipole or that between two dipolar entities.

Table.4.8

Influence of ionic strength on the rate of oxidation of 2-phenyl ethanol - influence of added salt

[KMnO4 : 7.57×10^{-4} mol dm^{-3} [2-phol] : 1.002×10^{-2} moldm^{-3}

Solvent : 10% aq.acetic acid (v/v) Temp : 308K

[NaCl]x 10^3 mol dm^{-3}	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ dm^{3}mol^{-1}s^{-1}	Corr:
0.00	7.86	7.85	0.9994
0.01	7.79	7.77	0.9991
0.04	8.36	8.35	0.9995

4.13. Effect of added mineral acid H^+ on the rate of oxidation of 2-phenyl ethanol

Addition of different amount of acid increased the rate of oxidation as is evident from Table: 4.9. By varying the concentration of H_2SO_4 from 0.00 mol dm^{-3} to 0.15 mol dm^{-3} the observed rate constant (k_{obs}) was found to be from 7.86×10^{-5} to 34.8×10^{-5} s^{-1}

Table 4.9

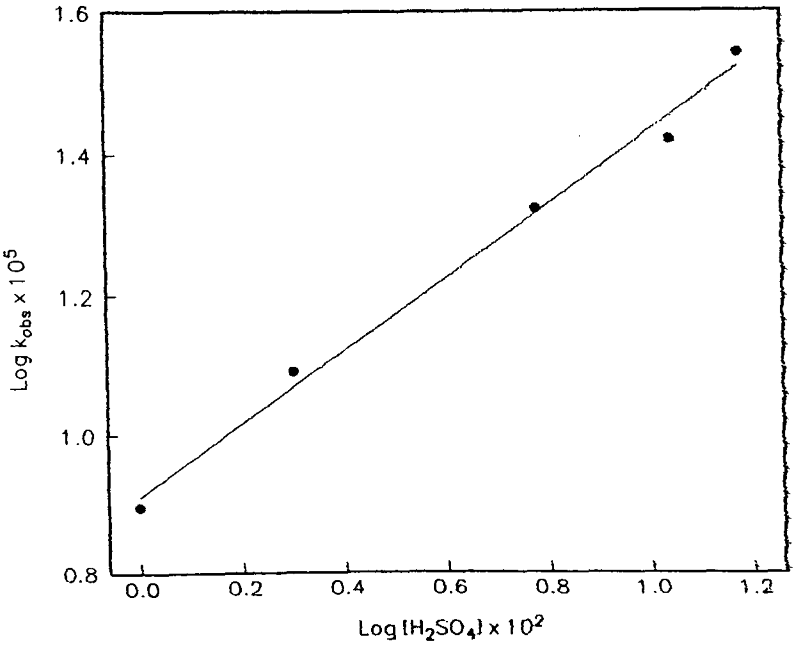
Effect of added mineral acid H$^+$ on the rate of oxidation of 2-phenyl ethanol

[KMnO$_4$] : 7.57x10^{-4} mol dm^{-3} [2-phol] : 1.025x10^{-2}mol dm^{-3}
Solvent : 10%aq.acetic acid(v/v) Temp : 308K

[H$_2$SO$_4$]x10^2 mol dm^{-3}	k$_{obs}$x10^5 s^{-1}	k$_2$ x 10^3 dm^3 mol^{-1} s^{-1}	Corr:
0.00	7.86	7.85	0.9994
2.00	12.28	12.22	0.9985
6.00	20.99	20.95	0.9951
11.00	26.25	26.20	0.9938
15.00	34.8	34.78	0.9889

A plot of k$_{obs}$ vs log[H$_2$SO$_4$] was found to be linear. This shows that the protonation of the substrate is one of the steps in the mechanism of oxidation.

Fig. 4.19. Plot of log k$_{obs}$ vs. log [H$_2$SO$_4$] in 10% aq. acetic acid



4.14. Effect of changing the polarity of the medium for the oxidation of 2-phenyl ethanol in aq. acetic acid

The results obtained shows that the rate increases with increase in the concentration of acetic acid. Increase in the concentration of acetic acid lowers the dielectric constant of the medium which favours reactions involving protonation.

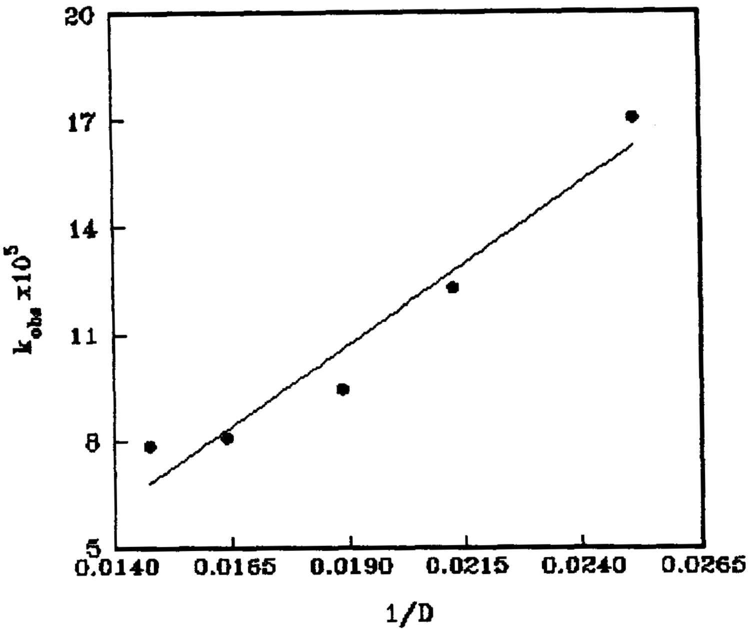
Table 4.10

Effect of changing the polarity of the medium for the oxidation of 2-phenyl ethanol in aq. acetic acid

[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3} Temp: 308K
[2-phol] : 1.002×10^{-2} mol dm^{-3}

%of aq:acetic acid (v/v)	10	20	30	40	50
Dielectric Constant	67.85	61	53.02	47	39.8
$k_{obs} \times 10^5$ s^{-1}	7.86	8.09	9.44	12.28	17.04
$k_2 \times 10^3$ s^{-1} mol dm^{-3}	7.85	8.08	9.42	12.25	17.008
Corr:	0.9994	0.9993	0.9991	0.9985	0.9972

Fig. 4.20. Plot of k_{obs} vs. 1/D



4.15. Effect of temperature on the rate of oxidation of 2-phenyl-ethanol in aq. acetic acid

The influence of temperature on the rate of oxidation of 2-phenyl ethanol were studied using aqueous $KMnO_4$ in 10% aqueous acetic acid at temperature from 303 K to 318K. The activation parameters were computed from the plot of log k_2 Vs. $1/T$(fig.43) and log (k_2 /T) vs.$1/T$ (fig.44). The results presented in table 4.11 shows that the rate constant k_2 increased from 5.05x10^{-3} to 20.57x 10^{-3} mol dm^{-3} for a temperature variation from 303K to 318K.

Table 4.11

Effect of temperature on the rate of oxidation of 2-phenyl-ethanol in aq. acetic acid

[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3}
[2-phol] : 1.002×10^{-2} mol dm^{-3}
Medium : 10% aq.acetic acid (v/v)

Temp:	$k_{obs} \times 10^5$ s^{-1}	$k_2 \times 10^3$ $dm^3\ mol^{-1}\ s^{-1}$
303	5.06	5.05
308	7.86	7.85
313	15.77	15.74
318	20.61	20.57

Fig. 4.21. Plot of log k_2 vs 1/T in 10% aq. acetic acid

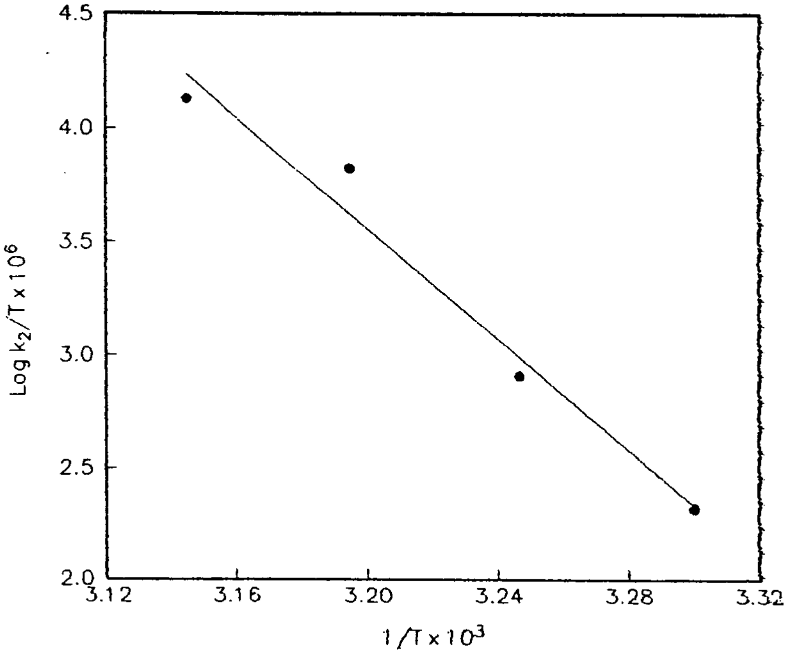


Fig. 4.22. Plot of log k_2/T vs $1/T$ in 10% aq. acetic acid

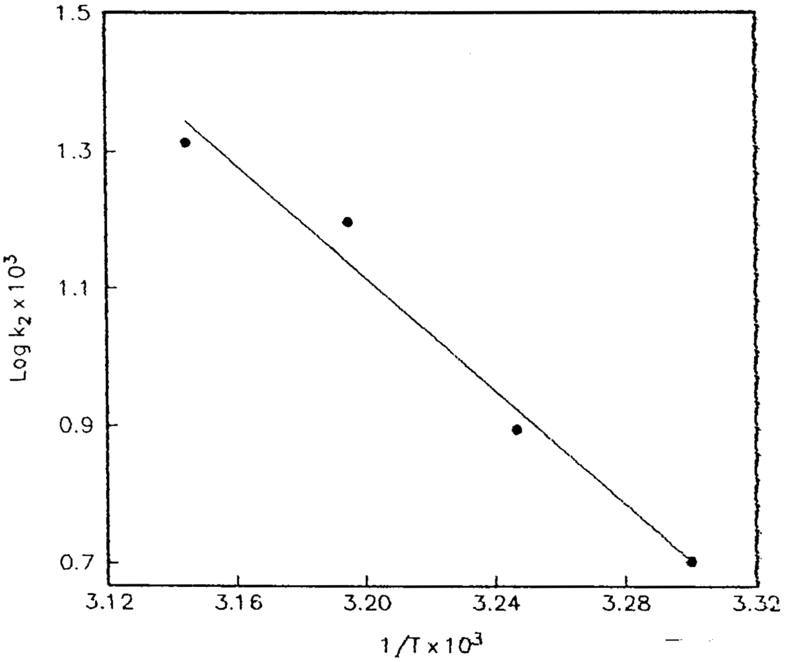


Table 4.12

Activation parameters for the oxidation 2-phenyl ethanol with $KMnO_4$ in aq 10% aq.acetic acid at 308k

k_2x10^3 dm^3 mol^{-1} s^{-1}	Ea kJmol^{-1}	ΔH$^{\#}$ kJmol^{-1}	ΔS$^{\#}$ K^{-1}Jmol^{-1}	ΔG$^{\#}$ kJmol^{-1}
5.05	78.8747	76.2841	37.3366	87.5970

From table 4.5, it appears that there is no gross change in the mechanism for the oxidation as reflected by the constant values of $\Delta G^{\#}$. However, the rates of the reaction with different catalysts are evidently entropy controlled. The oxidation with TBPB has lower rates compared to oxidation with TBAHS. But the activation energies are in the reverse order. Hence, the differences in the catalyts appears to change the randomness in the transition state configuration with more of disorder associated with the transition state when the catalyst is TBAHS. Consequently the reaction occurs faster with more positive activation entropy in this case.

B. HYDROLYSIS OF ESTERS, USING PTC

The results obtained for the alkaline hydrolysis of Benzyl Benzoate in aqueous-dioxane and aqueous-acetonitrile, with and without the presence of PTC under homogeneous conditions are presented and discussed in this chapter. Also the hydrolysis of Benzyl Benzoate was carried out under heterogeneous conditions with and without the presence of PTC and the yield of benzoic acid obtained was tabulated for different amount of catalyst for different stirring time. The heterogeneous condition was maintained by using a benzene solution of the ester and aqueous sodium hydoxide solution.

The activation parameters calculated for the hydrolysis of benzyl benzoate in the presence and absence of PTC under homogeneous conditions are tabulated in the table.

Fig. 4.23. Arrhenius plot for the alkaline hydrolysis of benzyl benzoate in 60% aqueous 1,4-dioxane without catalyst

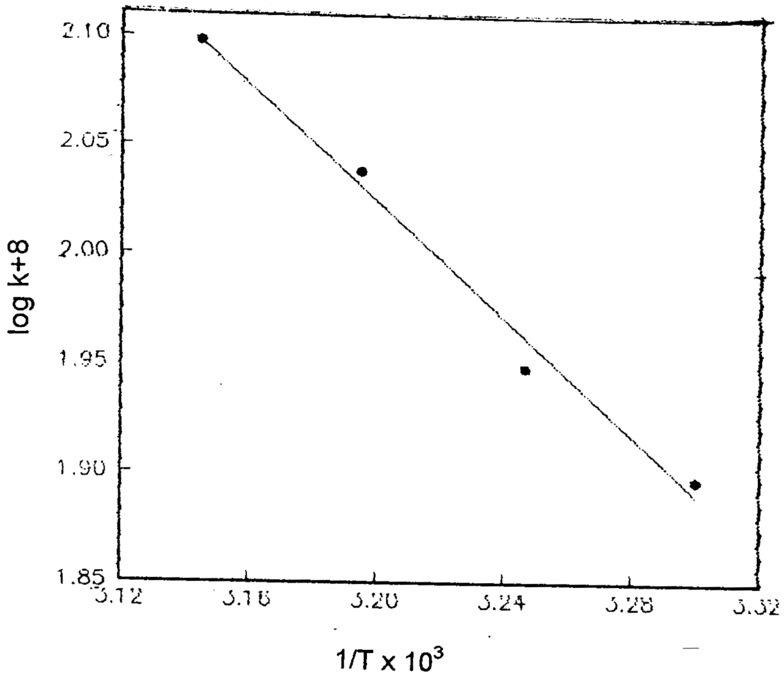


Fig. 4.24. Arrhenius plot for the alkaline hydrolysis of benzyl benzoate in 60% aqueous 1,4-dioxane with catalyst

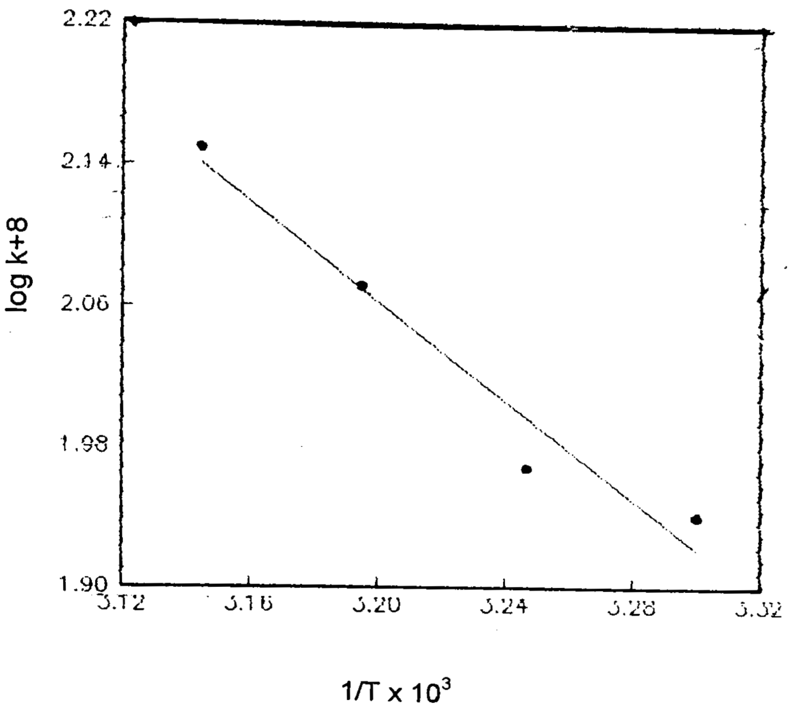


Fig. 4.25. Arrhenius plot for the alkaline hydrolysis of benzyl benzoate in 60% aqueous acetonitrile without catalyst

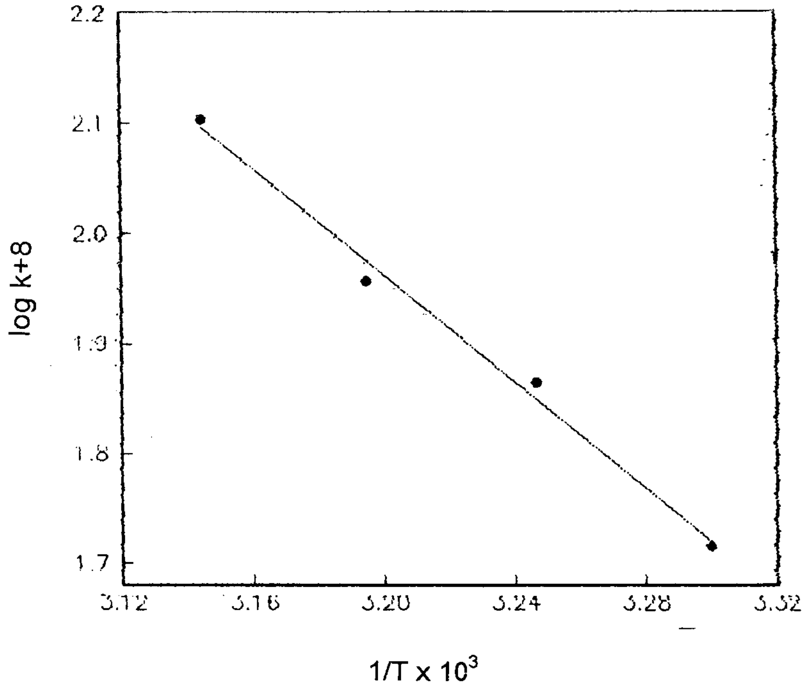


Fig. 4.26. Arrhenius plot for the alkaline hydrolysis of benzyl benzoate in 60% aqueous acetonitrile with catalyst

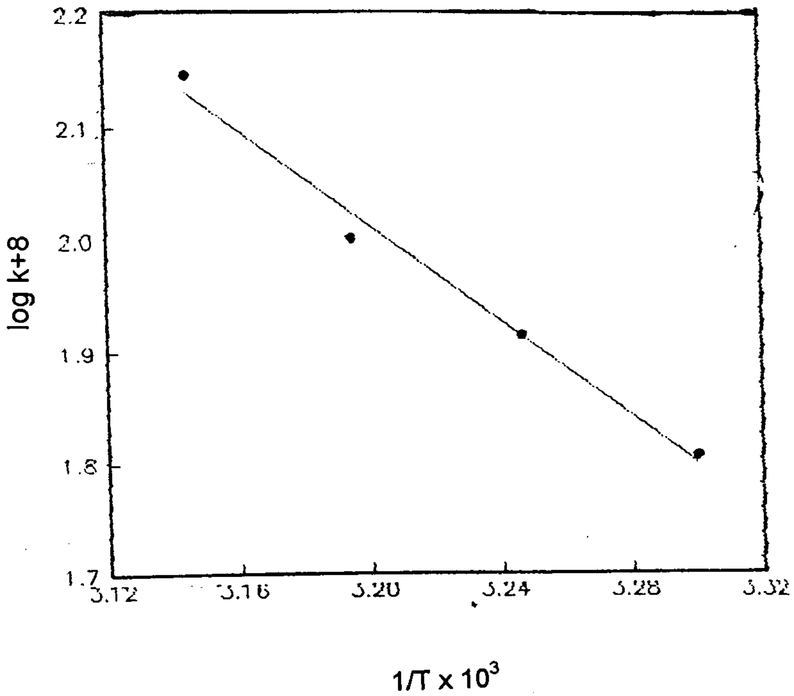


Fig. 4.27. **Plot of log k/T vs. 1/T for the alkaline hydrolysis of benzyl benzoate in 60% aqueous acetinotrile without catalyst**

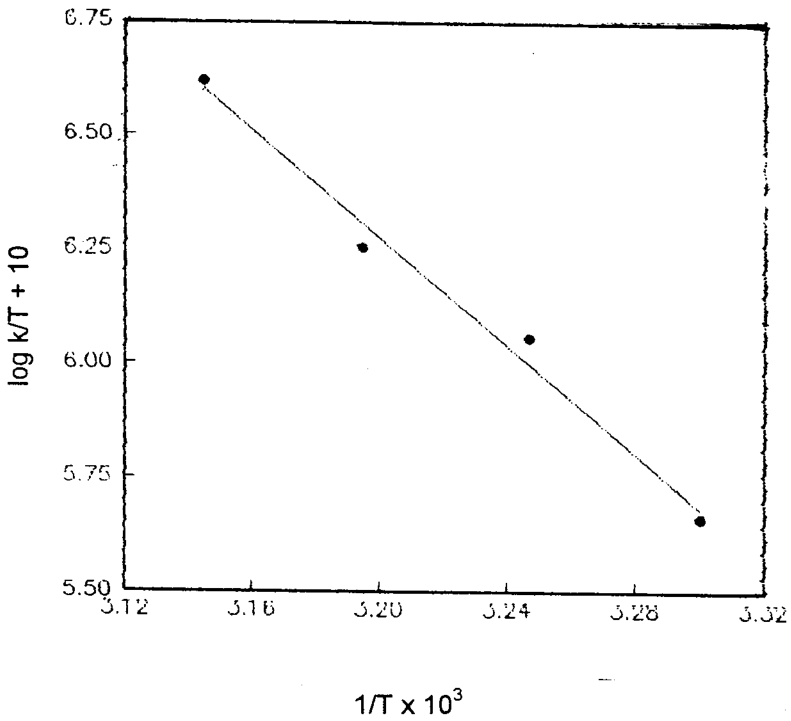


Fig. 4.28. **Plot of log k/T vs. 1/T for the alkaline hydrolysis of benzyl benzoate in 60% aqueous acetinotrile with catalyst**

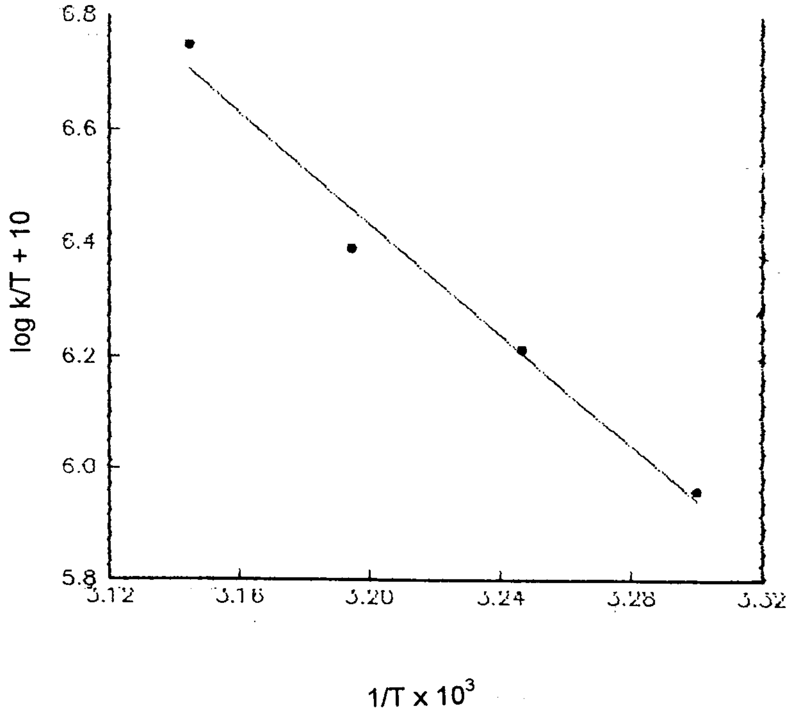


Fig. 4.29. Plot of log k/T vs. 1/T for the alkaline hydrolysis of benzyl benzoate in 60% aqueous 1,4-dioxane without catalyst

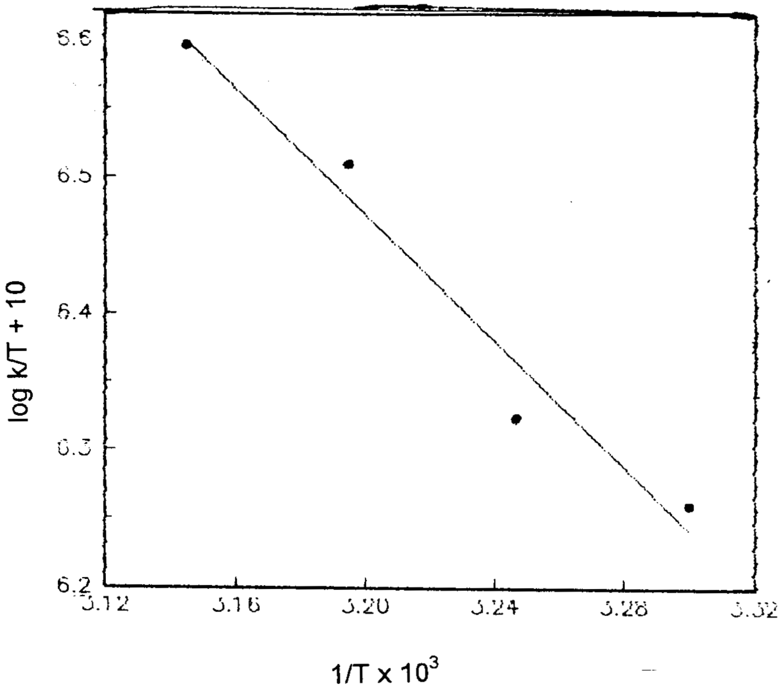


Fig. 4.30 Plot of log k/T vs. 1/T for the alkaline hydrolysis of benzyl benzoate in 60% aqueous 1,4-dioxane with catalyst

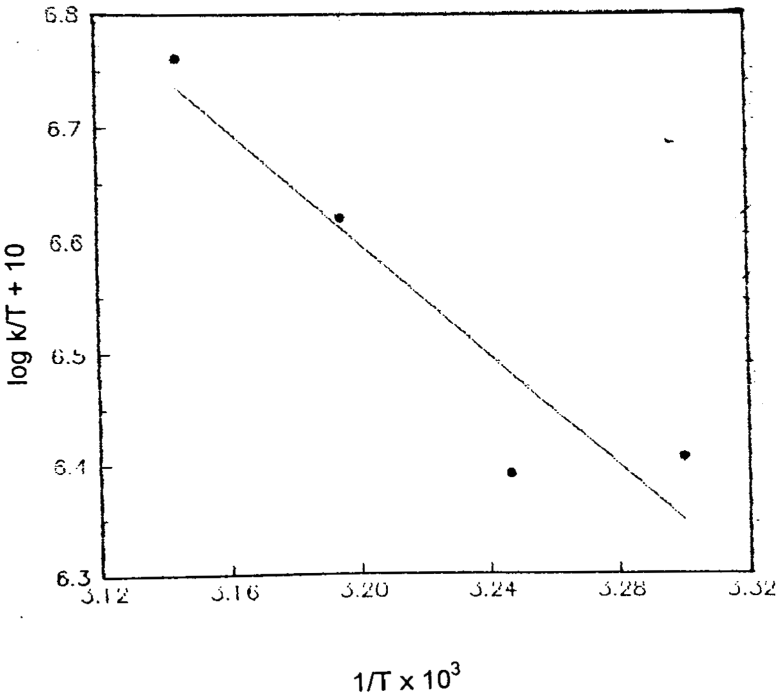


Table 4.13

Rate constants and activation parameters for the alkaline hydrolysis of benzyl benzoate in 60% aqueous acetonitrile (Homogeneous Reaction)

Ester : 0.04 M	Solvent : 60% Acetonitrile
NaOH : 0.05 M	Uncatalysed Reaction

Temperature	$k_2 \times 10^7$ dm^3mol^{-1} s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	$\Delta G^{\#}$ kJ mol^{-1}
303	5.1944	46.4471	43.8201	220.8166	110.7275
308	7.3284				
313	9.0552				
318	12.705				

Catalysed reaction

Temperature	$k_2 \times 10^7$ dm^3mol^{-1} s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	$\Delta G^{\#}$ kJ mol^{-1}
303	6.3902	40.9400	38.3632	237.0973	110.2036
308	8.2090				
313	10.024				
318	14.007				

Table 4.14

Rate constants and activation parameters for the alkaline hydrolysis of benzyl benzoate in 60% aqueous 1,4-dioxane (Homogeneous reaction)

Ester : 0.04 M	Solvent : 60% 1,4-dioxane
NaOH : 0.05 M	Uncatalysed Reaction

Temperature	$k_2 \times 10^7$ dm^3mol^{-1} s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	$\Delta G^{\#}$ kJ mol^{-1}
303	7.8946	25.5193	22.9478	286.2208	109.6727
308	8.8721				
313	10.901				
318	12.528				

Catalysed reaction

Temperature	$k_2 \times 10^7$ dm^3mol^{-1} s^{-1}	Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	$\Delta G^{\#}$ kJ mol^{-1}
303	8.7241	26.9993	24.4240	280.5475	109.4299
308	9.2936				
313	11.846				
318	14.114				

4.16. Mechanism of the hydrolysis of benzyl benzoate in aqueous dipolar aprotic solvents in the presence of PTC (homogeneous PTC reaction)

The results of the hydrolysis of benzyl benzoate in aq. dipolar aprotic solvents like acetonitrile and 1,4-dioxane, in the presence of TBAB have shown that the rate of the reaction increases when the reaction was carried in the presence of TBAB. Studies have shown that in the base catalysed hydrolysis of esters, nucleophilic attack on the cabronyl carbon atom by the hydroxide ion sets in the reaction. Here the nucleophilic attack by the hydroxide ion is augmented by the presence of the PTC probably due to release of more of active OH^- ions provided by Q^+OH^-.

The classical BAc_2 mechanism is supposed to be underway.

4.17 Mechanism of the hydrolysis of benzyl benzoate in non-polar medium with phase transferred OH^- ions (heterogeneous PTC reaction)

Ester bond cleavage in non-polar solvents like benzene, carbon tetrachloride etc. with hydoxyl group cannot be ordinarily carried out due to the immiscibility of aqueous solutions of sodium hydroxide in the non-polar media. The reaction readily takes place in the non polar medium and it could be due to the following phase transfer equilibrium. If 'Q' represents the TBAB cation, then the following equilibria will be obtained

$$\begin{tikzcd}
Q^+Br^- + NaOH \arrow[r, shift left] & Q^+OH^- + NaBr \text{ (aqueous layer)} \arrow[l, shift left] \arrow[d, shift left] \\
QOR + R\text{–}COOH \arrow[r, shift left] & Q^+\text{–}OH^- + R\text{–}COOR \text{ (Benzene layer)} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

It appears that a simple bimolecular nucleophilic displacement of the OR group by the hydroxyl as in an SN_2 reaction and takes place given in the following chemical equation

$$R-COOR + OH^- \longrightarrow R-COOH + OR^-$$

The tetrabutylammonium hydroxide formed in the aqueous layer gets phase transferred into the benzene layer where it provides very reactive and non solvated hydroxide which easily reacts with the ester in a nucleophilic substitution reaction to produce benzoic acid. The tetrabutylammonium alkoxide formed, having a better organic structure, would like to be more partitioned into the benzene layer. Hence the fraction of QOR getting phase transferred into the water layer to exchange the anion with NaOH would be less and hence more of the catalyst is needed for bringing about a greater percentage of the reaction. The very difficultly hydrolysable benzyl benzoates thus get 'hydrolysed'.

4.18 Mechanism of the oxidation of the carbinols in non-polar solvents using PTC[264]

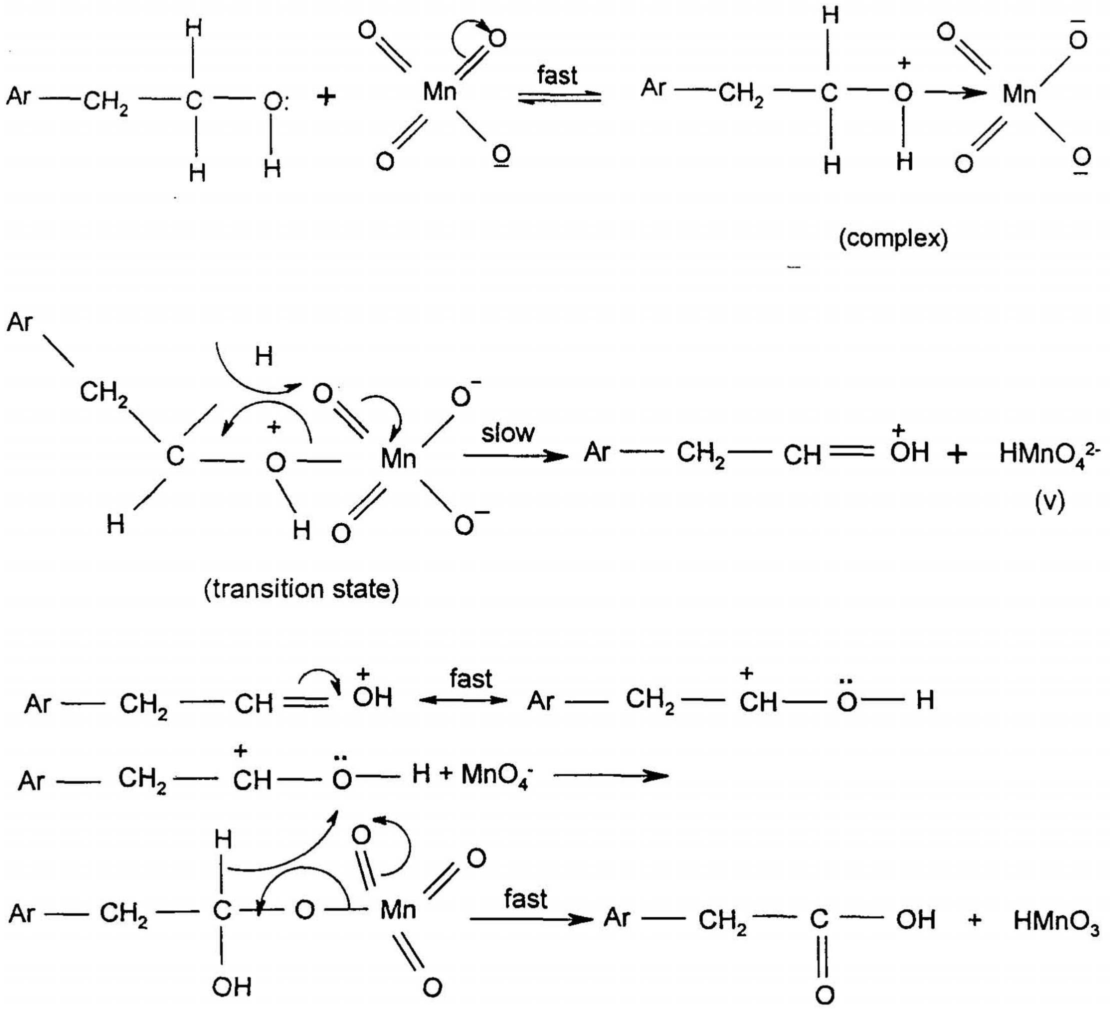
Kinetics studies on the oxidation of 2-phenyl ethanol, butanol and hexanol have been carried out. The mechanism of the oxidation of the carbinols in non-polar solvents can be formulated on the basis of the following experimental results. The results obtained for the oxidation of 2-phenyl ethanol is taken as a typical example. The plot of $\log_{(absorbance)}$ of $QMnO_4$ vs. time gave a linear relation indicating first order dependence of the reaction on the oxidant concentration, that is the reaction is first order with respect to the oxidant.

The observed rate constant $k_{(obs)}$ increased linearly with the increase in the concentration of the alcohol. The second order rate constant (k_2) is almost constant indicating first order behaviour with respect to the concentration of the alcohol. The double logarithmic plot of log k_{obs} vs. log[alcohol] is linear with a slope equal to unity further confirms the first order dependence of the alcohol concentration. The double reciprocal plot of $1/k_{obs}$ vs. 1/[2-phol] (Lineweaver-Burke plot) is linear passing through the origin which rules out the formation of a long lived intermediate. The rate determining step involves the interaction of a dipole or a neutral molecule with an ion or another polar entity since the addition of TBAB did not cause any effect on the rate of oxidation.

The plot of log k_2 vs 1/D of the solvent is linear with a negative slope indicating the interaction between an anion and dipole according to the Amis equation.[260] The possibility of greater charge separation in the transition state compared to the ground state is also evident. The results of the oxidation shows that the rate of the reaction increases with increase in the dielectric constant of the solvent employed.

The plot of log k_2 vs 1/T and log k_2/T vs 1/T are found to be linear and the results show that the oxidation increases with increase in temperature. The isosbestic point obtained is also suggestive of the formation of a single product only and rules out any complicated sequence of events during the oxidation reaction. Since the addition of acetonitrile did not produce any induced polymerisation, the reaction involving a free-radical mechanism can be ruled out. The reaction can be either an ion-dipole interaction or a dipole-dipole interaction. The negative value of $\Delta S^{\#}$ indicates a highly ordered transition state.

The probable mechanism can be as follows. The LUMO of the alcohol interacts with the HOMO of the permanganate to form a complex which is of short lived intermediate which in turn undergo rate determining slow decomposition forming the final product.



$$3\,Mn(V) \xrightarrow{\text{fast}} 2Mn(IV) + Mn(VII)$$

The resulting permanganate complex undergoes slow rate determining decomposition through a cyclic transition state involving α-CH bond cleavage and O-Mn bond cleavage.

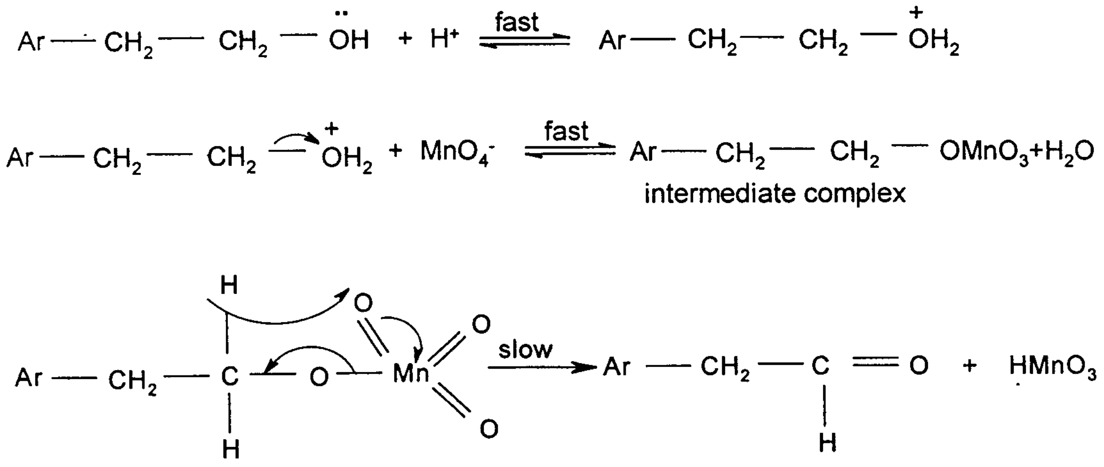
The alcohol formed in this state undergo fast oxidation with a second molecule of permanganate giving acid as the final product as shown in the scheme. The Mn(V) formed undergoes fast disproportionation to give more stable Mn(IV).

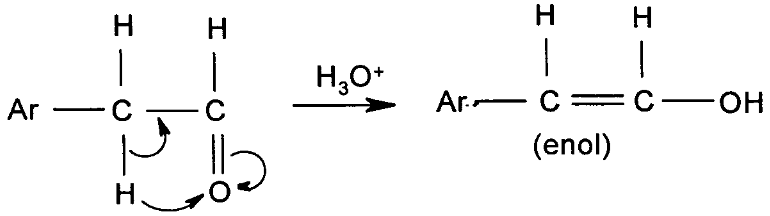
4.19 Mechanism of the oxidation of the carbinol in aqueous acetic acid[261-263]

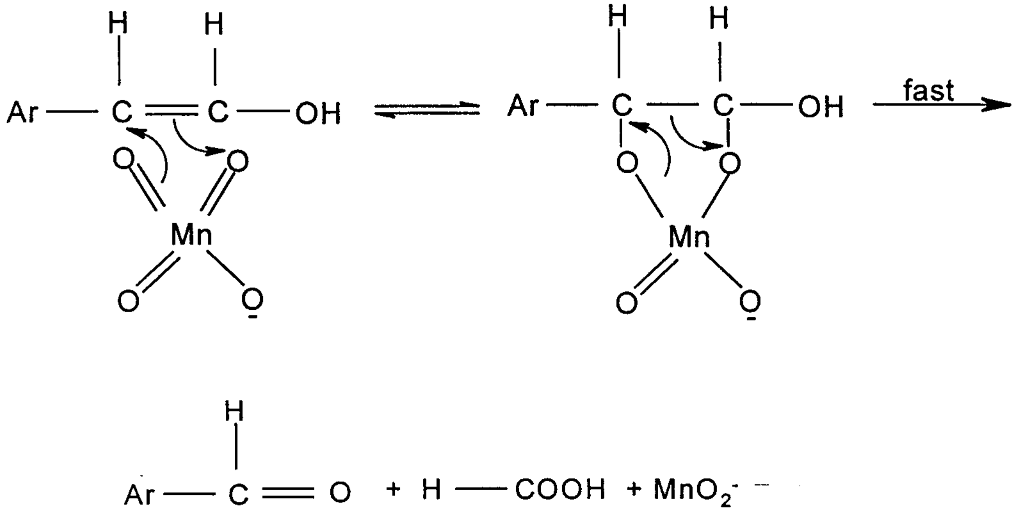
From the above results it is seen that the plot of log [$KMnO_4$] vs. time is linear showing first order dependence on the oxidant concentration. k_{obs} is independent for the initial concentration of $KMnO_4$. The plot of log k_{obs} vs. log [alcohol] is linear passing through the origin indicating first order dependence of the alcohol concentration. Moreover k_{obs} is found to be proportional to the [alcohol], and k_2 is almost found to be a constant.

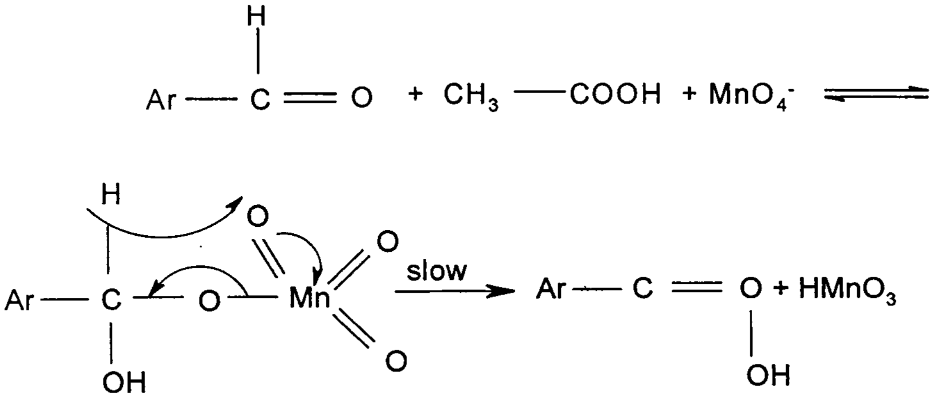
The plot of $1/k_{obs}$ vs. $1/$[alcohol] is also linear passing through the origin which rules out the formation of a long lived intermediate. However it may be considered that the substrate interacts with the oxidant and form a transient complex which immediately decomposes and the rate is controlled by the interaction of the alcohol with the oxidant. The addition of NaCl did not produce any primary kinetic salt effect. The rate constants remained practically constant with different concentrations of sodium chloride added. This suggests the absence of an ion-ion type interaction and hence the possibility could be that of an ion and dipole or that between two dipolar entities. The plot of log k_{obs} vs. log $[H_2SO_4]$ is linear and the rate of the reaction increases as the temperature is increased.

The probable mechanism for the oxidation of 2-phenyl ethanol in aqueous acetic acid medium can be suggested as follows:



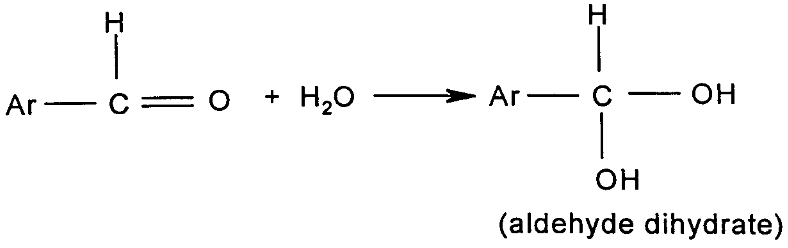


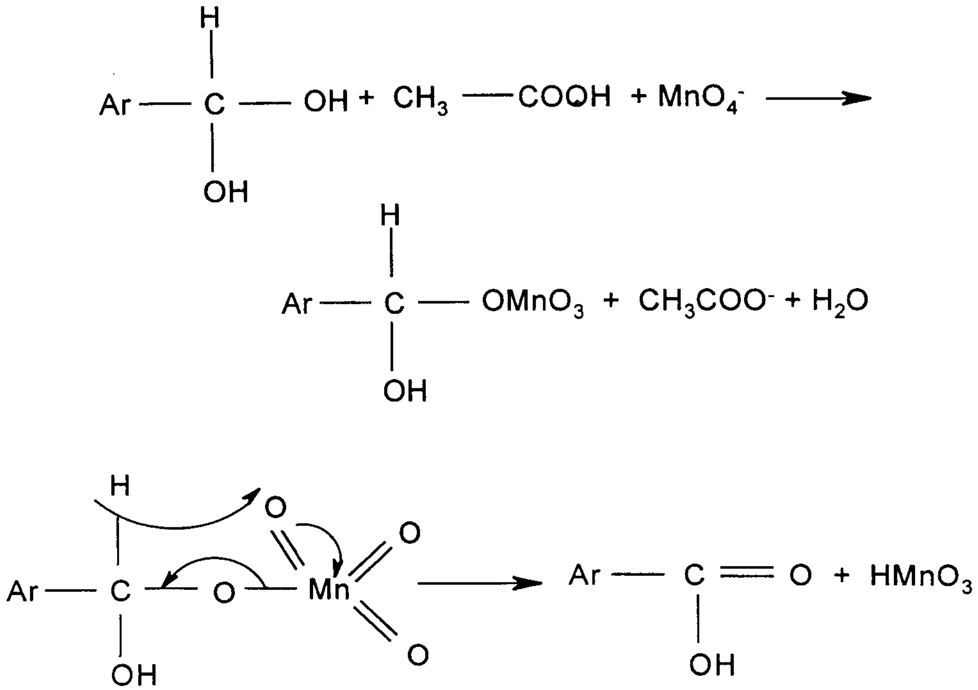




.... (1)

or step (I) can also be shown as follows:





$$2\mathrm{Mn(III)} \longrightarrow \mathrm{Mn(IV)} + \mathrm{Mn(II)}$$

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

In acetic acid medium alcohol undergo protonation to give protonated alcohol which combines with permanganate to form permanganate ester. This permanganate ester undergo slow rate determining decomposition to form, phenyl acetaldehyde and Mn(V). This phenylacetaldehyde in the acid medium undergo enolisation. This enol form of the aldehyde undergoes 1,2-electrocyclic addition to form a cyclic addition product which undergo fast decomposition to form benzaldehyde as an intermediate which further undergo fast oxidation by permanganate in the acid medium giving benzoic acid as the observed final product of the reaction. One of the reduced form of permanganate is MnO_2^- i.e., Mn(III) formed in the step (1) is converted to Mn(IV) and Mn(II) the stable form and Mn(V) is converted to Mn(IV) and Mn(VII).

SUMMARY

The kinetics of the oxidation of 2-phenyl ethanol and aliphatic primary alcohols like butanol and hexanol were carried out in benzene using phase transferred permanganate. Tetrabutylammonium bromide (TBAB), Tetrabutylammonium hydrogen sulphate (TBAHS) and Tetrabutylphosphonium bromide were used as the phase transfer catalysts. In order to carry out the kinetic studies the permanangate ions from the aqueous phase were first extracted into the organic phase with the use of PT catalyst. All the catalysts employed were found to be good in extracting the permanganate ions and TBAHS was found to be the best, among the three because the hydrogen sulfate anion associates much less strongly with the quaternary cation, which make the transfer of MnO_4^- ions from the aqueous to the organic phase more effectively.

In this present work, the effect of oxidant concentration, substrate concentration, solvent polarity, ionic strength variation and the effect of temperature were studied with respect to TBAB, TBPB and TBAHS. The reaction was found to be first order with respect to the oxidant concentration as well as with respect to the alcohol

concentration. The rate of the reaction was found to increase with increase in the polarity of the solvents employed and the rate of oxidation was found to be greatest for TBAHS than TBAB and TBPB. The product of the oxidation reaction was found to be the corresponding acid.

The kinetics of the oxidation of 2-phenylethanol was also carried out in aqueous acetic acid medium using $KMnO_4$. The comparison of kinetic data shows that the reaction takes place with a better rate when phase transfer catalysts were used. The rate of the reaction in aqueous acetic acid medium was found to increase with the increase in the percentage composition of acetic acid.

The hydrolysis of benzyl benzoate carried out in dipolar aprotic solvents in the presence and absence of phase transfer catalyst show that in the presence of PTC the rate of the reaction increased. The yield study conducted under heterogeneous conditions shows that esters can be hydrolysed in non-aqueous solvents using PTC, and in the absence of PTC hydrolysis was not observed.

CONCLUSION

The oxidation of 2-phenyl ethanol and some aliphatic primary alcohols like butanol and hexanol by phase transferred permanganate using TBPB, TBAB and TBAHS as phase transfer catalysts, occurred smoothly in benzene and other organic solvents like toluene and chloroform, at an appreciable rate. The alcohols were oxidised to the corresponding acids. Tetrabutylammonium hydrogensulphate (TBAHS) was found to be the best catalyst when compared with Tetrabutylphosphonium bromide and Tetrabutylammonium bromide for the extraction of MnO_4^- ions from the aqueous phase into the organic phase and also for effecting the oxidation reaction. Among the various organic solvents employed chloroform was found to be the best solvent for effecting oxidation. In methylene chloride the rate of the reaction was too fast to be measured.

The values of the activation parameters obtained for 2-phenyl ethanol under PTC condition are comparable to the oxidation of 2-phenyl ethanol in aqueous acetic acid media.

The hydrolysis of benzyl benzoate carried out in dipolar, aprotic solvents like acetontirile and 1,4-dioxane in the presence of TBAB as the catalyst showed an increase in the rate of the reaction, when the hydrolysis were carried out in the absence of TBAB. Of the two solvents employed for the hydrolysis reaction, 1,4-dioxane was found to be the best. The hydrolysis of benzyl benzoate carried out in heterogeneous condition using phase transfer catalyst have established that the hydrolysis reaction can be carried in non-aqueous solvents. Since the above reaction did not occur in the absence of a phase transfer catalyst, this method has been found to be very effective and convenient for the study of the kinetics and mechanism of the oxidation and hydrolysis of organic compounds in organic media.

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APPENDIX
KINETIC DATA

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TABLE 1

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

$[PhCH_2CH_2OH]$: 1.202×10^{-2} mol dm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBPB

$[QMnO_4] \times 10^4$ mol dm^{-3}	4.77	5.30	6.36	7.24
Time (min)	1 + [log (4 x Absorbance)]			
0	1.03981	1.10174	1.17026	1.23552
5	1.03019	1.08635	1.15594	1.22323
10	1.01367	1.06892	1.14238	1.21165
15	0.9965	1.05384	1.12580	1.19755
20	0.97498	1.03502	1.11126	1.18412
25	0.9542	1.01703	1.09621	1.16908
$k_{obs} \times 10^4$ s^{-1}	1.33	1.301	1.143	1.017
Correlation	0.9931	0.9994	0.9997	0.9990
Slope	-0.00349	-0.00339	-0.00298	-0.00265

TABLE 2

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

[$PhCH_2CH_2OH$]	: 1.202×10^{-2} mol dm^{-3}	Temp	: 308 K
Solvent	: Benzene	PT catalyst	: TBAB

[$QMnO_4$] x 10^4 mol dm^{-3}	4.77	5.30	6.36	7.24
Time (min)	1 + [log (4 x Absorbance)]			
0	1.04921	1.111262	1.18639	1.25139
5	1.03019	1.09342	1.17143	1.23754
10	1.01367	1.07627	1.15594	1.22427
15	0.994757	1.05994	1.14113	1.21165
20	0.98046	1.041392	1.125806	1.19755
25	0.94842	1.02036	1.108565	1.18298
k_{obs} x 10^4 s^{-1}	1.473	1.374	1.186	1.040
Correlation	0.9930	0.9992	0.9997	0.9997
Slope	-0.00384	-0.00358	-0.00309	-0.00271

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TABLE 3

Effect of varying the concentration of oxidant on the rate of oxidation of 2-phenyl ethanol

[$PhCH_2CH_2OH$] : 1.202×10^{-2} mol dm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBAHS

[$QMnO_4$] x 10^4 mol dm^{-3}	4.77	5.30	6.36	7.24
Time (min)	1 + [log (4 x Absorbabce)]			
0	1.05690	1.134814	1.19975	1.259115
5	1.03822	1.116607	1.18184	1.23954
10	1.020361	1.10037	1.16196	1.219060
15	0.99826	1.08206	1.14488	1.19975
20	0.97864	1.06145	1.12319	1.17724
25	0.95617	1.03981	1.10037	1.15472
$k_{obs} \times 10^5$ s^{-1}	1.546	1.443	1.512	1.596
Correlation	0.9993	0.9987	0.9988	0.9995
Slope	-0.00403	-0.00376	-0.00394	-0.00416

TABLE 4

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

[TBPP] : 5.30×10^{-4} moldm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBPB

[2-PhOl]x10^{2} mol dm^{-3}	1.202	2.003	3.005	4.007
Time (min)	1 + [log (4 x Absorbance)]			
0	1.101749	1.101747	1.10037	1.09898
5	1.08635	1.07335	1.06445	1.05230
10	1.06892	1.04139	1.02857	1.0000
15	1.05384	0.9914	0.99122	0.93852
20	1.03502	0.97681	0.94052	0.86688
25	1.01703	0.93852	0.88987	0.8400
$k_{obs} \times 10^{4}$ s^{-1}	1.301	2.533	3.205	4.183
Correlation	0.9994	0.9942	0.9963	0.9954
Slope	-0.00339	-0.0066	-0.00835	-0.0109

TABLE 5

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

[TBPP]	: 5.32×10^{-4} mol dm^{-3}	Temp	: 308 K
Solvent	: Benzene	PT catalyst	: TBAB

[2-PhOl]x10^{2} mol dm^{-3}	1.202	2.003	3.005	4.007
Time (min)	1 + [log (4 x Absorbance)]			
0	1.111262	1.10856	1.107209	1.10585
5	1.09342	1.07918	1.07040	1.05690
10	1.07627	1.04921	1.031812	0.9948
15	1.05994	1.01367	0.98945	0.94251
20	1.041392	0.97864	0.94251	0.86924
25	1.02036	0.93852	0.8921	0.8200
$k_{obs} \times 10^{4}$ s^{-1}	1.374	2.602	3.293	4.483
Correlation	0.9992	0.9983	0.9981	0.9987
Slope	-0.00358	-0.00678	-0.00858	-0.01168

TABLE 6

Effect of varying the concentration of substrate on the rate of oxidation of 2-phenyl ethanol

[TBPP] : 5.30×10^{-4} mol dm^{-3}

Solvent : Benzene

Temp : 308 K

PT catalyst : TBAHS

[2-PhOl]x10^{2} mol dm^{-3}	1.202	2.003	3.005	4.007
Time (min)	1 + [log (4 x Absorbance)]			
0	1.134814	1.13353	1.13225	1.13097
5	1.116607	1.09898	1.09201	1.07918
10	1.10037	1.05690	1.04921	1.01870
15	1.08206	1.01870	1.0000	0.95037
20	1.06145	0.97490	0.95037	0.86688
25	1.03981	0.9243	0.88987	0.8000
$k_{obs} \times 10^{4}$ s^{-1}	1.443	3.193	3.696	5.177
Correlation	0.9987	0.9983	0.9975	0.9973
Slope	-0.00376	-0.00832	-0.00963	-0.01349

TABLE 7

Effect of temperature on the rate of oxidation of 2-phenyl ethanol

$[PhCH_2CH_2OH]$: 1.202×10^{-2} mol dm^{-3} Solvent : Benzene
PT catalyst : TBPB

[TBPP] = 5.30×10^{-4} mol dm^{-3}	30^{0}C	35^0 C	40^0 C	45^0 C
Time (min)	1 + [log (4 x Absorbance)]			
0	1.103119	1.10174	1.10037	1.09898
5	1.090610	1.08635	1.07335	1.06445
10	1.07918	1.06892	1.046104	1.030194
15	1.06595	1.05384	1.02036	0.985876
20	1.05384	1.03502	0.9877	0.9345
25	1.04139	1.01703	0.95037	0.9000
$k_{obs} \times 10^4$ s^{-1}	0.9480	1.301	2.264	3.135
Correlation	0.9998	0.9994	0.9974	0.9975
Slope	-0.00247	-0.00339	-0.00590	-0.00817

TABLE 8

Effect of temperature on the rate of oxidation of 2-phenyl ethanol

[$PhCH_2CH_2OH$] : 1.202×10^{-2} mol dm^{-3} Solvent : Benzene
PT catalyst : TBAB

[TBAP] =5.30×10^{-4} mol dm^{-3}	30^0C	35^0 C	40^0 C	45^0 C
Time (min)	1 + [log (4 x Absorbance)]			
0	1.112605	1.111262	1.10856	1.1072
5	1.10037	1.09342	1.08062	1.0689
10	1.08778	1.07627	1.05230	1.02036
15	1.07481	1.05994	1.02201	0.97313
20	1.06295	1.041392	0.98945	0.9223
25	1.04921	1.02036	0.95037	0.90
$k_{obs} \times 10^4$ s^{-1}	0.9710	1.374	2.402	3.339
Correlation	0.9998	0.9992	0.9980	0.9960
Slope	-0.00253	-0.00358	-0.00626	-0.0087

TABLE 9

Effect of temperature on the rate of oxidation of 2-phenyl ethanol

[$PhCH_2CH_2OH$] : 1.202×10^{-2} moldm^{-3} Solvent : Benzene
PT catalyst : TBAHS

[TBAP] = 5.30×10^{-4} mol dm^{-3}	30^0C	35^0 C	40^0 C	45^0 C
Time (min)	1 + [log (4 x Absorbance)]			
0	1.1348	1.134814	1.13225	1.13097
5	1.1218	1.116607	1.10174	1.07627
10	1.1099	1.10037	1.06744	1.01535
15	1.0948	1.08206	1.02857	0.94646
20	1.0820	1.06145	0.99296	0.85974
25	1.06744	1.03981	0.94842	0.8100
$k_{obs} \times 10^4$ s^{-1}	1.067	1.443	2.817	5.097
Correlation	0.9983	0.9987	0.9984	0.9974
Slope	-0.00278	-0.00376	-0.00734	-0.01328

TABLE 10

Effect of solvent polarity on the rate of oxidation of 2-phenyl ethanol

[$PhCH_2CH_2OH$] : 1.202×10^{-2} mol dm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBPB

[TBPP] = 5.30×10^{-4} mol dm^{-3}	Benzene	Toluene	$CHCl_3$
Time (min)	1 + [log (4 x Absorbance)]		
0	1.10174	1.10174	1.1003
5	1.08635	1.0820	1.0659
10	1.06892	1.0629	1.0382
15	1.05384	1.0476	1.01367
20	1.03502	1.0301	0.9769
25	1.01703	1.0086	0.9657
Slope	-0.00339	-0.00364	-0.00551
Corr:	0.9994	0.9990	0.9938
$k_{obs} \times 10^4$ s^{-1}	1.30	1.39	2.11

TABLE 11

Effect of solvent polarity the rate of oxidation of 2-phenyl ethanol

$[PhCH_2CH_2OH]$: 1.202×10^{-2} mol dm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBAB

[TBAP] = 5.30×10^{-4} mol dm^{-3}	Benzene	Toluene	$CHCl_3$
Time (min)	1 + [log (4 x Absorbance)]		
0	1.11126	1.1112	1.1099
5	1.09342	1.0906	1.0762
10	1.07627	1.0718	1.0461
15	1.05994	1.0538	1.0170
20	1.041392	1.0366	0.9823
25	1.02036	1.0136	0.9406
Slope	-0.00358	-0.00382	-0.00661
Corr:	0.9992	0.9992	0.9982
$k_{obs} x 10^4 s^{-1}$	1.37	1.46	2.53

TABLE 12

Effect of solvent polarity the rate of oxidation of 2-phenyl ethanol

$[PhCH_2CH_2OH]$: 1.202 x 10^{-2} mol dm^{-3} Temp : 308 K
Solvent : Benzene PT catalyst : TBAHS

[TBAP] =5.30 x 10^{-4} mol dm^{-3}	Benzene	Toluene	$CHCl_3$
Time (min)	1 + [log (4 x Absorbance)]		
0	1.134814	1.1348	1.1335
5	1.116607	1.1099	1.0934
10	1.10037	1.0920	1.0569
15	1.08206	1.0733	1.0170
20	1.06145	1.0553	0.9841
25	1.03981	1.0334	0.9366
Slope	-0.00376	-0.00394	-0.00773
k_{obs}x10^4 s^{-1}	1.44	1.51	2.96
Corr:	0.9987	0.9987	0.9992

TABLE 13

Effect of [MnO_4^-] on the rate of oxidation of 2-phol in 10% aq. acetic acid

[2-Phol] = 1.002 x 10^{-2} mol dm^{-3}			Temp : 308 K	
[$KMnO_4$] x 10^4 mol dm^{-3}	3.27	4.48	6.07	7.57
Time (min)	4 + log [$KMnO_4$]			
0	0.5148	0.6520	0.7837	0.8792
10	0.4958	0.6335	0.7666	0.8573
20	0.4759	0.6142	0.7489	0.8400
30	0.4551	0.5940	0.7266	0.8159
40	0.4332	0.5728	0.7072	0.7968
50	0.4101	0.5505	0.6868	0.7769
k_{obs}x 10^5 s^{-1}	8.02	7.83	7.52	7.86
Corr. Coeff.	0.9994	0.9993	0.9992	0.9994

TABLE 14

Effect of [2-Phol] on the rate of oxidation of 2-phol in 10% aq. acetic acid

[KMnO$_4$] = 7.57 x 10^{-4} mol dm^{-3}			Temp : 308 K	
[2-phol] x 10^{2} mol dm^{-3}	1.002	1.6032	2.4048	3.006
Time (min)	4 + log [KMnO$_4$]			
0	0.8792	0.8792	0.8792	0.8792
10	0.8573	0.8516	0.8400	0.8311
20	0.8400	0.8281	0.7968	0.7769
30	0.8159	0.7903	0.7489	0.7189
40	0.7968	0.7561	0.6950	0.6475
50	0.7769	0.7266	0.6335	0.5674
k$_{obs}$ x 10^{5} s^{-1}	7.86	11.93	17.27	23.75
Corr. Coeff.	0.9994	0.9978	0.9985	0.9953

TABLE 15

Effect of [H_2SO_4] on the rate of oxidation of 2-phol in 10% aq. acetic acid

[2-Phol] = 1.0026×10^{-2} mol dm^{-3}
[$KMnO_4$] = 7.57×10^{-4} mol dm^{-3}
Temp. = 308 K

[H_2SO_4] x 10^2 mol dm^{-3}	2	6	11	15
Time (min)	4 + log [$KMnO_4$]			
0	0.8792	0.8792	0.8792	0.8792
10	0.8516	0.8370	0.8281	0.8190
20	0.8220	0.7903	0.7701	0.7453
30	0.7903	0.7379	0.7032	0.6610
40	0.7561	0.6741	0.6288	0.5562
50	0.7189	0.6042	0.5331	0.4179
$k_{obs} \times 10^5$ s^{-1}	12.28	20.99	26.25	34.80
Corr. Coeff.	0.9985	0.9951	0.9938	0.9889

TABLE 16

Effect of [NaCl] on the rate of oxidation of 2-phol in 10% aq. acetic acid

[2-Phol]	:	1.0026×10^{-2} mol dm^{-3}
[$KMnO_4$]	:	7.57×10^{-4} mol dm^{-3}
Temp.	:	308 K

[NaCl] x 10^2 mol dm^{-3}	0	2	4
Time (min)	4 + log [$KMnO_4$]		
0	0.8792	0.8792	0.8792
10	0.8573	0.8573	0.8573
20	0.8400	0.8341	0.8341
30	0.8159	0.8159	0.8159
40	0.7968	0.7968	0.7903
50	0.7769	0.7769	0.7701
$k_{obs} \times 10^5$ s^{-1}	7.86	7.79	8.36
Corr. Coeff.	0.9994	0.9991	0.9995

TABLE 17

Effect of percentage variation of acetic acid (change of polarity of medium) on the rate of oxidation of 2-phenyl ethanol

[2-Phol] : 1.002×10^{-2} mol dm^{-3}
[$KMnO_4$] : 7.57×10^{-4} mol dm^{-3}
Temp. : 308 K

% of acetic acid	10	20	30	40	50
Time (min)	4 + log [$KMnO_4$]				
0	0.8792	0.8792	0.8792	0.8792	0.8792
10	0.8573	0.8601	0.8573	0.8516	0.8429
20	0.8400	0.8400	0.8341	0.8220	0.8033
30	0.8159	0.8190	0.8096	0.7903	0.7596
40	0.7968	0.7968	0.7837	0.7561	0.7111
50	0.7769	0.7735	0.7561	0.7189	0.6565
$k_{obs} \times 10^5$ s^{-1}	7.86	8.09	9.44	12.28	17.04
Corr. Coeff.	0.9994	0.9993	0.9991	0.9985	0.9972

TABLE 18

Effect of temperature on the rate of oxidation of 2-Phol in 10% aq. acetic acid

[2-Phol] : 1.002×10^{-4} mol dm^{-3}
[KMnO$_4$] : 7.570×10^{-4} mol dm^{-3}

Temp (K)	303	308	313	318
Time (min)	4 + log [KMnO$_4$]			
0	0.8792	0.8792	0.8792	0.8792
10	0.8684	0.8573	0.8458	0.8370
20	0.8573	0.8400	0.8096	0.7903
30	0.8458	0.8159	0.7666	0.7379
40	0.8341	0.7968	0.7228	0.6783
50	0.8281	0.7769	0.6741	0.6093
$k_{obs} \times 10^5$ s^{-1}	5.06	7.86	15.77	20.61
Corr. Coeff.	0.9867	0.9976	0.9959	0.9994

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TABLE 19

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.4	
1800	8.1	2.6663
2400	8.3	2.7017
3000	8.45	2.6301
3600	8.6	2.6269
4200	8.75	2.6747
α	9.65	

k= 5.1944×10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 20

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M		Solvent = 60% Acetonitrile	
[NaOH] = 0.0502 M		[HCl] = 0.0976 M	
		Temp. = 308 K	

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.4	
1800	8.35	3.8541
2400	8.55	3.7142
3000	8.75	3.7445
3600	8.9	3.7000
4200	9.05	3.7584
α	9.65	

k = 7.3284 x 10^{-7} lit. mol^{-1}sec^{-1}

TABLE 21

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.4	–
1800	8.5	4.6626
2400	8.75	4.6807
3000	8.95	4.6909
3600	9.1	4.6512
4200	9.2	4.5089
α	9.65	

$k = 9.0552 \times 10^{-7}$ lit. $mol^{-1} sec^{-1}$

TABLE 22

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0408 M
[NaOH] = 0.0502 M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3 mol^{-1} sec^{-1}$
0	7.4	–
1800	8.8	6.6029
2400	9.05	6.5773
3000	9.2	6.3125
3600	9.35	6.4743
4200	9.45	6.5763
α	9.65	

$k = 1.2705 \times 10^{-6}$ lit. $mol^{-1}sec^{-1}$

TABLE 23

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M
[NaOH] = 0.0525 M
[TBAB] = 0.0601M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} $dm^3 \, mol^{-1} \, sec^{-1}$
0	7.5	–
1200	8.1	3.4909
1800	8.3	3.2632
2400	8.5	3.2426
3000	8.7	3.3345
3600	8.85	3.3227
4200	8.95	3.2053
α	9.65	

k = 6.3902 x 10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 24

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M
[NaOH] = 0.0525 M
[TBAB] = 0.0601M

Solvent = 60% Acetonitrile
[HCl] = 0.0976 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$kx10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.5	
1200	8.3	4.8948
1800	8.5	4.3235
2400	8.7	4.1681
3000	8.9	4.2297
3600	9.05	4.2153
4200	9.15	4.0902
α	9.65	

k = 8.2090×10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 25

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M		Solvent = 60% Acetonitrile	
[NaOH] = 0.0525 M		[HCl] = 0.0976 M	
[TBAB] = 0.0601M		Temp. = 313 K	

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.5	
1800	8.65	5.2290
2400	8.9	5.2872
3000	9.05	5.0584
3600	9.2	5.0909
4200	9.3	5.0105
α	9.65	

$k = 1.0024 \times 10^{-6}$ lit. $mol^{-1} sec^{-1}$

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TABLE 26

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate in the presence of TBAB

[Ester] = 0.0408 M	Solvent = 60% Acetonitrile
[NaOH] = 0.0525 M	[HCl] = 0.0976 M
[TBAB] = 0.0601M	Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.5	–
1800	8.9	7.0496
2400	9.15	7.1578
3000	9.3	7.0147
3600	9.4	7.5028
4200	9.5	7.1539
α	9.65	

k = 1.4007 x 10^{-6} lit. mol^{-1}sec^{-1}

TABLE 27

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	–
1200	8.45	4.5364
1800	8.7	4.2500
2400	8.9	4.0507
3000	9.1	4.0668
3600	9.25	4.0176
α	9.9	

k = 7.8946×10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 28

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	-
1800	8.8	4.8025
2400	9.0	4.5412
3000	9.2	4.5533
3600	9.35	4.5166
α	9.9	

k = 8.8721×10^{-7} lit. $mol^{-1}sec^{-1}$

Fpt

TABLE 29

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	–
1800	8.95	5.7202
2400	9.2	5.6916
3000	9.4	5.7588
3600	9.5	5.4549
α	9.9	

$k = 1.0901 \times 10^{-6}$ lit. $mol^{-1} sec^{-1}$

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TABLE 30

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate without catalyst

[Ester] = 0.0403 M
[NaOH] = 0.0510 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.65	-
1800	9.1	6.7781
2400	9.3	6.3861
3000	9.5	6.5459
3600	9.6	6.2917
α	9.9	

k = 1.2528×10^{-6} lit. $mol^{-1}sec^{-1}$

TABLE 31

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester]	= 0.0403 M	Solvent	= 60% 1,4-dioxane
[NaOH]	= 0.0510 M	[HCl]	= 0.096 M
[TBAB]	= 0.0620 M	Temp.	= 303 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.8	
1800	8.85	4.5992
2400	9.05	4.4330
3000	9.25	4.5234
3600	9.4	4.5509
α	9.9	

$k = 8.7241 \times 10^{-7}$ lit. $mol^{-1} sec^{-1}$

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TABLE 32

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M
[NaOH] = 0.0510 M
[TBAB] = 0.0620 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 308 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.8	–
1800	8.9	4.9047
2400	9.1	4.7114
3000	9.3	4.811
3600	9.45	4.8615
α	9.9	

k = 9.2936×10^{-7} lit. $mol^{-1}sec^{-1}$

TABLE 33

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M	Solvent = 60% 1,4-dioxane
[NaOH] = 0.0510 M	[HCl] = 0.096 M
[TBAB] = 0.0620 M	Temp. = 313 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	$k \times 10^{-5}$ $dm^3\ mol^{-1}\ sec^{-1}$
0	7.8	
1200	8.85	6.8988
1800	9.1	6.2818
2400	9.3	6.0139
3000	9.5	6.2842
3600	9.6	6.0435
α	9.9	

k = 1.1846×10^{-6} lit. $mol^{-1} sec^{-1}$

TABLE 34

Illustrating the effect of temperature on the alkaline hydrolysis of benzyl benzoate with TBAB

[Ester] = 0.0403 M
[NaOH] = 0.0510 M
[TBAB] = 0.0620 M

Solvent = 60% 1,4-dioxane
[HCl] = 0.096 M
Temp. = 318 K

Title value are expressed as ml of 0.05 M NaOH per 5 ml of the reaction mixture quenched by 10 ml of 0.03 M HCl

Time	Volume of alkali ≡ Excess Acid	kx10^{-5} dm^3 mol^{-1} sec^{-1}
0	7.8	–
1800	9.25	7.5390
2400	9.45	7.2922
3000	9.6	7.2523
3600	9.7	7.2105
α	9.9	

k = 1.4114 x 10^{-6} lit. mol^{-1}sec^{-1}

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