KINETIC STUDIES ON THE OXIDATION OF CARBONYL COMPOUNDS IN THE PRESENCE OF PHASE TRANSFER CATALYSTS

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DOCTOR OF PHILOSOPHY
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By

SHEEBA P.S.

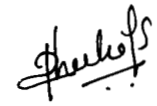
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA - 676 635 INDIA

Dedicated to the loving memories
of my beloved father

P.V. Sadasivan Pillai

DECLARATION

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by me under the guidance of **Dr. T. D. Radhakrishnan Nair**, Professor of the 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.



SHEEBA. P. S

Dr. T. D. Radhakrishnan Nair
Professor of the Department of Chemistry
University of Calicut

Calicut University
Kerala 673 635

CERTIFICATE

The thesis presented herewith embodies the observations on the Kinetics of Oxidation of two Carbonyl Compounds *viz.* Acetophenone and Benzaldehyde and some of its derivatives in aqueous acetic acid medium and in a few organic solvents in the presence of Phase Transfer Catalysts. This is an authentic record of research work carried out by **Sheeba. P. S** 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 there of has not been presented for the award of any other degree.

Dr. T. D. Radhakrishnan Nair
Supervising Teacher

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This thesis is inevitably the fruit of a collective and cooperative labour of many people; hence I wish to express my tribute to all of them.

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PREFACE

This thesis reports in four chapters the results of the investigation carried out independently by the author on the kinetics studies on the oxidation of carbonyl compounds in the presence of phase transfer catalysts.

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

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

The last chapter, which is the core of this thesis includes the results and discussion of the work done. Mechanism and rate law of the oxidation of benzaldehyde and acetophenone using both the methods have been discussed separately. Finally a conclusion of the work is given at the last of this chapter.

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

LIST OF ABBREVIATIONS

Abbreviations

PTC	Phase Transfer Catalysis
PT	Phase Transfer
TCMAC	Tricaprylmethylammonium chloride
TBAB	Tetrabutylammonium bromide
Q^+	Quaternary ammonium cation
$Q^+MnO_4^-$	Quaternary ammonium permanganate
AcPh	Acetophenone
PNA	*p*- nitro Acetophenone
MNA	*m*- nitro Acetophenone
PCA	*p*- chloro Acetophenone
PBA	*p*- chloro Acetophenone
PMA	*p*- methyl Acetophenone
PMyA	*p*- methoxy Acetophenone
PhCHO	Benzaldehyde
PNB	*p*- nitro Benzaldehyde
MNB	*m*- nitro Benzaldehyde
PCB	*p*- chloro Benzaldehyde
PMB	*p*- methyl Benzaldehyde
PMyB	*p*- methoxy Benzaldehyde
MMyB	*m*- methoxy Benzaldehyde
aq. HOAc	Aqueous acetic acid

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INTRODUCTION

Sheeba P.S. “Kinetic studies on the oxidation of carbonyl compounds in the presence of phase transfer catalysts” Thesis. Department of Chemistry, University of Calicut

CHAPTER 1

INTRODUCTION

1 PHASE TRANSFER CATALYSIS

Phase transfer catalysis (PTC) has emerged as a technique for conducting useful synthetic reactions under heterogeneous conditions. This field indeed is a tribute to the chemists involved in process development and research. PTC is a welcome cost-effective process in general, and is a solution to problems related to yield and purity usually encountered in industrial and developmental laboratories. Many excellent chemists are employing their skills for the development of this technique into a versatile, convenient, and cost-effective method, and developmental work is being carried out in leading laboratories the world over.

1.1 WHAT ARE PHASE TRANSFER CATALYSTS?

They are agents used to transfer one of the reactants in active form from its normal phase into the normal phase of the other reactant for causing higher reaction rates. The phase transfer agent, however, is not consumed during the course of the reaction and it performs the transport duty repeatedly and efficiently. The catalysts most commonly used are quaternary salts and crown ethers. Polyethylene glycols, which are known as 'poor chemists crown' also, come under this category.

1.2 NATURE OF PHASE TRANSFER CATALYSIS

Interaction of a substrate with a reactant located in two different phases is often inhibited because of the inability of the reactant and the substrate to cross over the phase boundary barrier and come together. The fundamental requirement for a bimolecular chemical process to occur is collision or interaction between the reactant and the substrate entities. Chemists frequently encounter the problems associated with the difficulty in bringing together two mutually insoluble reagents in sufficient concentration to attain conveniently rapid reaction rates. Regardless of the amount of energy, external agitation or time of exposure, the reaction will not occur if the reactants cannot come into contact with each other.

Such problems have traditionally been overcome by utilizing a solvent or cosolvent, which exhibits both lipophilic and hydrophilic properties, provided one of them is water. For example, methanol, ethanol, acetone and dioxane have all been used as solvents in reactions involving salts and organic substrates. However, the salts are usually less soluble in organic solvents than in water and the organic reagents are less soluble in water. This problem has been partly solved by using dipolar aprotic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetonitrile, hexamethylphosphoramide(HMPA), *etc.* These solvents have made possible the mutual dissolution of both salts and the organic substrates. In these cation solvating solvents, the anion associated with the solvated cation is relatively unhindered by solvation, and therefore they become very reactive. The principal difficulty with such solvents is that they are costly and difficult to purify. To keep such solvents in an anhydrous state and to recover once the solvent has been used are also difficult, and they can cause health hazards to the user.

However, these difficulties are normally not there with phase transfer (PT) catalysts, which permits and accelerates reactions between ionic compounds and organic, water-insoluble substrates in solvents of low polarity. The basic convenience

of PTC of two-phase reactions is that one can select a PT agent, and use it in catalytic quantities. The function of the catalyst is to transfer or carry the anionic reactant in the form of its onium salt, from the aqueous to the organic phase where the reaction can take place. The isolated onium salts show two properties of great importance – the anions can be alkylated extremely rapidly and the position of alkylation (C vs O in enolate ions) appears to be much more specific than in the usual alcoholic or aprotic reaction solvents[1,2]. A number of PT agents like quaternary salts[3], phosphoramides, crown ethers[4] and cryptands, which can mask and thereby solubilize alkali metal ions, have been used to catalyze a variety of organic transformations. Recently, it has been shown that carbowax, *i.e.* linear polyethylene glycol (PEG), can complex with alkali ions (notably K^+) and transfer the complexed salt into organic phases[5,6], whose catalytic action is mechanistically similar to that of crown ethers. It can be seen now-a-days that PEG is also being used commonly to carry out organic reactions[7-14].

The novel PT technique is superior to the conventional methods in many respects and some of the important advantages are given below:

- expensive anhydrous or aprotic solvents are no longer required
- improved reaction rates are found
- lower reaction temperatures are only needed
- synthetically easier to work-up
- increased yields through suppression of side reactions are found.

The great beauty of the PT method, however, is in the fact that it is usually mild and efficient. The simplicity of operation, the rapid reaction rates and the generally high yields of products, ensure that the technique will grow in importance and gain more reviews of application.

The PT method has been shown to be applicable to 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], polmerization[85-92], isomerization[93-98], rearrangements[99,100], hydrolysis[101-107], oxidation, reduction[108-114] reactions *etc.*

Additionally, PTC may function not only through liquid-liquid systems, but also with liquid-gas[115], liquid-solid[116-122], solid-gas and presumably solid-solid systems.

1.3 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. The foundations in this area were laid in the late 1960s by M. Makosza, C. M. Starks, and A. Brandstrom.

Mieczyslaw Makosza and coworkers of the Technical University in Warsaw published the first of a long series of papers in 1965[123]. They began a systematic exploration of alkylation and subsequently of other reactions in two-phase systems containing mainly concentrated alkali metal hydroxides. The descriptive terms used by them were "Catalytic two-phase reactions", "Catalytic alkylations of anions", "Catalytic generations of carbenes", *etc.* This work became more widely known with his dichlorocarbene discovery[34,35].

Almost simultaneously, patents on the "Catalysis of heterogeneous reactions" were issued to Charles. M. Starks of the Continental Oil Company in Ponca City, Oklahoma[124]. It was Starks who named the process "Phase transfer catalysis" and who clearly outlined the scope of the method and extended it beyond the original applications, *i.e,* alkylation and carbene generation. Furthermore a unifying mechanistic concept was proposed for all these types of reactions. This has provided an enormous impetus for the development of the field.

At about the same time, Arne Brandstrom of AB Hassle, Sweden developed a process that he called "Ion-pair extraction"[125]. Brandstrom's ion-pair extraction technique logically leads to the technique of PTC. The ion-pair extraction method is used to extract anions from an aqueous layer into chloroform or methylene chloride. Most anions can be extracted as ion-pairs in the organic phase, with the quaternaryammonium as 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. One such example, which is unquestionably important and deserves inclusion in any discussion of PTC is the method reported by Gibson and Hosking in 1965[126]. They have shown that triphenylmethylarsonium permanganate could be prepared, isolated and dissolved in chloroform, where it can act as an excellent oxidizing reagent.

1.4 COMMONLY USED PHASE TRANSFER CATALYSTS

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 second is that the transferred reagent in the new phase be available in a highly reactive form.

Although transfer of many species such as anions, cations, hydrogen peroxide, ammonia, hydrogen, oxygen, olefins, alcohols, acetylenes, *etc.* from their normal phase to a second phase are known to occur, the bulk of literature on PTC is, in fact, concerned with reactions involving anion transfer and activation. Hence, the basic requirements of a PT catalyst for anion transfer reactions are considered.

In the first place 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 secondly the effective cation-anion bonding must be "loose" enough to allow high anion reactivity to occur.

In addition to the above essential requirements, several additional parameters need to be considered, *viz.* 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, and whether or not anhydrous conditions are desirable

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

1) Quaternary salts - Charged catalysts

2) Macrocyclic ethers (Crown ethers) - Uncharged catalysts

1.4.1 Quaternary Salts

Numerous quaternary ammonium, phosphonium, arsonium, antimonium, bismuthonium, and tertiary sulfonium salts have been claimed to be catalysts. However, in practice only a limited number of ammonium and phosphonium salts are widely being used[125,127,128]. This is based on some factors involved in the selection of quaternary salts as catalysts for anion transfer[129].

The simple notation $R_4N^+X^-$, *etc.* for quaternary salts conceal the wide range of structures and properties possible in this kind of PT catalysts.

a) Various Combinations of the R Groups

The primary requirement of the groups R is that they collectively have sufficient organic structure to transfer the desired anion into the organic phase. The required amount of organic structure will depend on the anion transferred, the polarity

of the organic phase, the concentration of inorganic reagent in the aqueous phase, and sometimes, the presence of solvating organic compounds. It has generally been found that tetramethyl- and tetraethylammonium salts do not have sufficient oleophilicity to function well as anion transfer catalysts.

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 catalysts 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 $R\text{-}N^{+}(R^{1})_{3}\ X$ are frequently used because of their ease of preparation or commercial availability. Catalysts where R^{1}=butyl or larger appear to activate anions more strongly because they provide for near-maximum cation-anion interionic distances. These catalysts are particularly useful when the organic phase reaction is relatively slow as in simple displacement reactions. The cheapest catalyst available is "tricaprylmethylammonium chloride", a technical mixture containing C_8-C_{10} alkyl groups, which is sold under the trade names "Aliquat 336" (Fluka A G, Buchs, Switzerland; General Mills Co., Kankasee, Illinois, USA) or "Adogen 464" (Aldrich Chemical Comp., Milwaukee, Wisconsin, USA) belong to this group.

b) Different Central Onium Atom

Quaternary ammonium and phosphonium salts have been successfully used as PT catalysts, 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 available. But phosphonium salts are more thermally stable than the corresponding ammonium salts in some environments. Phosphonium salts are reasonably stable upto

temperatures of 150-170^{0}C, whereas ammonium salts lose their activity rather rapidly at temperatures greater than about 110-120^{0}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^{0}C. On an industrial scale, however, this difference may be significant, since reaction rates can be increased by conducting reactions under pressure, which invariably causes an increase in temperature. It may also be noted in this connection that phosphonium cations are exceedingly sensitive to hydroxide ion[130,131], and they undergo a reaction of the type

$$R_4P^+OH^- \longrightarrow R_3PO + RH \qquad (1.1)$$

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

c) Different Anions with the given Catalyst Cation

The activity of a quaternary salt selected for use as a PT catalyst may depend markedly on the anion originally present. The quaternary salts are useful as PT catalysts only if the anion accompanying the catalyst is distributed in the organic phase to a much lesser extent than the anion to be reacted. In general, the large, lipophilic quaternary cations are soft in the HSAB sense[132], so that this cation tends to pair with the softest anions 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 would be convenient to use as PT catalysts. However, iodide ion associates much more strongly with quaternary cations in organic media than many other anions. This problem can be overcome by renewing the aqueous phase periodically[15]. Various studies suggest that the nucleophilicity of halide ions under PT conditions are approximately equal[133] or slightly reversed[134] from the usual accepted order, *i.e.*, $F \geq Cl \geq Br \geq I$. Thus the more commonly used

catalysts have hydrogen sulfate or chloride as the anionic moiety. Bromide also is reasonably good in many cases.

Taking into consideration the above factors, the catalysts which have been used most commonly to date are benzyltriethylammonium chloride ("Makosza's catalyst", BTEAC, TEBAC), trioctylmethylammonium chloride ("Starks catalyst", Aliquat 336, tricaprylmethylammonium chloride, TCMAC, TOMAC) and tetrabutylammonium hydrogen sulfate ("Brandstrom's catalyst", TBAHS). Makosza's catalyst is quite easy to prepare, and can be recrystallized to purity and kept in a reasonably anhydrous state with little difficulty. Aliquat 336 is readily available as yellow oil from General Mills and is quite inexpensive. It is more efficient than either Brandstrom's or Makosza's catalyst according to the Herriott-Picker study[24].

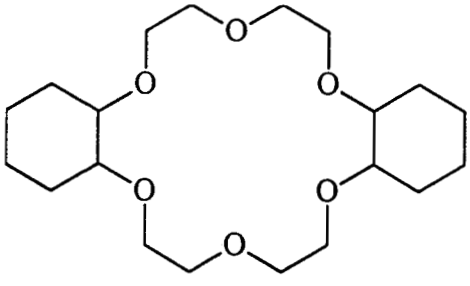
Even though tetrabutylammonium hydrogen sulfate is a bit more expensive, it has two important advantages. The hydrogen sulfate anion is highly hydrophilic and readily partitions into the aqueous phase where it plays no further role in the reaction. Moreover, the crystalline hydrogen sulfate can be treated with a variety of salts and it enables anion exchange reactions. Brandstrom and coworkers have prepared numerous salts by this anion exchange reaction, details of which are given in his book on ion pair extraction[135].

1.4.2 Macrocyclic Ethers (Crown Ethers)

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 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,

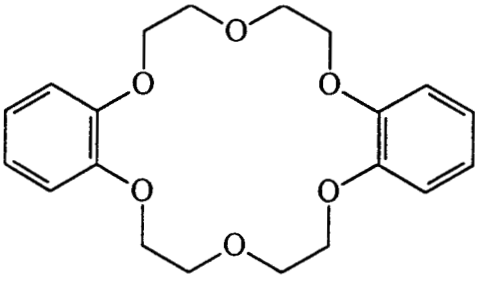
to 'crown' a metal ion, the members of this series were referred to as crown compounds.

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)



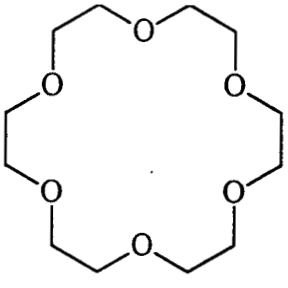
dibenzo-18-crown-6

(I)



dicyclohexyl-18-crown-6

(II)



18-crown-6

(III)

Figure 1.1 Structures of three important crown ethers

Using the simple "lock and key" approach, it is evident that these crowns have cavity dimensions (2.6-3.2) of the potassium ion (2.66), hence these crowns are more

specific for potassium ion than sodium or lithium ion whose ionic diameters are 1.94 and 1.36 respectively.

The dibenzo crown (I) owes its popularity 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 better cation complexing crown[137,138], and secondly, its solubility in hydrocarbon media is marginal. More popular than (I) is dicyclohexyl-18-crown-6 (II), which is prepared from (I) by hydrogenation[105]. Compound (II) is quite soluble in a variety of organic media, is a strong cation complexer and is a stable white solid. Unfortunately, it is a skin irritant[106] and is relatively expensive to make. The most widely used crown catalyst has been 18-crown-6. This compound is somewhat less lipophilic than (II), but much more than (I). Moreover, 18-crown-6 can be prepared quite readily by several methods and can be obtained in a pure form[139]. Finally, 18-crown-6 is effective in a wide variety of PT processes.

In most reactions, quaternary salts and macrocyclic ethers give roughly equal success, although often under different reaction conditions. General comparisons of these two catalyst types are given in Table 1.1. Selection of one or the other of these two general types of catalyst will usually be made on the collective importance of the factors listed in the table to the particular conditions and the problems faced.

Table 1.1

General Comparison of Quaternary Salts and Macrocyclic Ethers as Phase Transfer Catalysts

Factor	Quaternary Salts	Macrocyclic Ethers
Activity	Generally high; depends on the structure of the catalyst	Generally high; depends on the structure
Stability	Generally stable to ~150 ^{0}C, but < 70-80^{0}C when strong alkalies are used.	Stable.
Ease of preparation or availability	Wide varieties of quaternary ammonium salts are available or prepared; other functional groups are easily introduced.	Certain macrocyclic ethers are easily prepared and commercially available.
Recovery	Lower salts are easily recovered; higher ones may be difficult.	Easily recovered.
Cost	Relatively low.	Relatively high.
Use of water for the dissolution of inorganic reagent	Addition of some water is usually, but not always required.	Addition of water is not required. Sometimes, added water inhibits reaction
Inorganic cation	The kind of inorganic cation is not usually important.	A specific cation must be used, depending on the macrocyclic ether.

1.5 THE PRINCIPLE OF PHASE TRANSFER CATALYSIS

Though quaternary salts and crown ethers bring about phase transfer catalysis they involve different mechanistic pathways.

Phase transfer catalysis utilizing either a quaternary ammonium or phosphonium salt as a 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 base or 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 amount 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 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 1.2.

$$Q^+X^-_{(aq)} + M^+Nu_{(aq)} \rightleftharpoons Q^+Nu^-_{(aq)} + M^+X^-_{(aq)} \qquad (1.2)$$

Not only that the anion, which is functioning as 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 1.3.

$$Q^+Nu^-_{(aq)} \rightleftharpoons Q^+Nu^-_{(org)} \qquad (1.3)$$

Once the nucleophile or base (represented by Nu) is in solution in nonpolar (organic) media, the displacement or deprotonation can take place with product formation. In the case of a nucleophile displacement reaction, Q^+ would ultimately be ion-paired with the nucleofuge. If the leaving group were X^-, the ion-pair QX would be generated and would be subject to the equilibria formulated as shown above. Starks has offered a classic diagram of the phase transfer catalytic cycle[15] as given in Figure 1.2.

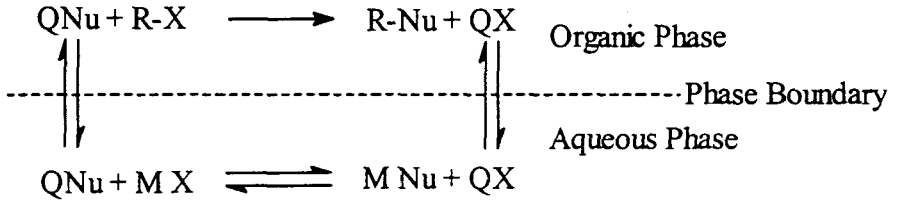
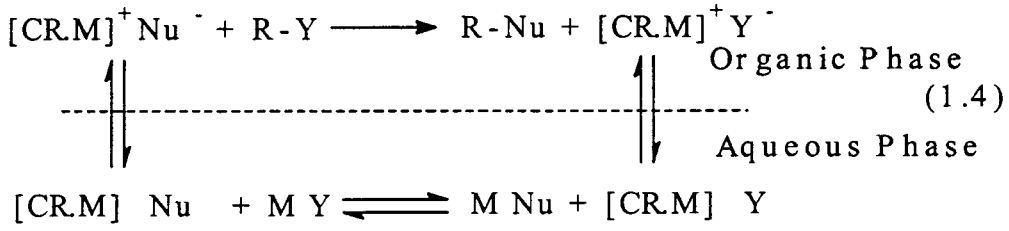


Figure 1.2 Starks 'Phase transfer catalytic cycle'

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 there be present in solution a lipophilic cation, Q^+, or some equivalent cation solvator and that whatever the identity of X, it must be exchangeable with 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 complete.

Crown ethers function in a fashion similar to quaternary salts. They envelop 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 1.4 in which 'CR' represents the crown.



(1.4)

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.

1.6 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 the 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].

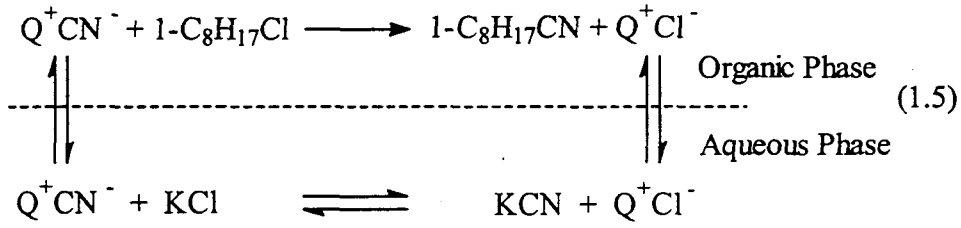
Since PTC involves a sequence of several steps, detailed understanding of the factors which influence each step and a knowledge of the relationships between the various steps are desirable for enabling one for the application of the technique for useful synthetic or mechanistic study purposes. Much experimental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

The mechanism of PTC in anion-promoted reactions, proposed by Starks[15,16] and supported by other authors[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 amount of data is available, is simply the cyanide displacement on alkyl chloride (Equation 1.5).



(1.5)

From the above equation, it is clear that the anion transfer step involves all the three equilibria pictured above, while reaction of the transferred reagent, CN^-, with alkyl chloride takes place in the non-aqueous phase. Therefore an understanding of this 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 (Equation 1.6)

$$Q^+Cl^-_{(org)} + CN^-_{(aq)} \rightleftharpoons Q^+CN^-_{(org)} + Cl^-_{(aq)} \qquad (1.6)$$

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.

1.6.1 Transfer of Anions from Aqueous to Organic Phases

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 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 greater charge on it.

Inorder to transfer most 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 organic phase solvation of the cation is stronger than aqueous phase solvation of the anion. To be highly effective in phase transfer for two-phase displacement reactions, the catalyst cation-anion pair need to be strongly partitioned into the organic phase. Therefore the factors affecting the partition of cations between aqueous and organic phases are to be taken into consideration.

A. Factors Affecting the Distribution of Catalyst Cations between Aqueous and Organic Phases

The optimum distribution of catalyst cation in anion transfer catalysis is that the rate of the organic phase reaction be equal to the rate of catalyst regeneration. For example, in the cyanide displacement reaction sequence,

$$RCl + Q^+CN^- \xrightarrow{k_0} R\text{-}CN + Q^+Cl^- \quad \begin{matrix}\text{Organic Phase}\\ \text{Reaction}\end{matrix} \qquad (1.7)$$

$$Q^+Cl^- + NaCN \xrightarrow{k_r} Q^+CN^- + NaCl \quad \begin{matrix}\text{Catalyst}\\ \text{Regeneration}\end{matrix} \qquad (1.8)$$

the maximum rate is obtained when

$$k_0 (RCl) (QCN) = k_r (QCl) (NaCN) \qquad (1.9)$$

If we assume that catalyst regeneration takes place only in the aqueous phase, then a definite aqueous phase concentration of the catalyst cation would be required. Values of k_r typical for anion exchange reactions in aqueous media are 5-10 orders of magnitude greater than k_0, so that even if catalyst regeneration occurred only in the aqueous phase, only a few hundredths of a percent of the catalyst need be in the aqueous phase to satisfy or exceed the criteria represented by Equation (1.9). Thus for most PT catalyzed reactions involving anion transfer from aqueous to organic phases, we select a catalyst which is soluble in the organic phase.

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

In fact, 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 inorganic salt in the aqueous phase, and the presence of foreign salts.

1. The Organic Structure of the Catalyst Cation

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

$$\alpha = (QX \text{ in the organic phase}) / (QX \text{ in the aqueous phase}) \quad (1.10)$$

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

$$\log \alpha = 0.5\ n + \text{constant} \quad (1.11)$$

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 center 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 quaternary ammonium 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.

2. The Anion Associated with the Catalyst Cation

The kind of anion associated with the catalyst cation has enormous influence on the extent 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 catalyst cation for transfer. First, anions are hydrated to different extents, 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 of 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 catalysts.

3. The 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 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 behavior 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 "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 (dichloromethane, 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.

4. Concentration of Inorganic Salt in the Aqueous Phase

Increasing the concentration of inorganic salts 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 is illustrated by Herriott and Picker[24] for the 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.

5. Salting – out Effects

Extraction constants are not only influenced by solvent systems, but also by 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 sodium hydroxide. In this medium almost all-quaternary ammonium salts are sparingly soluble and easily extracted.

1.6.2 Ionic Reactions in Non-Polar Media

Not only must a phase transfer agent bring one reactant from its 'normal' phase into the phase of the second reactant, but also it must make 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 ions exhibit 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 high activity.

Ugelstand and co-workers[71] have measured rates for the reaction of potassium and tetrabutylammonium 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 the 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.

1.6.3 Evidence for the Mechanism of Phase Transfer Catalysis

A difficult problem in the kinetics of PT catalyzed 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 slow step being the displacement reaction in the organic phase. Detailed work has been carried out by several groups, and their conclusions are in substantial agreement.

Starks[15] examined the reaction of cyanide ion with n-octyl bromide (Equation 1.12) and found that

$$Q^+CN^- + C_8H_{17}Br \longrightarrow C_8H_{17}CN + Q^+Br^- \qquad (1.12)$$

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 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 fashion. 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 favor substitution, it was inferred that 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 important factors.

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 concomitant transfer of the organic cation[158]. The kinetic measurements indicate that the effectiveness of a PT catalyst depends mainly on its organophilicity.

1.7 PHASE TRANSFER ASSISTED PERMANGANATE OXIDATION

Potassium permanganate is probably the most powerful of the oxidizing agents in the organic chemist's armory. It has been used both as a selective oxidant and as a scavenger to remove small amounts of organic material present as contaminants in either water or air.

The great reactivity of permanganate as an oxidant is reflected in its ability to use different reaction paths, depending on the structure of the organic substrate, and depending on the acidity and basicity of the solution[159,160]. Low enthalpies of activation, frequently in the range 5 to 10 K Cal $mole^{-1}$, 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 has 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 properties.

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 the reductant at the interface and the rate of reaction is drastically reduced[166]. The classical way of overcoming the solubility problem has been by use of polar organic solvent 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 catalyzed permanganate oxidations are usually 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 the titration of reducible substances. For permanganate oxidations in non-aqueous solvents, quaternary salts, crown ethers and poly (ethylene glycol) ethers have been used as catalysts. Taking into account of the high cost of crown ethers, it has been reported to be more reasonable and advantages to use quaternary ammonium salts as PT catalysts for $KMnO_4$ oxidation either in L-L system or L-S system.

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 potassium permanganate by exchange of the chloride ion of methyltriphenylarsonium chloride. The methyltriphenylarsonium permanganate thus prepared in chloroform was found to oxidize olefins, alcohols, nitroalkanes, nitriles, and 1,3,5-trimethyl benzene, but it didn't oxidize t-butanol, benzene, toluene, ethyl acetate, diethyl ether, acetone, or dipropyl ketone.

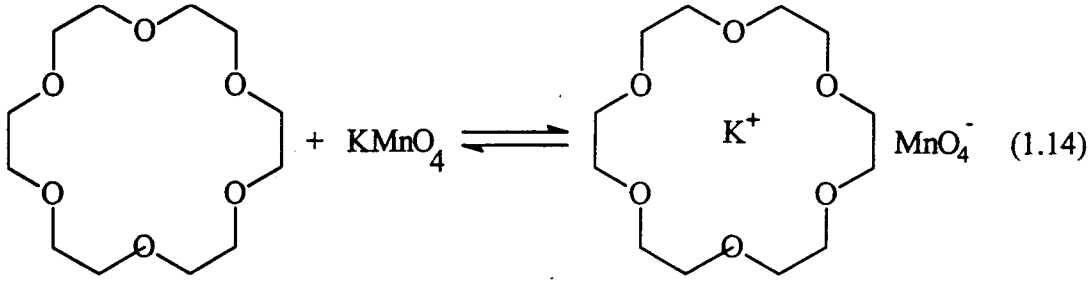
Another more recent approach involves the use of salts such as tetrabutylammonium permanganate[167] or benzyltriethylammonium permanganate[168], which, because of the organophilicity of the quaternary ammonium cations, are soluble in non-polar solvents. These salts may be prepared by adding a solution of the corresponding quaternary ammonium halide to a solution of potassium permanganate. However, caution should be exercised because above a certain temperature most quaternary ammonium permanganates 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 quaternary ammonium halide (Q^+X^-) with potassium permanganate. Anion exchange (Equation 1.13) then produces a quaternary ammonium ion-pair that is soluble in non-polar solvents.

$$Q^+X^- + K^+MnO_4^- \rightleftharpoons Q^+MnO_4^- + K^+X^- \qquad (1.13)$$

This exchange usually takes place with a change of phase by the permanganate ion. Typically, the quaternary ammonium halide dissolved in an organic solvent such as methylene chloride is added to either solid $KMnO_4$ or an aqueous solution of potassium permanganate. During the exchange, the 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 organophilic and thereby produces an ion-pair that is soluble in organic solvents (Equations 1.14 and 1.15).



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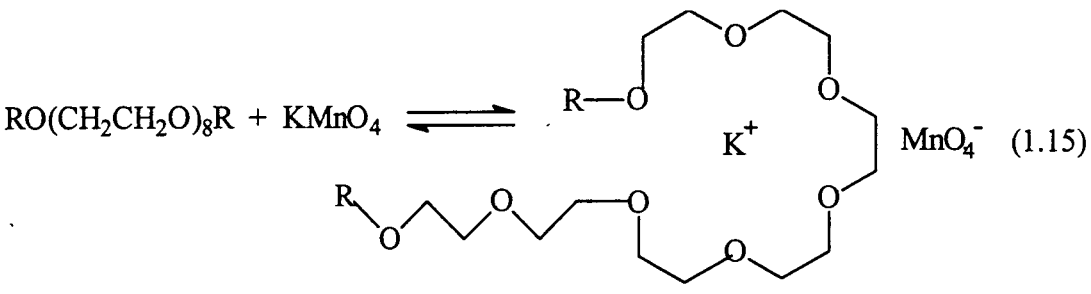

(1.15)

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

Poly (ethylene glycol) mono[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 the PEG-purple benzene is identical with that reported by Sam[45] 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.

1.7.1 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 solution in the organic phase.

It is well known that potassium permanganate exists in an ionic form when dissolved in water. However, when a quaternary ammonium permanganate salt

dissolves in an organic solvent it exists predominantly as an ion-pair. This can be seen from the calculations described in 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 equation 1.16, where R is the radius of the solvent sphere, k is the Boltzmann constant, and T is the temperature[178].

$$dP = (3/4\pi R^3)\, 4\pi r^2 \exp(-e^2/DkTr)\, dr \qquad (1.16)$$

Assuming that the sphere is large enough to give ideal behavior 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 center of an ion Q^+ when more ions are present is given by equation (1.17)

$$dH = [Q^+]\,[X^-]\,(4\pi N/1000)^2\,(R^3/3)\,r^2 \exp(-e^2/DkTr)\, dr \qquad (1.17)$$

A plot of dH/dr against r passes through a minimum at $r = e^2/2DkT$ (Figure 1.3).

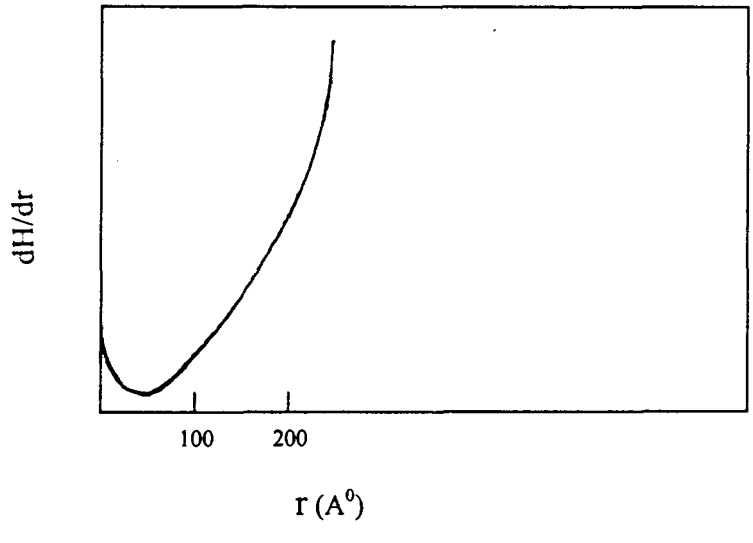

Figure. 1.3 Plot of dH/dr against r

The significance of this 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 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] (Table 1.2).

Table 1.2

Solvent Parameters

Solvent	Dielectric Constant	$e^2/2DkT$ (A^0)
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 an 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 A^0 for the ionic radius of the permanganate ion[179] and the value of about $3A^0$ and $6A^0$ for tetramethyl and tetraoctyl ammonium 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.

Some studies regarding the effectiveness of various PT agents with potassium permanganate have been tried by Okimoto and Swern[181], Herriott and Picker[173] and Cram and Co-workers[182]. 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 at least on three factors:

1) the structure of an organic cation,
2) the polarity of the organic phase, and
3) the nature of anions involved.

REVIEW & SCOPE OF PRESENT WORK

Sheeba P.S. "Kinetic studies on the oxidation of carbonyl compounds in the presence of phase transfer catalysts" Thesis. Department of Chemistry, University of Calicut

CHAPTER 2

REVIEW AND SCOPE

OF THE PRESENT WORK

2 REVIEW & SCOPE OF THE PRESENT WORK

2.1 REVIEW OF THE PRESENT WORK

2.1.1 Kinetics of Oxidation of Benzaldehyde

The kinetics and mechanism of oxidation of benzaldehyde by various oxidants have been reported.

Radhakrishnamurti and Sarangi[183] have reported the Ru(III)-catalyzed oxidation of benzaldehyde and substituted benzaldehydes by acid bromate. The reaction is first order each in [substrate] and [Ru(III)], independent of acid and zero order with respect to [bromate]. The reaction indicates acceleration in rate with increase in the percentage of acetic acid in the reaction medium.

Kinetics and mechanism of Ru(III)-catalyzed and uncatalyzed oxidation of hydroxy benzaldehyde by CAT in $HClO_4$ medium containing 20% MeOH was studied by Ali and Upadhyay[184]. The order with respect to CAT was found to be unity and that in substrate and acid decreases from unity. The corresponding carboxylic acids were obtained as the product.

Radhakrishnamurthy and Sahu[185] have studied the kinetics of Os(VIII)-catalyzed oxidation of benzaldehyde and substituted benzaldehydes in alkaline

medium and in aqueous t-butanol medium. The loss of HO^- by single electron transfer in the transition state has been proposed.

Oxidation of cinnamaldehyde by CAT in perchloric acid and in alkaline medium catalyzed by Os(VIII) has been kinetically investigated by Mahadevappa *et al*[186]. Addition of Cl^- ions in the form of NaCl increases the rate of reaction. The mechanism suggested by them is in agreement with the zero salt effect and the solvent effect showing reaction of neutral species in the rate-determining step.

The kinetics of oxidation of substituted benzaldehydes by quinolinium chlorochromate (QCC) has been studied in aquo-acetic acid in the presence of perchloric acid[187]. The rates of oxidation show first order kinetics each in [substrate], [QCC], and $[H^+]$. Electron-releasing substituents retard and the electron-withdrawing groups enhance the rate.

The first kinetic study of the chromic acid oxidation of aldehydes was reported by Lucchi[188]. He studied the oxidation of a series of aromatic aldehydes in acetic acid solution using sulfuric acid as the catalyst. The reaction was first order in the aldehyde and in chromium (VI). Electron-withdrawing substituents were found to facilitate the reaction.

Studies of benzaldehyde oxidation using chromic acid were also reported by Graham and Westheimer[189], and by Wiberg and Mill[190], and have arrived at the following conclusions. In aqueous sulfuric acid solution, the reaction had the rate law:

$$\upsilon = k_a [RCHO] [HCrO_4^-] [H^+] + k_b [RCHO] [HCrO_4^-] [H^+]^2$$

whereas in aqueous acetic acid the rate of oxidation is approximately proportional to the first power of the Hammett acidity function

$$\upsilon = k [RCHO] [HCrO_4^-] h_0$$

The reaction also shows a kinetic isotope effect, indicating that carbon-hydrogen bond cleavage occurs in the rate-determining step.

Tompkins[191] found that the oxidation of benzaldehyde with potassium permanganate showed a linear increase of rate with increasing hydroxyl ion concentration over a very limited concentration range, and also noted catalysis by strong acids.

The rate of oxidation of eight aromatic aldehydes by potassium permanganate has been determined from pH 5 to 13[192]. The rate of reaction was found to be proportional to the first powers of the permanganate and the aldehyde concentrations. The reaction in neutral solution probably involves the formation of a permanganate ester of the hydrate of the aldehyde, followed by a rate-determining loss of the aldehyde hydrogen as a proton.

2.1.2 Kinetics of Oxidation of Acetophenone

The kinetics and mechanistic aspects of oxidation of acetophenones by a number of oxidants have received considerable attention. Mechanism of oxidation of acetophenones with two-electron oxidants differs from that of one-electron oxidants mainly in the involvement of enol or keto-form of the substrate.

In the Ru(III)-catalyzed oxidation of acetophenone by NBS[193] in aqueous acetic acid, a zero order dependence on [NBS] and first order dependence on [AcPh] and [H^+] have been noticed in uncatalyzed reaction. The catalyzed reaction was first order in [NBS] and fractional order in [AcPh] and [Ru(III)]. The order of reactivity observed among different acetophenones studied is *p*-NO_2 > *m*-NO_2 > *p*-Cl > *m*-OCH_3 > H > *m*-CH_3 > *p*-CH_3 > *p*-OCH_3.

In thallium(III) oxidation[194] of substituted acetophenones, a mechanism is postulated through rate-determining enolization. The electron-releasing groups

accelerate the reaction and electron-withdrawing groups retard the rate. The value of Hammett's reaction constant (ρ), obtained is –0.3, indicate that both the equilibrium protonation of carbonyl group and deprotonation of α-carbon of the conjugate acid, control the rate of enolization. The reaction is first order in substrate and zero order in oxidant. Dependence on acidity is unity. A decrease in the rate has been observed with increasing percentage of acetic acid upto 60% of HOAc, beyond which increase in acetic acid content increases the rate.

Kinetics of uncatalyzed and Os(VIII)-catalyzed oxidation of acetophenone and some substituted acetophenones by diperiodatoargentate(III) (DPA) have been investigated spectrophotometrically[195]. Both the catalyzed and uncatalyzed reactions follow first order kinetics in [substrate] while the order in [Ag(III)] is one in the absence and zero in the presence of Os(VIII). Addition of KIO_4 and KOH affects the reaction rates. The order of reactivities is found to be *p*-Cl ~ *p*-Br > H > *m*-CH_3 > *p*-CH_3 > *p*-OCH_3-acetophenones. The Hammett's plots yield a ρ-value of +1.33 for the uncatalyzed and +2.00 for the catalyzed systems.

Phenacyl was reported as the final product in Ce(IV) oxidation[196] of acetophenone in aqueous acetic acid. The substituents attached to the acetophenone ring were found to accelerate the oxidation rate regardless of the sign and magnitude of σ-value.

Micellar catalysis in the oxidation of acetophenone by Ce(IV) [197] has been employed in aqueous acetic acid. The rate is found to increase sharply as the surface concentration increases with no sign of reaching a maximum or constant value.

Mishra *et al* employed vanadium(V) for the oxidation of acetophenone[198]. They suggested a direct attack on the keto-form, without the involvement of intermediate complex formation, and benzoic acid was the end product

In the oxidation of acetophenones under alkaline conditions using hypohalite[199], it was observed that the cyclodextrins catalyzed the oxidation reaction

The oxidation of acetophenone using NBSac in aqueous acetic acid has been reported by Sundaram *et al*[200]. The order with respect to substrate, oxidant and $[H^+]$ is one each. Phenyl glyoxal is the reported product.

Kinetics of oxidation of acetophenone and substituted acetophenones has been carried out using NBP and NBSac in aqueous acetic acid[201]. The rate is found to be first order with respect to the substrate and zero order with respect to oxidants. The stoichiometry of the reaction was found to be 1:3 AcPh: oxidant in either case. The dielectric constant of the media has a negative influence. The effect of ionic strength is found to be negligible Besides this the effect of cyclodextrins was also studied.

In the CAT oxidation of acetophenone in aqueous ethanol under alkaline medium, phenacyldehyde is detected as the product of oxidation by Radhakrishnamurthy *et al*[202]. The observed reactivity in the case of substituted acetophenones is *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > H > *p*-CH_3. Electron-withdrawing groups accelerate the process while electron-releasing groups retard the oxidation process. The ionic strength effect is negligible. Solvent effects indicate the involvement of atleast one neutral molecule in the rate-determining step.

Kinetics of oxidation of acetophenone by CAT in aqueous acetic acid medium has been studied by K. J. Singh and N. Raina[203]. The rate of the reaction was found to increase with decrease in dielectric constant of the medium, and the reaction showed positive salt effect. The rate-determining step has been postulated to be between the enol-form of the ketone and HOCl.

Phenacylalcohol was the reported product in the chromic acid oxidation of acetophenones[204] and the oxidation rate was not very much affected by electron-

withdrawing groups whereas it was susceptible to electron demand at the seat of reaction.

The kinetics of oxidation of acetophenone and substituted acetophenones by acid iodate in 50% aqueous methanol medium is reported[205]. The reaction is first order with respect to [AcPh] and [iodate]. The oxidation process is catalyzed by H_2SO_4 and increase in the proportion of methanol in the reaction mixture enhances the rate. The order of reactivity observed among different acetophenones studied is H > *p*-OCH_3 > *p*-CH_3 > *p*-Cl > *m*-CH_3 > *m*-OCH_3 > *p*-NO_2 > *m*-NO_2. The plot of log k_{obs} vs σ_p^+ is linear, suggesting through conjugation between substituent and reaction centre. A probable mechanism involving the rate limiting electrophilic attack of IO_2^+ on methyl carbon atom of the acetophenone is proposed.

The bromate oxidation of acetophenone and substituted acetophenones was carried out by Sundaram *et al*[206] in acid medium. The reaction is first order each in [oxidant] and [substrate], and the rate increases with the acidity of the medium. A decrease in the proportion of acetic acid in the reaction mixture decreases the rate. The products of oxidation were identified as benzoic acid and formic acid. Added salts have no effect on the reaction rate, indicating the reaction to be of ion-dipole type. The rate constants of various acetophenones correlated well with σ+, the Okamato-Brown's constant, suggesting a cross-conjugation and/or a resonance interaction between the substituent and the reaction center. The reaction is susceptible to polar influences and the reaction constant (ρ) evaluated at various temperatures and solvent compositions is ~ 0.8 + 0.02 indicating an electron-deficient transition state.

Kinetics of oxidation of acetophenone using Mn(III) sulfate was investigated by Nath and Banerji[207]. The order with respect to each of the oxidant and ketone detected is first order. The rate is independent of acidity and solvent composition. The product of oxidation is reported as benzoic acid and formaldehyde. The mechanism of acetophenone in this case involves a direct attack of Mn(III) on the keto-form of the acetophenone.

Kinetics of oxidation of some substituted acetophenones by potassium permanganate[208] in aqueous acetic acid at constant ionic strength is reported. The reactions are first order each in the substrate and the oxidant. Change in acetic acid content of the solvent doesn't affect the kinetic rate.

2.1.3 Phase Transfer Catalysis Applied to Oxidation

Phase transfer catalysis has become a pervasive and widely accepted synthetic tool. However, there is very limited information on the kinetics of multiphase PTC reactions, in liquid-liquid, liquid-solid, liquid-liquid-solid (triphase) systems, particularly those involving complex mechanisms.

It has been reported that many inorganic oxidants can be transferred into the organic phase using PTC[129,141,142]. On laboratory scale, inorganic oxidizing agents like hypochlorite, chromic acid, chromates, dichromates, hydrogen peroxide, potassium permanganate *etc.* have been reported for the oxidation of organic substrates. Various PT catalysts, such as quaternary onium salts, crown ethers, and poly(ethylene glycol)s, have been used for the oxidation of organic substrates.

A. Hypochlorite

Hypochlorite ion is an effective oxidizing agent for a variety of substrates when the reactions are conducted under PT conditions.

Since Lee and Freedman[208,209] have demonstrated that hypochlorite ion can be transferred into an organic phase by using quaternary ammonium salts for the oxidation of alcohols and amines, the oxidation of alcohol by hypochlorite ion in the presence of PT catalyst has been reported by several investigators. In these studies the main reaction in the organic phase was claimed to be rate-determining, because the experiment was carried out under conditions in which the mass-transfer resistance of relevant species might be made negligible by high stirring. An interesting and

unexpected specific solvent effect has also been discovered with the use of ethyl acetate.

The oxidation of benzyl alcohol was conducted using hypochlorite as the oxidizing agent and triethylbenzylammonium chloride as PT catalyst in a two-phase system[210]. 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[211]. The results show that the oxidation of benzyl alcohol in two immiscible aqueous/dichloromethane systems was reaction controlled and occurred in the organic phase when the stirring rate was larger than 500 rpm. The experimental results also reveal that the reaction orders 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[212]. 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 anodic oxidation of benzyl alcohol in the two-phase system involving both, the redox mediator, OCl^-/Cl^-, and a PT catalyst were investigated[213]. The reaction order of the anodic oxidation of chloride ion in the aqueous phase was unity. The charge-transfer parameters, α, k_2^0, and exchange current density, i_0, of chloride ion oxidized on the graphite anode are obtained in the temperature range

from 5 to 45 ^{0}C. The model calculation of the anodic oxidation of benzyl alcohol by the theoretical analysis correlates well with the experimental results.

The synergetic action of the electron-transfer catalyst, meso-tetraphenyl porphyrin Mn(III) chloride complex with a common PT catalyst, trioctylmethylammonium chloride to promote the oxidation of alcohols has been reported[214]. Direct oxidation of benzyl alcohol with sodium hypochlorite was very slow, but was accelerated by electron-transfer or phase-transfer catalyst. In the presence of both, the oxidation was very fast.

Do and Do have carried out the indirect anodic oxidation of benzyl alcohol[215,216] in the presence of PT catalyst in a CSTER (continuous stirred tank electrolysis reactor). Effects 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. The conversion of benzyl alcohol and yield of benzaldehyde increased, and the selectivity of benzaldehyde decreased at a high organic flow rate when both the current density and the concentration of PT catalyst increased. The power consumption was confirmed by the experimental results as having decreased when the current density decreased and the concentration of PT catalyst increased.

Rapid spectroscopic assessment of reaction rates in PTC has been carried out by Trifonov and Kuzmanova[217]. The reactions examined include the hypochlorite oxidation of benzyl alcohol, and the plot of E (optical density) vs $t^{1/2}$(t-time) was found to be linear. The PT catalysts used were aliquat 336, $Bu_4N^+HSO_4^-$ and Bu_4PBr.

Amsterdamsky[218] 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 sulfate as the PT catalyst. The oxidation is essentially complete in 30 min., and the yields range from 70% to 85% after recrystallization.

Alkyl and aryl-substituted hydroquinones are rapidly oxidized to *p*-benzoquinones by stirring their solution in an organic solvent with aqueous sodium hypochlorite in the presence of catalytic amounts of tetrabutylammonium hydrogen sulfate[219]. In the oxidation of mono-substituted hydroquinones, dichloromethane or chloroform is more suitable solvents than ethyl acetate or benzene whereas the oxidation of di-, tri-, and tetra-substituted hydroquinones gave comparable results in dichloromethane, chloroform, ethyl acetate or benzene.

Using a PT catalyst, the kinetics of oxidation of benzaldehyde with hypochlorite was carried out in a batch reactor[220]. The reaction orders were both unity with respect to benzaldehyde and tetrabutylmmonium hypochlorite ion-pair in the organic phase.

Aromatic aldehydes were oxidized to carboxylic acids in high yields and selectivity using aqueous sodium hypochlorite as oxidant in a PTC system[221]. The reaction was strongly influenced by the pH of the aqueous phase, with maximum reaction rates at pH 9-11. Similarly, extraction of the hypochlorite ion was maximal at these pHs. The maxima are attributed to co-extraction of hypochlorous acid together with the hypochlorite anion into the organic phase, the former significantly increasing the reaction rate.

A. Chromate

Hutchins *et al*[222] showed that a fascile solubilization of potassium dichromate was effected in several organic solvents using a 2:1 ratio of adogen 464 to dichromate. The resulting orange solutions are fairly stable at ambient temperature but slowly darken after several days. These solutions were used for the neutral oxidation of activated alcohols especially where acid or base would be detrimental.

Pletcher and Tait[223,224] have studied the oxidation of alcohols with stoichiometric quantity of dichromate in 3M aqueous sulfuric acid using

tetrabutylammonium bisulfate as the PT catalyst. They have suggested that the reaction proceed *via* disproportionation of chromate ester in which the proton catalyzed disproportionation of Cr(V) or Cr(IV) to Cr(VI) is important. Cr(VI) in aqueous solution exists as a pH-dependent mixture of several species.

The kinetics of oxidation of benzyl alcohol by chromic acid was determined in two-phase system and in aqueous solution[225]. 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 one with respect to both reactants and a partial order two with respect to the acid concentration. 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*[226] have demonstrated the use of onium salts as PT catalysts to get complex chromate salts which is soluble in aprotic organic solvents such as dichloromethane. This complex chromate was used for the oxidation of several alcohols.

In consideration of low cost and easy availability of tricaprylmethylammonium chloride[227], this PT reagent was used with chromium trioxide as oxidant in dichloromethane medium for the conversion of alcohols to corresponding carbonyl compounds in excellent yields under mild conditions.

Dey and Mahanti[228] have studied the kinetics of oxidation of substituted benzyl alcohols by quinolinium dichromate in the presence of an acid and found that no further oxidation of benzaldehyde occurred under their experimental conditions.

A thorough and systematic analysis of the mechanism and kinetics of the oxidation of benzyl chloride by dichromate in L-L phase transfer catalysis has been provided to throw light on the course of reaction[229]. The rate of reaction depends on

the pH of the aqueous phase in view of the fact that chromium exists as dichromate, perchromate, or chromate depending on the pH. It was observed that $Q^+HCrO_4^-$ was the active species for oxidation. The reaction proceeds *via* the formation of benzyl alcohol, which is oxidized to benzaldehyde.

B. Hydrogen Peroxide

Quaternary ammonium salts assist the extraction of both hydrogen peroxide and metal salts like ruthenium or palladium chloride from the aqueous to the non-aqueous component of a two-phase system. This system has been used for the oxidation of styrene[230] with H_2O_2 in H_2O-dichloroethane containing both $RuCl_3$ and a PT catalyst to give mainly PhCHO. Similar oxidation of styrene in the presence of $PdCl_2$ gave PhCOMe.

A phase-transfer procedure for the oxidation of terminal alkynes under mild conditions was described[231]. The catalytic system involves dilute H_2O_2, Na_2MO_4 salts (M = Mo, W), and Hg (OAc) $_2$. In the absence of mercuric derivative no oxidation takes place. By changing the pH of the aqueous phase and the nature of the PT agent, either cationic or neutral, as well as the metal (Mo or W), carboxylic acids or α-keto aldehydes may be selectively obtained in fairly good yields.

The selective oxidation of primary aliphatic alcohols to carboxylic acids (60-70% selectivity), secondary alcohols to ketones (100% selectivity), and primary benzylic alcohols to aldehydes (95-100% selectivity) or carboxylic acids as well as the selective oxidation of allylic alcohol to ketones (80% selectivity) was performed in a H_2O_2-$RuCl_3.3H_2O$ PT catalyst system at a high substrate:$RuCl_3$ (625:1) ratio[232]. It has also been found that the PT catalyst not only has a role in the extraction of $RuCl_3$ and H_2O_2 in the organic phase but also protects the metallic catalyst against reduction.

In the presence of quaternary ammonium PT agents copper salts catalyze the selective oxidative dehydrogenation of alcohols and hydroxy acids by tert-butyl hydroperoxide in aqueous-organic two-phase systems[233].

C. Permanganate

Starks has reported that terminal olefins can be oxidized by $KMnO_4$ using PT catalyst to the one carbon shorter carboxylic acid[234]. Similarly, Sam and Simmons found that dicyclohexyl-18-crown-6 ether complex of $KMnO_4$ is effective in quantitatively oxidizing internal olefins to diacids[235]. Weber and Shepherd[236] had reported the controlled oxidation of olefins to the corresponding *cis*-glycols in moderate yields by $KMnO_4$ in dichloroethane using benzyltriethylammonium chloride as catalyst.

Herriott and Picker[237] has carried out the oxidation of several organic substrates (phenyl acetonitrile, benzyl alcohol, trans-stilbene, 1-octanol, 1-octene) by $KMnO_4$ under PTC conditions using tricaprylmethylammonium chloride with very good yields.

The instability of the solutions of $KMnO_4$ solubilized in benzene, toluene, and chloroform by the action of 15-crown-5, 18-crown-6, dibenzo-18-crown-6, tetrabutylammonium bromide and triaurylmethylammonium bromide as PT catalysts was reported[238]. The kinetic parameters depend markedly on the catalyst used, and the solvation of reactants is also important.

Styrene and acrolein diethyl acetal were oxidized at 0-2% with $KMnO_4$ under PT conditions[239] using chiral ammonium salts such as benzyl-l-methyl dimethyl ammonium bromide, l-methyl trimethyl ammonium iodide and benzyl dimethyl [(+)-1-phenyl ethyl] ammonium bromide as well as benzyl triethyl ammonium chloride as PT catalysts and pure water and CH_2Cl_2 as solvents.

The oxidation rates of 3,5-di-tert-butylcatechol (3,5-DtBC) to 3,5-di-tert-butyl-o-benzoquinone (3,5-DtBBQ) with $KMnO_4$ in both the L-L phase and S-L systems were found to increase by adding a crown ether, which functions as a PT catalyst[240]. The rate of the L-L phase oxidation was larger in a non-polar organic solvent, whereas a polar organic solvent was more effective for the S-L phase oxidation. The crown ether with a cavity that is the best match with the K^+ ion was found to function as the most effective PT catalyst, regardless of the reaction system used. The addition of an inorganic or organic acid was found to increase the rate of the L-L phase oxidation using crown ether as a PT catalyst. The oxidation step of 3,5-DtBC and MnO_4^- (in the form of the K^+-crown ether-MnO_4^-) in the organic layer, rather than the PT step of the K^+-crown ether-MnO_4^- complex from the aqueous phase to the organic phase, was suggested to be the rate-determining step of the L-L phase oxidation of 3,5-DtBC with $KMnO_4$ using a crown ether.

Kinetics of the cyclohexene oxidation with potassium permanganate in mono or biphasic systems, using the initial rates method has been investigated spectrophotometrically[241]. Kinetic parameters in presence of the PT agent and of small quantities of acetic acid have been determined. The results obtained during the kinetic investigations have been compared with those determined in the PT catalytic reactor (*i.e.* in conditions of $KMnO_4$ excess and ratio of the organic phase volume to the aqueous phase volume of 0.16).

Phase transfer has assisted the permanganate oxidation of primary aromatic amines to their corresponding azo compounds in good yields[242].

Permanganate, solubilized in methylene chloride with the aid of a PT agent, oxidizes benzyl alcohol to benzaldehyde and benzyl ethers to benzoate esters[243]. Although the rate of oxidation of the ether is about an order of magnitude slower than alcohol oxidation, both respond in an identical way to the unique effects caused by the

introduction of substituents into the ring. In addition, primary kinetic isotope effects are observed for both reactions. Because of these similarities, it is proposed that benzyl alcohols and benzyl ethers are oxidized by similar mechanisms, the difference in rate being ascribed to steric effects.

Oxidation of benzaldehyde, nitro-, chloro-, and methyl-substituted benzaldehydes and benzyl cyanide by potassium permanganate under PTC conditions using different catalysts and solvents were reported[244]. A correlation of structure-activity relationship of the catalysts is made and a comparison is made of the efficacies of the solvents used. It was found that tetrabutylammonium bromide and tricaprylmethylammonium chloride functioned as better catalysts and benzene as best solvent.

Polypropylene was oxidized with the help of tetrabutylammonium permanganate, and characterized by infrared and X-ray photoelectron spectroscopy (XPS) studies[245]. Scanning electron microscopy (SEM) was utilized to examine the surface topography, and peel strength measurements were employed to examine the bond strength.

2.2 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

It is important to note that although phase transfer catalysis has been in vogue for almost a quarter century, kinetic oriented research in this area are seldom reported.

The present investigation was undertaken with the object to determine the kinetic results for the oxidation of two important carbonyl compounds *viz.* Benzaldehyde and Acetophenone, and some of its substituents using potassium permanganate. Both the traditional method, which uses a co-solvent and the modern technique of phase transfer catalysis have been employed to study the kinetics.

The traditional method of oxidation of the substrates were carried out using aqueous acetic acid and in this solvent, the effect of the concentration of oxidant, substrate and hydrogen ion were examined. In addition the effect of solvent polarity, ionic strength of the medium, temperature and substituents on the rate have also been determined. The thermodynamic and kinetic parameters such as enthalpy of activation, free energy of activation and entropy of activation have also been evaluated to throw some light on the energetic and mechanistic details of the reaction.

The phase transfer (PT) technique was carried out using benzene, toluene, dichloromethane, chloroform and carbon tetrachloride as organic solvents. Tetrabutylammonium bromide (TBAB) and tricaprylmethylammonium chloride (TCMAC) were employed as phase transfer catalysts. In order to carry out the kinetic investigation in the organic solvent, the permanganate ions were extracted first from the aqueous to the organic phase. The efficiency of extraction was determined with respect to the

1) Concentration of MnO_4^- in aqueous phase
2) Structure of quaternary ammonium salt
3) Concentration of the quaternary ammonium salt and
4) Nature of the solvent

Although potassium permanganate was widely used as oxidant under phase transfer conditions, only little attention was paid to the investigation of the stability of its solutions in organic solvents. Hence the stability of the solution of permanganate ion, prepared in organic solvents were determined to show that such solutions are stable enough for satisfactory period of time in order to carry out the oxidation reactions.

This reasonably stable homogeneous oxidant in organic solvent was used to carry out the kinetic runs of phase transfer catalyzed oxidation of the carbonyl compounds. This particular kinetic study has been employed to find out the effect of substrate, oxidant, solvent, catalyst, temperature and substituents. The rates obtained under PT catalytic conditions were compared with the rates obtained in aqueous acetic acid media.

The yield study under heterogeneous oxidation conditions using phase transfer catalyst and the yields obtained were correlated with the efficiency of extraction.

Thus in the present study, attempts were made to study the stoichiometry and kinetics of phase transfer catalyzed oxidation of the aldehydes and ketones with permanganate ion and to compare these with the traditional method.

The following substrates were employed in the present investigation

01. Acetophenone (AcPh)
02. *p*-NO_2 AcPh
03. *m*-NO_2 AcPh
04. *p*-Br AcPh
05. *p*-Cl AcPh
06. *p*-OCH_3 AcPh
07. *p*-CH_3 AcPh
08. Benzaldehyde (PhCHO)
09. *p*-NO_2 PhCHO
10. *m*-NO_2 PhCHO
11. *p*-Cl PhCHO
12. *p*-CH_3 PhCHO
13. *o*-OCH_3 PhCHO
14. *p*-OCH_3 PhCHO

EXPERIMENTAL

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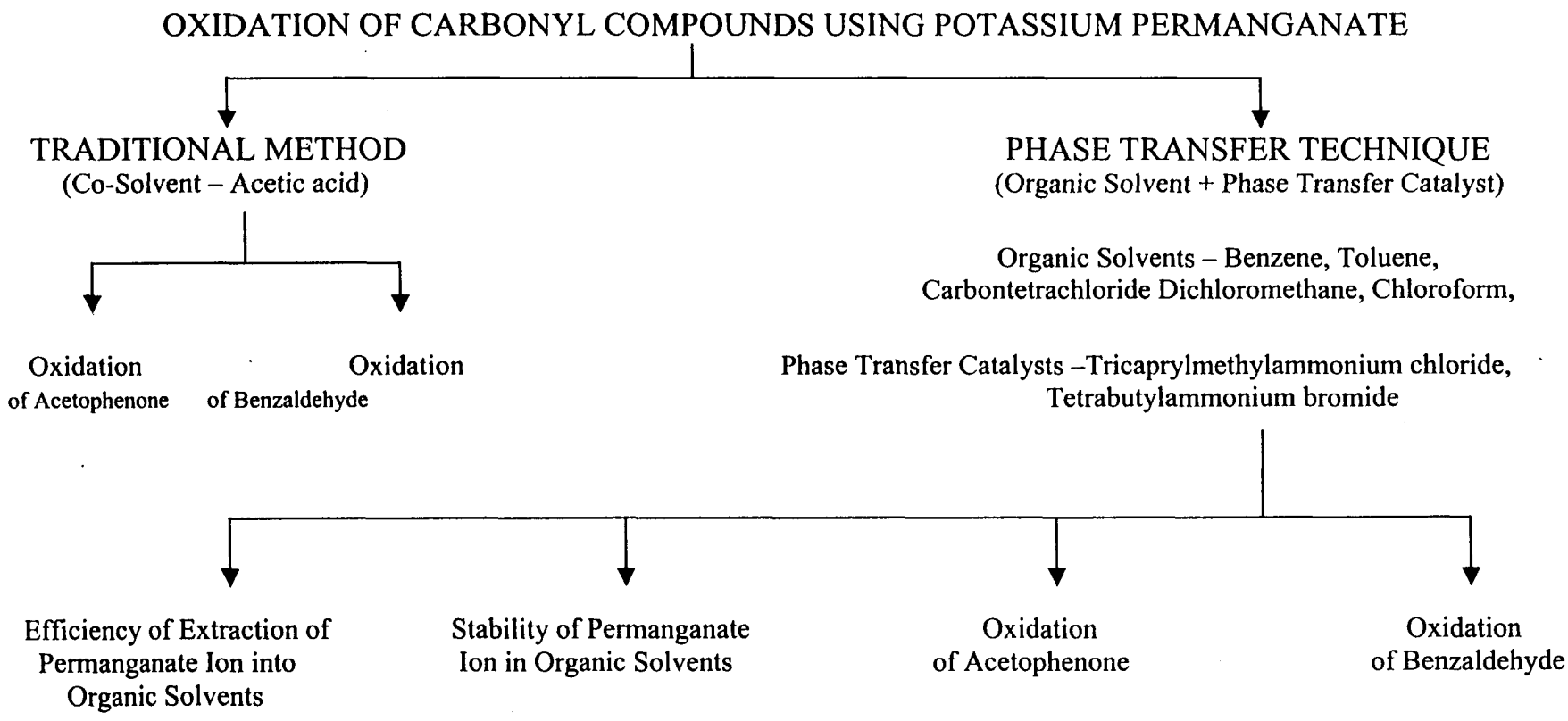
CHAPTER 3

EXPERIMENTAL

3 EXPERIMENTAL

This chapter deals with the materials and methods employed for the kinetic investigation. In this present project the kinetics of oxidation of two important carbonyl compounds *i.e.* Benzaldehyde and Acetophenone and some of its substituents were carried out using potassium permanganate with and without the use of phase transfer catalysts. Both, the traditional method, which uses a co-solvent and the modern technique of phase transfer catalysis, have been employed to study the kinetics. Hence the experimental part has been divided into different sections depending upon the materials and methods employed for the kinetic study.

EXPERIMENTS AT A GLANCE



3.1 TRADITIONAL METHOD – OXIDATION OF CARBONYL COMPOUNDS IN AQUEOUS ACETIC ACID MEDIUM

3.1.1 Materials

Acetophenone (BDH, AR grade) and Benzaldehyde (AR grade) was distilled under reduced pressure before use. The substituted acetophenones and benzaldehydes were of BDH, Fluka or Analar samples and were used without further purification.

Acetic acid (Analar quality) was purified by refluxing with potassium dichromate and the fraction boiling between 117^0 – 118^0C was collected and used. All other chemicals used were of analytical grade. Potassium permanganate (M&B, AR grade) was used as such, but its solutions were prepared in doubly distilled water.

3.1.2 Kinetic Measurements

Unless mentioned other wise, all the rate measurements were carried in 50% (V/V) aqueous acetic acid medium in a thermostatic waterbath in the temperature range 308-323 K. The reaction was initiated by adding to an equilibrated mixture of acetophenone in acetic acid, requisite quantity of pre-equilibrated solution of potassium permanganate. The concentration of substrate was always maintained in large excess over [permanganate] to ensure pseudo-first order conditions. 1ml aliquots were withdrawn at various known time intervals from the reaction mixture, diluted to one-fourth its concentration and the progress of the reaction were followed by measuring the absorbance of the unreacted permanganate (λ_{max} 526 nm) using Shimadzu double beam UV-Vis Spectrophotometer (UV-1602). The pseudo-first order rate constants, k_{obs} were computed by the method of regression analysis (method of least squares). Duplicate experiments were carried out to estimate the experimental errors. It was observed that the rate constants could be reproduced with sufficient accuracy.

By this experiment the effect of oxidant, substrate, hydrogen ion, ionic strength, temperature and substituents on the rate of oxidation of carbonyl compounds using potassium permanganate in aqueous acetic acid was determined.

3.1.3 Stoichiometry

The stoichiometry of the reaction between the substrate and the oxidant was determined by taking excess of [permanganate] over [substrate] and allowing the reaction to go for completion. Since the concentration of the substrate taken is less compared to that of the oxidant, all the substrate taken would have completely reacted leaving behind the unreacted oxidant. The concentration of the remaining oxidant was estimated iodimetrically. From the amount of the substrate reacted and the amount of permanganate consumed, the stoichiometry [substrate]: [permanganate] was estimated. The estimation was repeated at different time intervals to get concordant thiosulphate titre values, inorder to make sure that the reaction was complete.

3.1.4 Product Analysis

The products of oxidation was isolated and identified as follows. A reaction mixture containing excess of permanganate over acetophenone in 50% aqueous acetic acid were refluxed in a round-bottomed flask with a reflex condenser. Then sodium bisulphite and 50% hydrochloric acid was added to it till the precipitated MnO_2 dissolved and a colorless mixture was obtained. The resulting mixture was filtered off from impurities and suspended matter. The resulting liquid was saturated with NaCl and extracted with ether. The ethereal layers were combined, dried over anhydrous $MgSO_4$ and on evaporation of it gave a solid residue, which was then analyzed by qualitative as well as spectral data.

3.2 PHASE TRANSFER TECHNIQUE – OXIDATION OF CARBONYL COMPOUNDS USING QUATERNARY AMMONIUM HALIDES AS PHASE TRANSFER CATALYSTS

3.2.1 Materials

Carbonyl compounds *viz.* Acetophenone and Benzaldehyde was distilled under reduced pressure before use. The substituted acetophenones and benzaldehydes were of BDH, Fluka or Analar samples and are used without further purification. The organic solvents *viz.* benzene, toluene, dichloromethane, chloroform, carbontetrachloride, ethyl acetate *etc.* used in all of the experiments was purified by refluxing with potassium permanganate followed by distillation. The quaternary ammonium salts *viz.* tricaprylmethylammonium chloride (TCMAC) and tetrabutylammonium bromide (TBAB) were used as such. The distilled water used for these experiments was specially purified by distillation from alkaline permanganate.

3.2.2 Methods

As the phase transfer technique includes several steps, the method has been divided into several sections.

3.2.2.1 Extraction of Permanganate ion from Aqueous into Organic Phase

The aqueous solution of potassium permanganate was mixed with the organic solvent containing quaternary ammonium salts as phase transfer catalysts. The mixture was stirred at room temperature for half an hour using a magnetic stirrer and the concentration of MnO_4^- in each phase was estimated spectrophotometrically. This experiment has been carried out to find out the efficiency of extraction under different conditions and the optimum concentration of catalyst required for the complete transference of MnO_4^- from the aqueous phase was calculated.

The purple organic layer containing the MnO_4^- was separated, dried with $MgSO_4$ and stored in amber colored bottles. Its stability was determined by measuring the decrease in absorbance of MnO_4^- after regular intervals of time.

3.2.2.2 Kinetics of Oxidation of Carbonyl Compounds using Phase Transferred Potassium Permanganate as Oxidant

The concentration solution of permanganate ion in organic solvents prepared by the above method was adjusted by dilution and determined accurately by spectrophotometric method. Aliquots of substrate in organic solvent and the phase transferred permanganate ion were mixed together in such a way that reactions are performed under pseudo-first order conditions *i.e.* [substrate] > [MnO_4^-]. The kinetics were determined by the measurement of the decrease in absorbance of $Q^+MnO_4^-$. The wavelength of the most intense peak of $Q^+MnO_4^-$ is slightly different for different solvents. Hence the corresponding calibration line in each solvent was made before measuring the samples (λ_{max} of $Q^+MnO_4^-$: 527 nm in benzene, 526 nm in toluene, 524 nm in chloroform, 528 nm in dichloromethane and 524 nm in carbontetrachloride).

The above kinetic experiment was carried out to find out the effect of oxidant, substrate, catalyst, polarity of the organic solvent, temperature and substituents on the rate of oxidation of carbonyl compounds using phase transfer technique.

3.2.3 Stoichiometry

The stoichiometry of the reaction was performed in the same way as mentioned above with the aqueous solvent, and the amount of unreacted permanganate ion in the organic solvent was estimated spectrophotometrically by diluting to appropriate concentration.

3.2.4 Product Analysis

The product analysis was carried out in a heterogeneous system. To substrate (0.1 mole) dissolved in 50 ml of organic solvent (benzene), 0.01 mole of PTC was dissolved. To it was added a solution of $KMnO_4$ (0.5 mole) in 50 ml water. This mixture was stirred vigorously using a magnetic stirrer. The excess permanganate was destroyed with sodium bisulphite and 50% HCl. The benzene layer was separated and extracted several times with 10% aqueous NaOH solution. The combined alkaline phase was acidified and extracted with ether. Evaporation of ether gives the product, which was then analyzed with its melting point and qualitative analysis.

RESULTS AND DISCUSSIONS

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CHAPTER 4

RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSIONS

The most important carbonyl compounds are aldehydes and ketones. In aldehydes one of the available valencies of carbonyl carbon is satisfied by hydrogen *i.e.* R-CHO, whereas in ketones both the valencies are satisfied by same or different alkyl or aryl groups *i.e.* R-C(R')=O. Because of this particular difference, aldehydes are easily oxidized to carboxylic acid.

Though many researchers have carried out the kinetics of oxidation of Acetophenone and Benzaldehyde using different oxidizing agents, a detailed study of the oxidation of these compounds with potassium permanganate is lacking. The present investigation is an attempt in this direction. In this present work an attempt has been made to study the kinetics of oxidation of Acetophenone, Benzaldehyde and some of its substituents using the traditional method, which uses the co-solvent and the modern technique of phase transfer catalysis. The results obtained are presented and discussed in this chapter.

4.1 OXIDATION OF ACETOPHENONE USING POTASSIUM PERMANGANATE IN 50% AQUEOUS ACETIC ACID MEDIUM

Acetophenone is a stable substrate and it does not undergo oxidation very easily.

4.1.1 Stoichiometry and Product Analysis

Stoichiometry of the reaction has been investigated by equilibrating known amounts of acetophenone and potassium permanganate at room temperature for two days. The completion of the reaction was ensured by estimating the oxidant remaining in excess at various intervals of time. From the amount of acetophenone taken and the permanganate reacted, the stoichiometry of the reaction, [Acetophenone] : [$KMnO_4$] was found to be 1 : 1 *i.e.* one mole of acetophenone consumed one mole of permanganate.

A qualitative analysis of the reaction product showed that the product of the oxidation is carboxylic acid, which was identified as benzoic acid from the melting point and IR data.

4.1.2 Kinetic Studies

The specific rates for the reaction of acetophenone and some of its substituents using potassium permanganate in 50% aqueous acetic acid determined under different experimental conditions *i.e.* by changing the concentration of the oxidant, substrate, mineral acid, solvent polarity, ionic strength, temperature *etc.* are given in detail.

Effect of [MnO_4^-] on the oxidation of AcPh in 50% aq. HOAc.

The order with respect to oxidant was determined by the method of isolation. In all experiments the concentration of the substrate was always taken ten to fifteen

times in excess compared to that of the oxidant. The influence of the oxidant on the rate of oxidation was followed by taking fixed concentration of acetophenone (1.0 x 10^{-2} mol dm^{-3}) and varying [MnO_4^-] in the range 0.5 x 10^{-3} to 2.0 x 10^{-3} mol dm^{-3}. Under the conditions of [AcPh] >> [MnO_4^-], the plots of log [MnO_4^-] versus time were found to be linear indicating a first order dependence on [MnO_4^-] (Fig. 4.1.1).

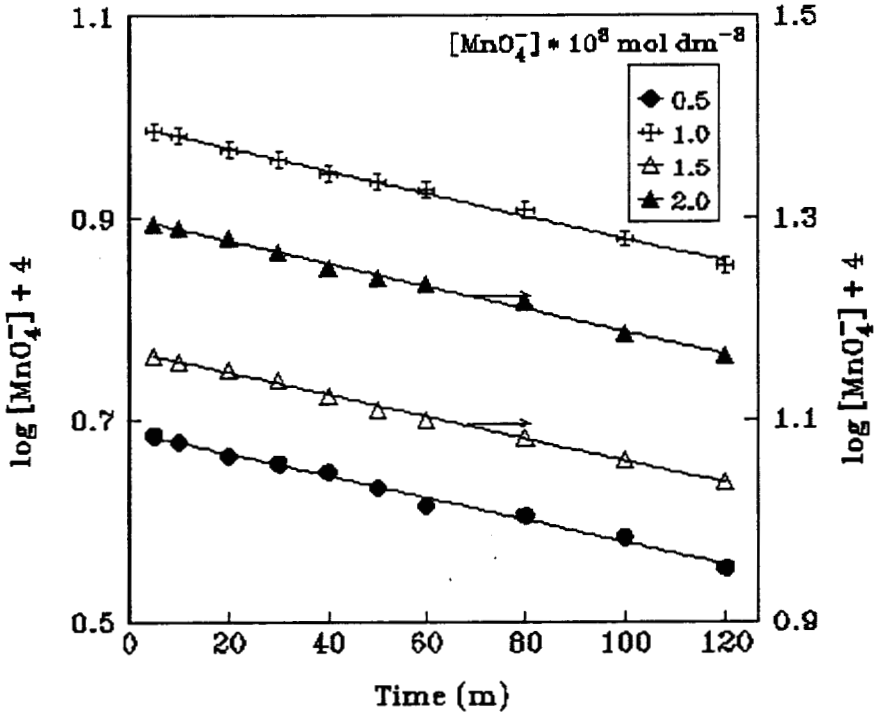


Fig. 4.1.1 Effect of [MnO_4^-] on the oxidation of AcPh in 50% aq. HOAc

It was further confirmed by the constancy in the pseudo-first order rate constants (k_{obs}) for various [MnO_4^-] (Table 4.1.1).

Table 4.1.1 Effect of $[MnO_4^-]$ on the oxidation of AcPh in 50% aq.HOAc

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3} Temp. = 308 K

$[MnO_4^-] \times 10^3$ mol dm^{-3}	0.5	1.00	1.50	2.0
$k_{obs} \times 10^5$ sec^{-1}	4.22	4.29	4.26	4.33
Correlation Coefficient	0.9957	0.9977	0.9985	0.9970

Effect of [Acetophenone]

The effect of varying the concentration of acetophenone was studied for a range of $1.0 - 2.5 \times 10^{-2}$ mol dm^{-3}, keeping all the other conditions the same. Here also the plots of log $[MnO_4^-]$ versus time were linear (Fig. 4.1.2) and the values of k_{obs} evaluated from the slopes were found to be dependent on initial concentration of acetophenone (Table 4.1.2).

Table 4.1.2 Effect of [Acph] on the oxidation of AcPh in 50% aq. HOAc

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[AcPh] \times 10^2$ mol dm^{-3}	1.00	1.50	2.00	2.50
$k_{obs} \times 10^5$ sec^{-1}	4.29	6.25	8.98	10.82
$k_2 = k_{obs}/[AcPh]$	4.29	4.17	4.49	4.32
Correlation Coefficient	0.9977	0.9979	0.9993	0.9984

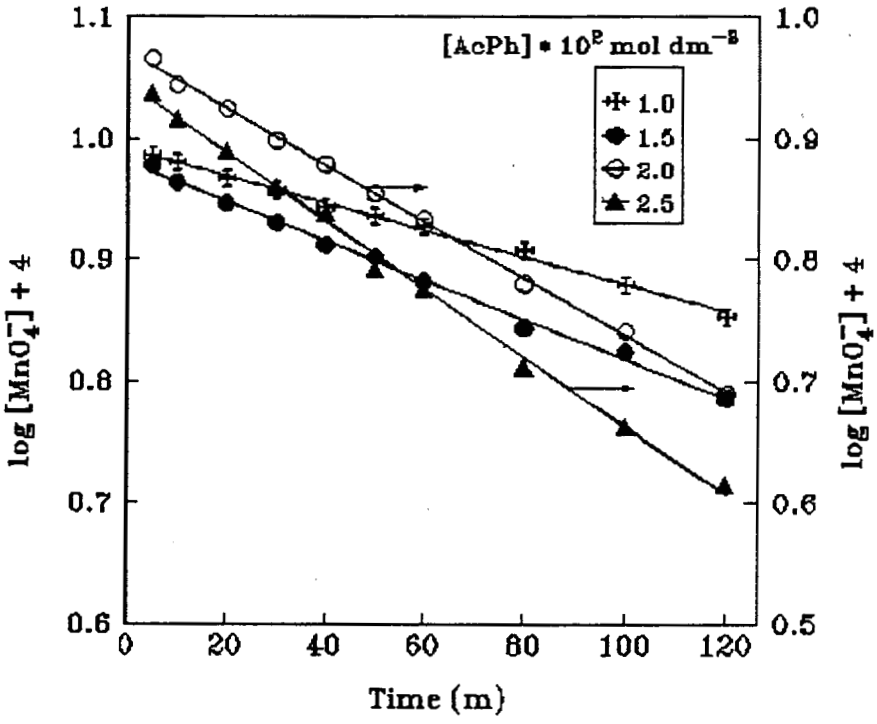


Fig. 4.1.2 Effect of [AcPh] on the oxidation of AcPh in 50% aq. HOAc

Since [AcPh] >> [MnO_4^-], the order obtained would be that with respect to MnO_4^-. The observed pseudo-rate constant (k_{obs}) would be the product of [AcPh] and k_2 (second order rate constant). Therefore the rate constant with respect to acetophenone was found by dividing k_{obs} with the concentration of acetophenone *i.e.* k_{obs}/[AcPh]. The second order rate constant obtained are found to be almost identical, which indicates the first order dependence with respect to acetophenone (Table 4.1.2). Moreover the plot of log k_{obs} vs log [AcPh] (Fig. 4.1.3) were linear with unit slope confirming the order with respect to acetophenone to be unity.

The Lineweaver – Burke plot of $1/k_{obs}$ vs 1/[AcPh] (Fig. 4.1.4) were linear passing through the origin, indicating that no complex is formed during the reaction or the complex formed has only a transitory existence.

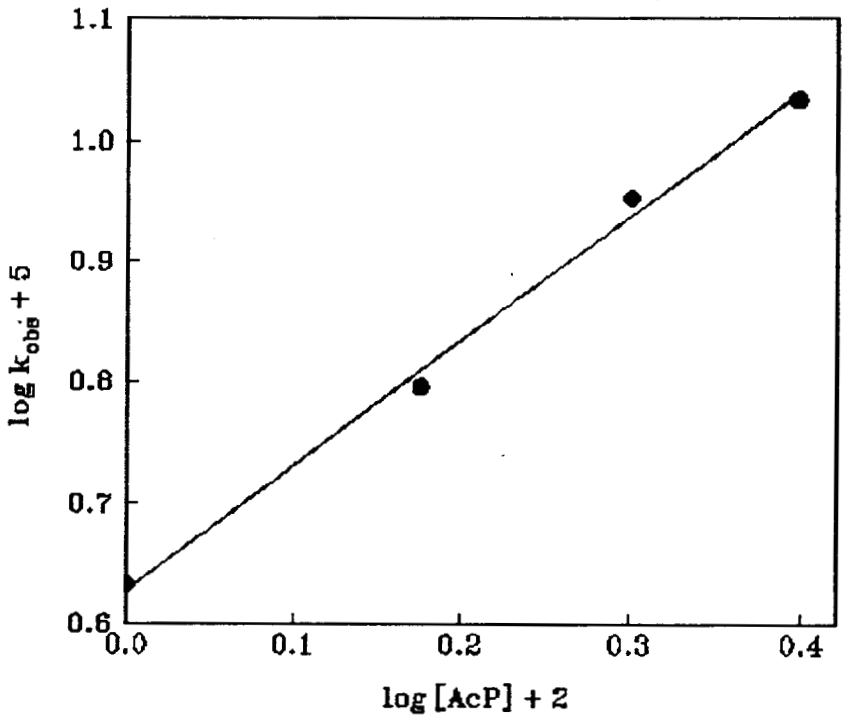


Fig. 4.1.3 Order with respect to Acetophenone

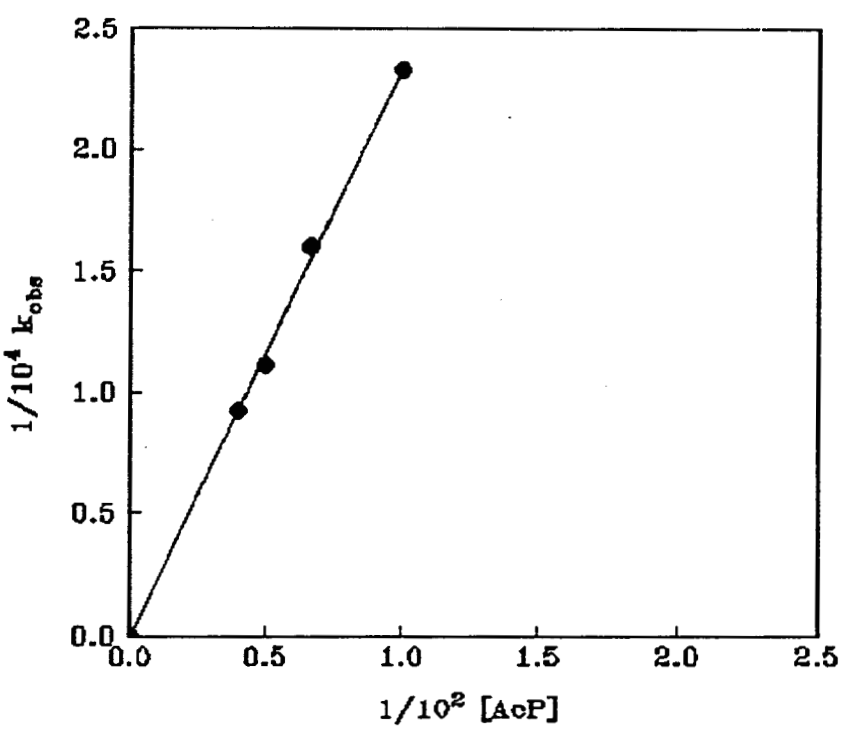


Fig. 4.1.4 Lineweaver – Burke Plot of $1/k_{obs}$ vs 1/[AcPh]

Effect of added mineral acid

The influence of added mineral acid was studied for the system by varying the concentration of added H_2SO_4. Keeping the concentration of MnO_4^- and Acetophenone constant, the concentration of H_2SO_4 in the system was varied over a range of 0.0–20.0 x 10^{-3} mol dm^{-3} (Fig. 4.1.5).

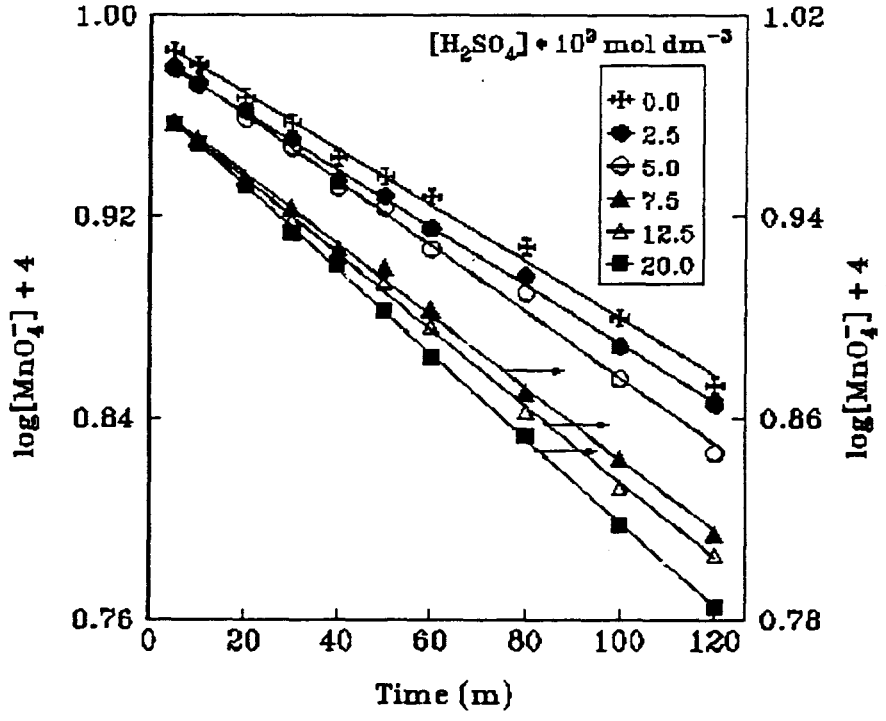


Fig. 4.1.5 Effect of [H_2SO_4] on the oxidation of AcPh in 50% aq.HOAc

The first order rate constants obtained confirm the dependence of the [H_2SO_4] on the reaction rate. The rate constants were found to increase with the increase of [H_2SO_4] (Table 4.1.3).

Table 4.1.3 Effect of $[H_2SO_4]$ on the oxidation of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} , $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} , Temp. = 308 K

$[H^+]$ x 10^3 mol dm^{-3}	0.0	2.5	5.0	7.5	12.5	20.0
k_{obs} x 10^5 sec^{-1}	4.29	4.41	4.98	5.45	5.79	6.41
Correlation Coefficient	0.9977	0.9990	0.9982	0.9992	0.9995	0.9998

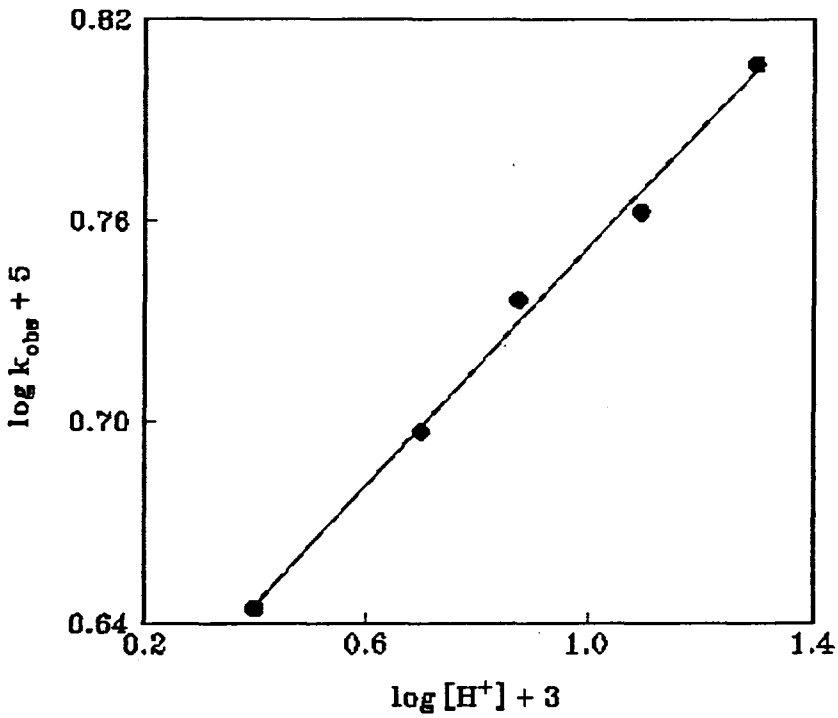


Fig. 4.1.6 Order with respect to Acid

The plot of log k_{obs} vs log $[H^+]$ (Fig. 4.1.6) were linear with a positive slope and the order with respect to $[H^+]$ is found to be fractional. This suggests that H^+ is

not directly involved in the rate-determining step, but it is an acid - catalyzed reaction.

Effect of added salts

The effect of added neutral salt (NaCl) was studied by varying the concentration of NaCl in the range 0.0-5.0 x 10^{-2} mol dm^{-3} (Fig. 4.1.7).

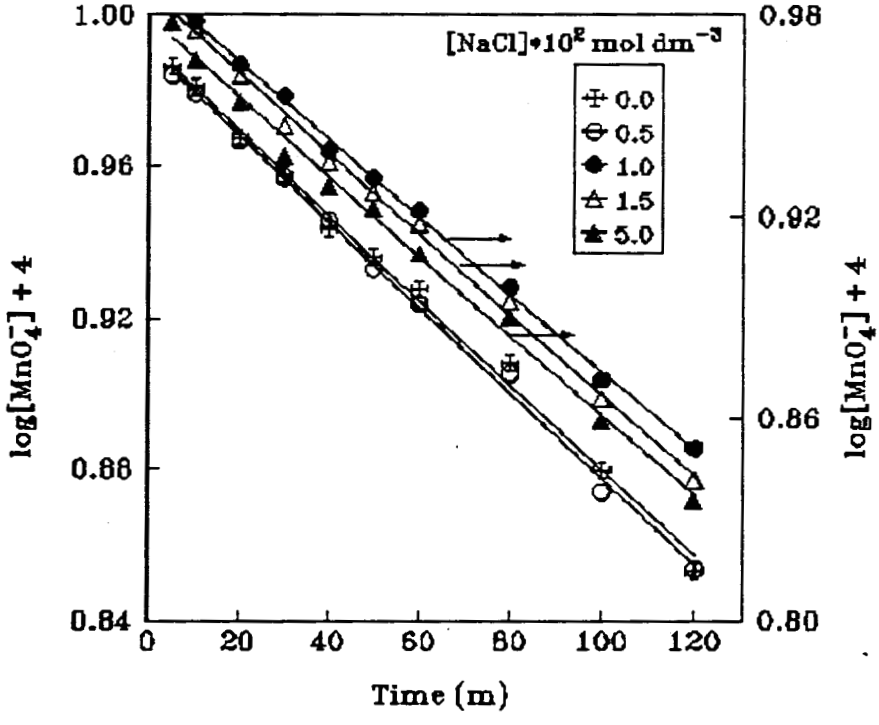


Fig. 4.1.7 Effect of [NaCl] on the oxidation of AcPh in 50% aq. HOAc

It was found that an increase in [NaCl] doesn't affect the kinetic rate significantly (Table 4.1.4). This clearly points out the absence of primary salt effect and hence it is assumed that the rate-determining step consists of either two neutral molecules or a neutral molecule and an ion.

Table 4.1.4 Effect of [NaCl] on the oxidation. of AcPh in 50% aq. HOAc

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} , [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3} , Temp. = 308 K

[NaCl] x 10^2 mol dm^{-3}	0.0	0.5	1.0	1.5	5.0
k_{obs} x 10^5 sec^{-1}	4.29	4.33	4.41	4.60	4.52
Correlation Coefficient	0.9977	0.9987	0.9992	0.9985	0.9970

However the addition of $MnSO_4$ in the range 0.0-2.0 x 10^{-2} mol dm^{-3} decreased the rate (Fig.4.1.8 and Table 4.1.5).

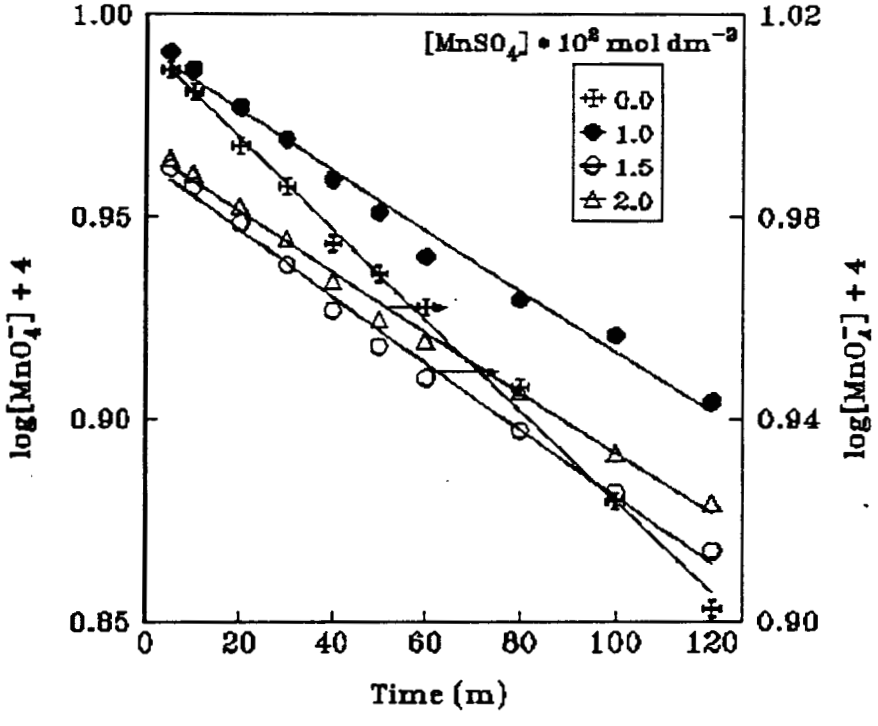


Fig. 4.1.8 Effect of [$MnSO_4$] on the oxidation of AcPh in 50% aq. HOAc

The effect of [$MnSO_4$] could be understood from the following reaction

$$MnO_4^- + 3\ Mn^{2+} + 8\ H^+ \longrightarrow 3\ Mn^{3+} + Mn^{4+} + 4\ H_2O$$

If MnO_4^- is primarily responsible for the oxidation, the addition of Mn^{2+} should reduce the concentration of the permanganate and hence cause retardation, whereas acceleration should be observed if Mn^{3+} ions are the oxidizing species. In the present study the addition of $MnSO_4$ decreases the rate of the reaction, which shows that permanganate ion is the initial oxidizing species.

Table 4.1.5 Effect of [$MnSO_4$] on the oxidation of AcPh in 50% aq. HOAc

[AcPh] = 1.0×10^{-2} mol dm^{-3}, [MnO_4^-] = 1.0×10^{-3} mol dm^{-3}, Temp. = 308 K

[$MnSO_4$] x 10^3 mol dm^{-3}	0.0	1.0	1.5	2.0
k_{obs} x 10^5 sec^{-1}	4.29	2.84	2.53	2.30
Correlation Coefficient	0.9977	0.9934	0.9962	0.9971

Effect of polarity of the solvent

The effect of polarity of the solvent on the reaction rate was investigated by varying the percentage of acetic acid in the reaction mixture (20 – 80% v/v) (Fig. 4.1.9). It was observed that the rate constants decreased as the percentage of acetic acid in the solvent increased. In other words the rate decreased as the dielectric constant of the medium decreased (Table 4.1.6).

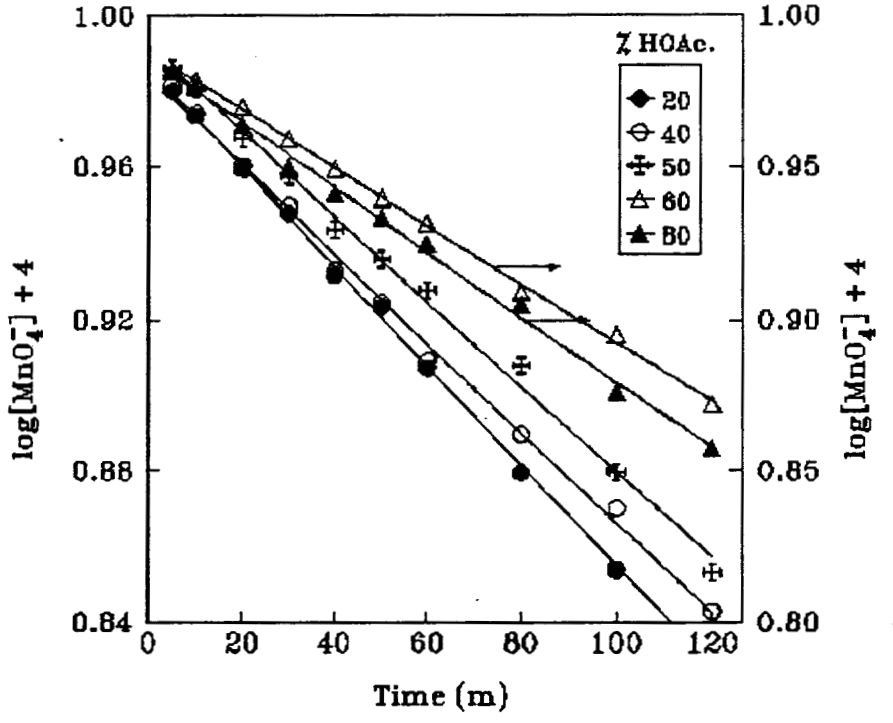


Fig. 4.1.9 Effect of solvent polarity on the oxdn. of AcPh in 50% aq. HOAc.

Table 4.1.6 Effect of solvent polarity on the oxdn. of AcPh in 50%aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} , [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3} , Temp. = 308 K

HOAc %	20	40	50	60	80
Dielectric constant	61	47	39.8	32	17.5
k_{obs} x 10^5 sec^{-1}	4.64	4.33	4.29	3.68	3.41
Correlation Coefficient	0.9969	0.9923	0.9977	0.9990	0.9957

The plot of log k_{obs} vs 1/D (Fig. 4.1.10) were with negative slope indicating the anion–dipole nature of the reaction. The curved nature of the graph shows that there is some other factor enhancing the rate with the increase in acetic acid composition.

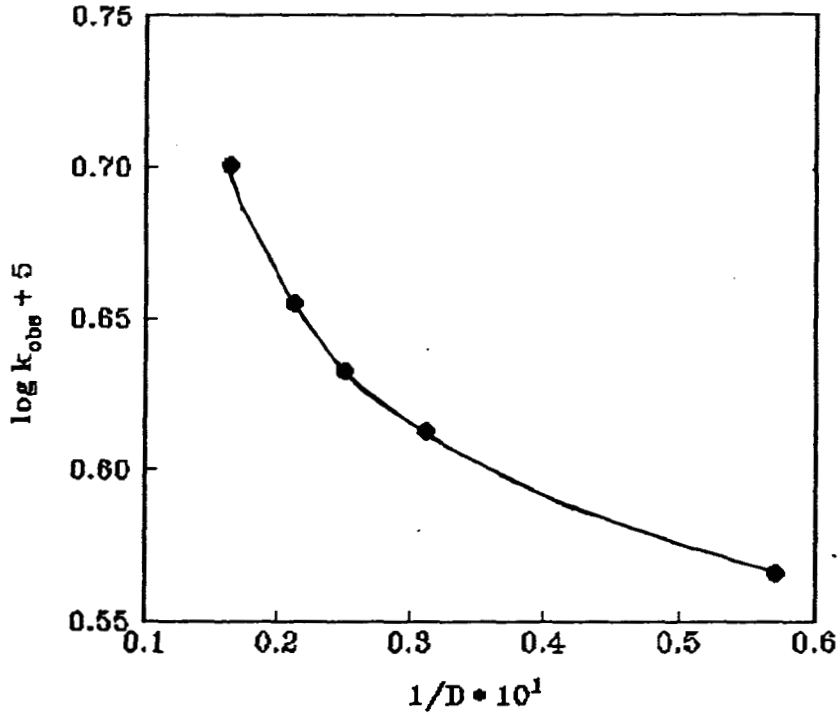


Fig. 4.1.10 Plot of log k_{obs} vs 1/D for the oxidation of AcPh in 505 aq. HOAc.

This may be due to the increase in the rate of enolization of acetophenone with increase in acetic acid[246]. The dielectric constant values used above were obtained according to the literature[247].

Effect of substituents on the benzene ring of acetophenone

The effect of substituents on the benzene ring of acetophenone was studied using *m*- nitro, *p*-nitro, *p*-bromo, *p*-chloro, *p*-methyl, and *p*-methoxy acetophenones (Fig. 4.1.11).

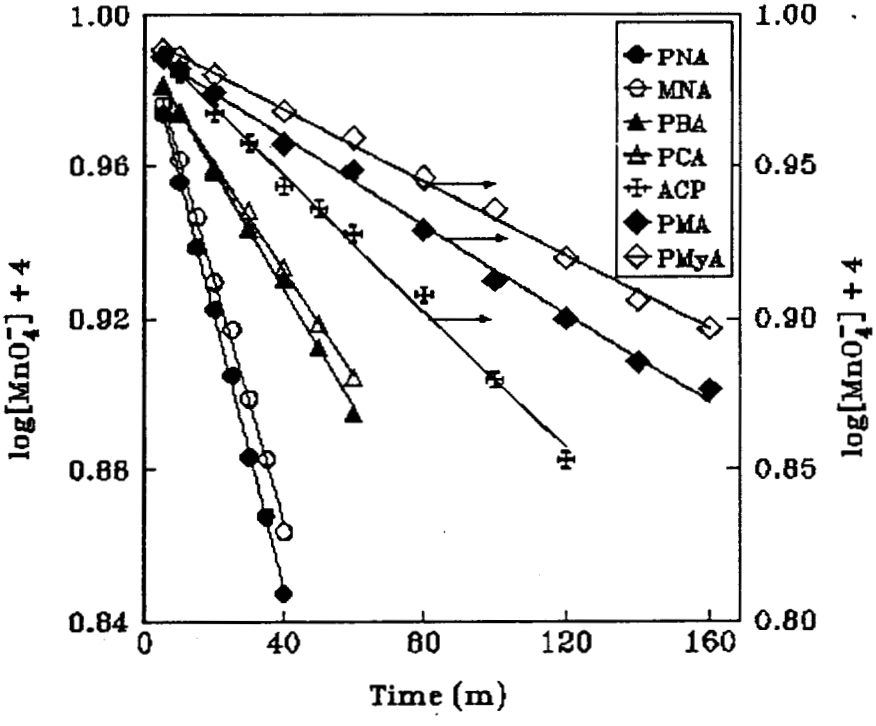


Fig.4.1.11 Effect of Substituents on the oxdn. of AcPh in 50% aq.HOAc.

The order of reactivities of various substituted acetophenones were found to be *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > Acph > *p*-CH_3 > *p*-OCH_3 (Table 4.1.7).

Table 4.1.7 Effect of Substituents on the benzene ring on the oxdn. of AcPh in 50% aq. HOAc

Substrate	MNA	PNA	PBA	PCA	AcPh	PMA	PMyA
k_{obs} x 10^5 sec^{-1}	13.81	12.20	5.94	5.33	4.29	2.80	2.30
Corr. Coefficient	0.9995	0.9990	0.9993	0.9995	0.9977	0.9978	0.9986

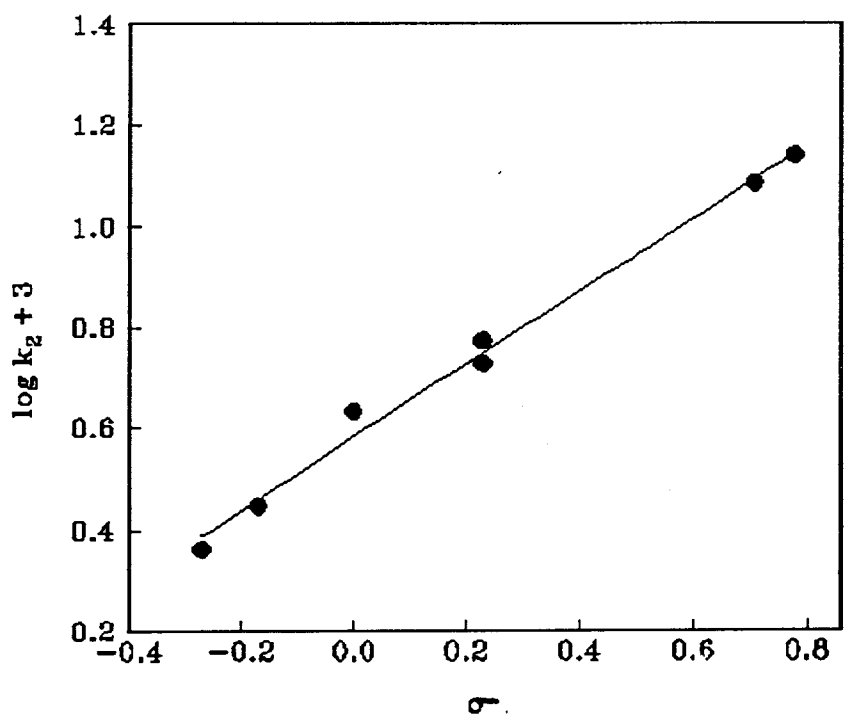


Fig. 4.1.12 Hammett plot for the oxidation of AcPh in 50% aq. HOAc.

The log k_2 values for the various substituted acetophenones were found to correlate well with the Hammet's σ values and a reaction constant of +0.7210 was obtained (Fig. 4.1.12). This +ve value indicates that electron-withdrawing substituents accelerate the process while electron-donating substituents retard the process.

Effect of Temperature on the rate of oxidation and evaluation of the thermodynamic parameters

The effect of temperature on the rate of oxidation of acetophenone and some substituted acetophenones were studied for a range of 308 – 323 K (Fig. 4.1.13). The overall second order rate constants for the acetophenone and its derivatives were found to increase with increase in temperature (Table 4.1.8).

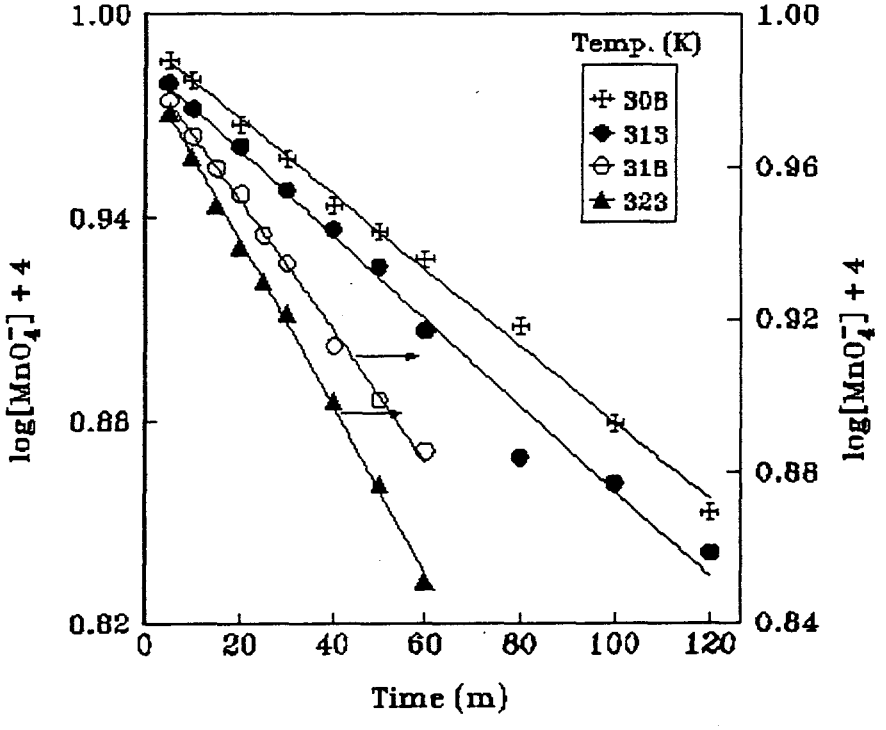


Fig. 4.1.13 (a) Effect of Temp. on the oxdn. of AcPh in 50% aq. HOAc.

Table 4.1.8 (a) Effect of Temp. on the oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}

Temperature (K)	308	313	318	323
$k_{obs} \times 10^5$ sec^{-1}	4.29	4.83	6.56	8.36
Correlation Coefficient	0.9977	0.9929	0.9982	0.9991

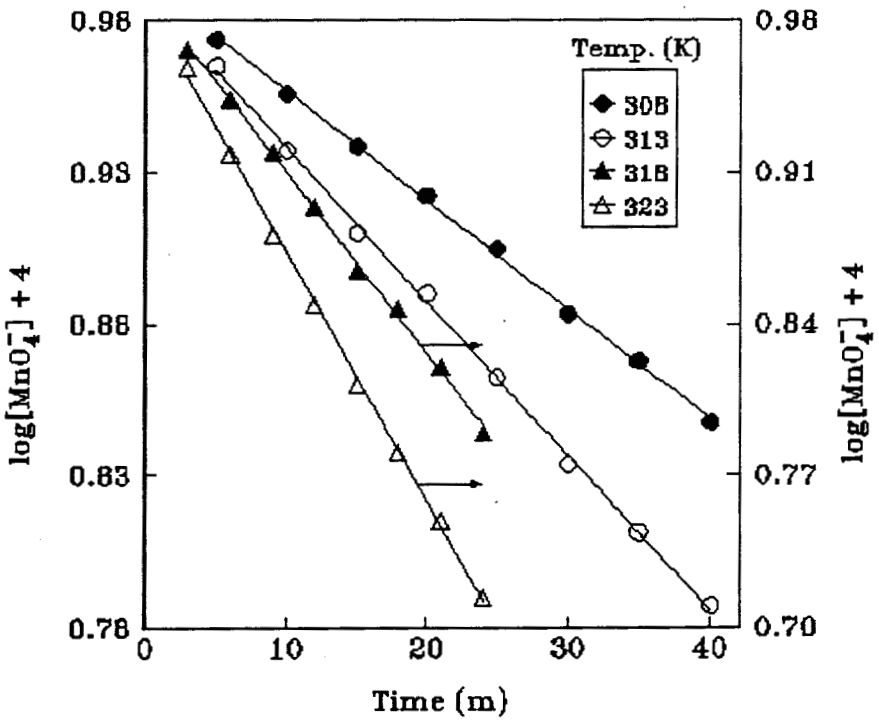


Fig. 4.1.13 (b) Effect of Temp. on the oxdn. of PNA in 50% aq. HOAc.

Table 4.1.8 (b) Effect of Temp. on the oxdn. of PNA in 50% aq. HOAc.

[PNA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	13.81	19.49	32.05	44.14
Correlation Coefficient	0.9995	0.9995	0.9990	0.9995

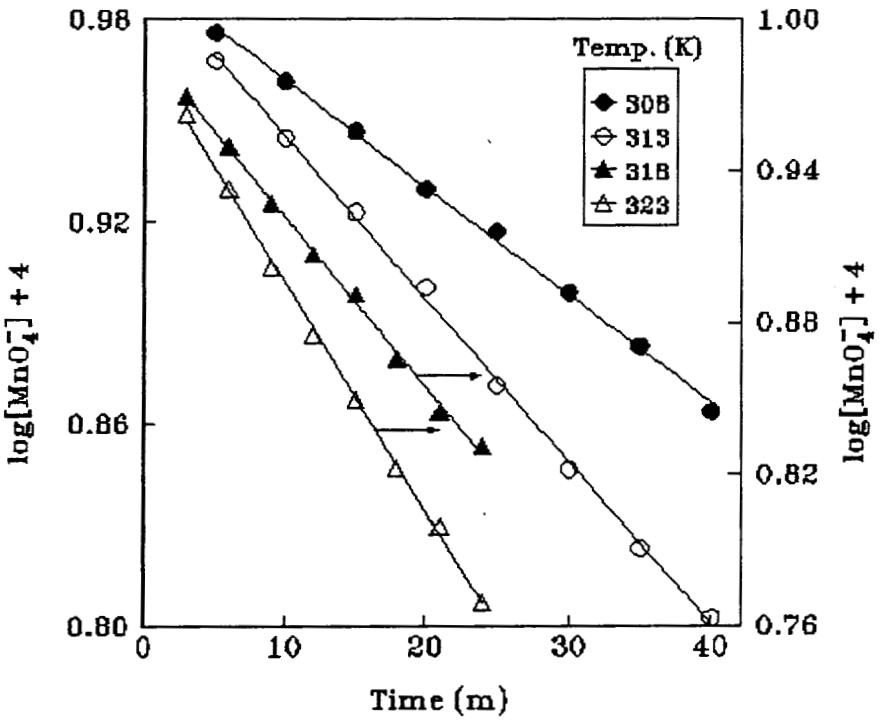


Fig. 4.1.13 (c) Effect of Temp. on the oxdn. of MNA in 50% aq. HOAc.

Table 4.1.8 (c) Effect of Temp. on the oxdn. of MNA in 50% aq. HOAc.

[MNA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	12.20	18.50	25.71	34.73
Correlation Coefficient	0.9990	0.9994	0.9987	0.9993

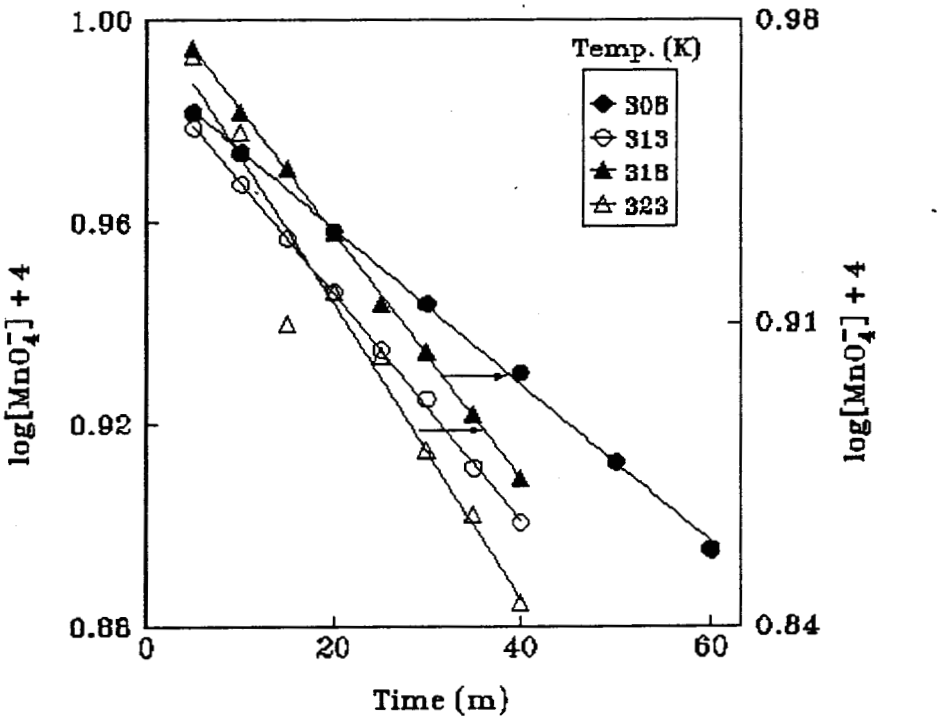


Fig. 4.1.13 (d) Effect of Temp. on the oxdn. of PBA in 50% aq. HOAc.

Table 4.1.8 (d) Effect of Temp. on the oxdn. of PBA in 50% aq. HOAc.

[PBA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	5.94	8.55	10.90	13.80
Correlation Coefficient	0.9993	0.9996	0.9996	0.9992

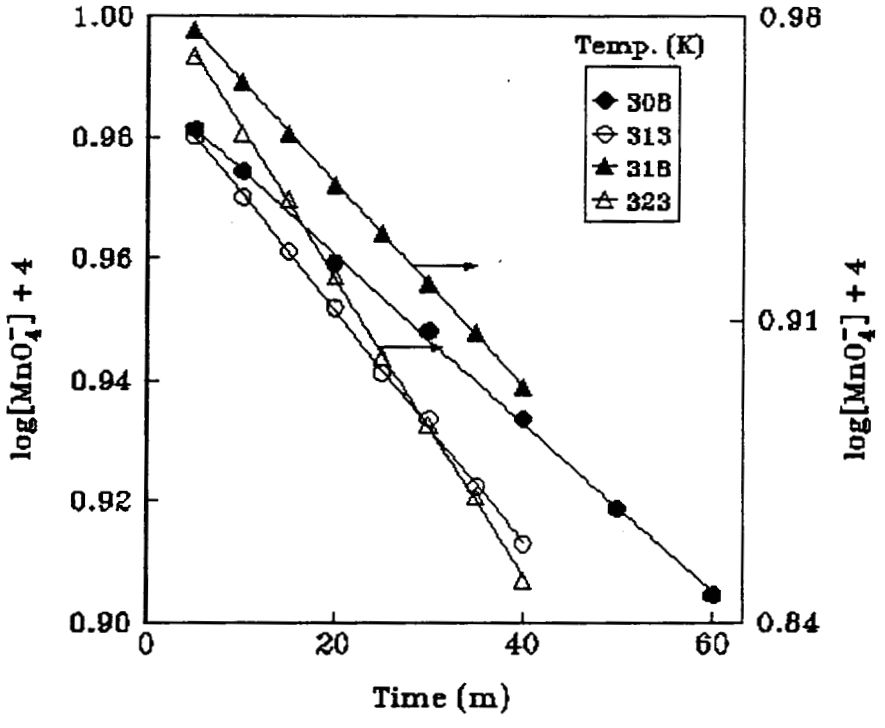


Fig. 4.1.13 (e) Effect of Temp. on the oxdn. of PCA in 50% aq. HOAc.

Table 4.1.8 (e) Effect of Temp. on the oxdn. of PCA in 50% aq. HOAc.

[PCA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	5.33	7.33	8.98	13.20
Correlation Coefficient	0.9995	0.9996	0.9999	0.9998

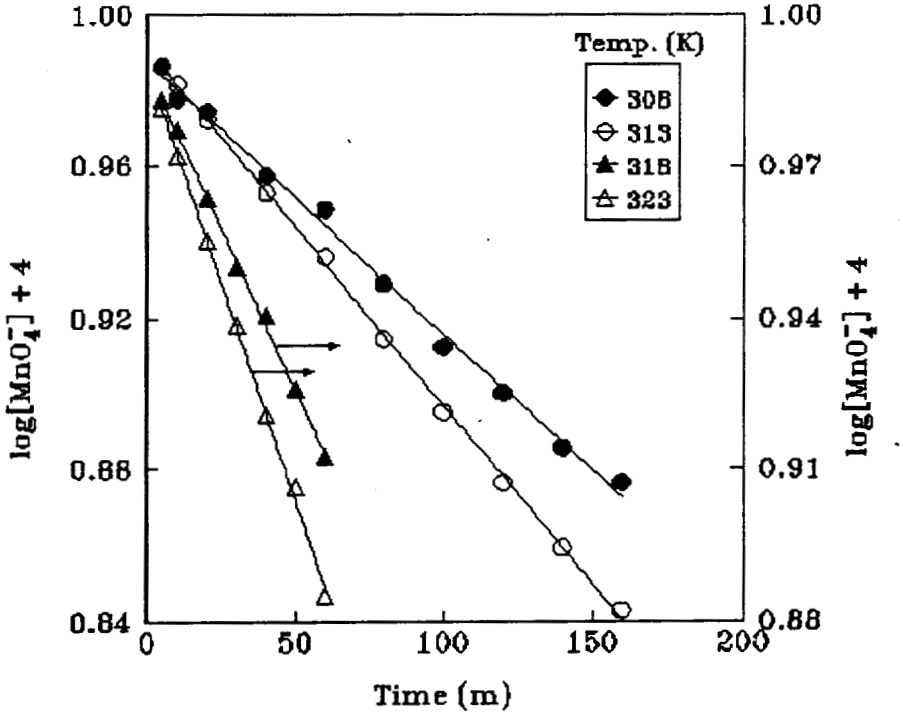


Fig. 4.1.13 (f) Effect of Temp. on the oxdn. of PMA in 50% aq. HOAc.

Table 4.1.8 (f) Effect of Temp. on the oxdn. of PMA in 50% aq. HOAc.

[PMA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	2.80	3.60	4.87	6.60
Correlation Coefficient	0.9978	0.9997	0.9991	0.9993

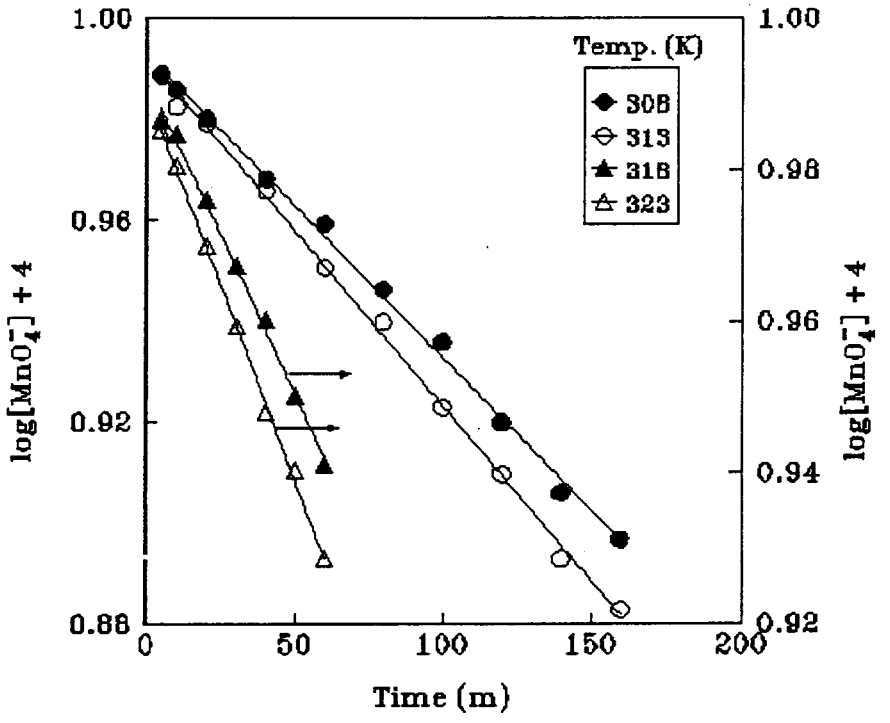


Fig. 4.1.13 (g) Effect of Temp. on the oxdn. of PmyA in 50% aq. HOAc.

Table 4.1.8 (g) Effect of Temp. on the oxdn. of PMyA in 50% aq. HOAc.

[PMyA] = 1.0 x 10^{-2} mol dm^{-3} [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^5 sec^{-1}	2.30	2.64	3.22	3.95
Correlation Coefficient	0.9986	0.9990	0.9984	0.9994

The plots of log k_2 vs 1/T were linear indicating that Arrhenius law is being obeyed (Fig. 4.1.14).

The various thermodynamic parameters namely, the energy of activation (E_a), the enthalpy of activation ($\Delta H^{\#}$), the entropy of activation ($\Delta S^{\#}$), and the free energy of activation ($\Delta F^{\#}$) were calculated by plotting log k_2 vs 1/T (Fig. 4.1.14) and log k_2/T vs 1/T (Fig. 4.1.15) and are given in Table 4.1.9. The details of calculation are given in the Appendix.

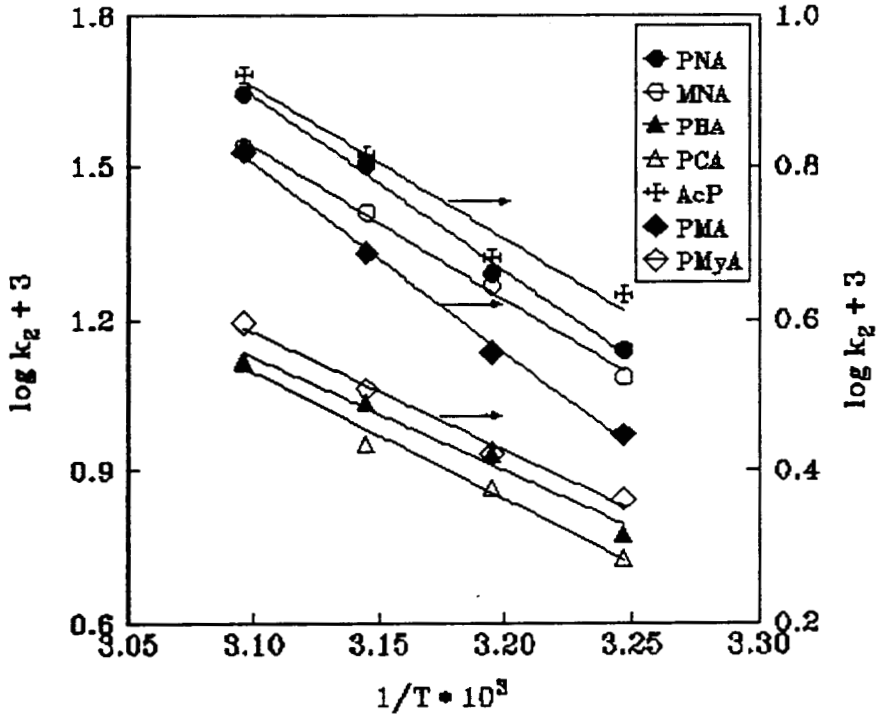


Fig. 4.1.14 Plot of log k_2 vs 1/T for the oxdn. of AcPh in 50% aq. HOAc.

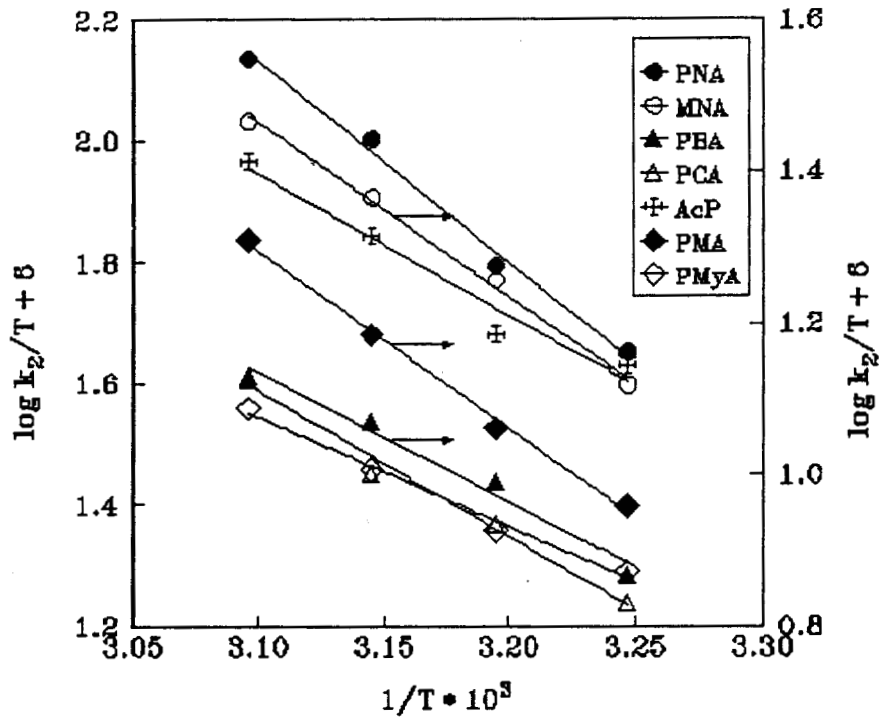


Fig. 4.1.15 Plot of log k_2/T vs 1/T on the oxdn. of AcPh in 50% aq. HOAc.

Table 4.1.9 Activation Parameters for the oxdn. of AcPh and its substituents in 50% aq. HOAc.

Substrate	k_{obs} x 10^5 sec^{-1}	E_a KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
PNA	13.81	65.83	63.24	75.05	86.36
MNA	12.20	57.37	54.73	103.65	86.65
PBA	5.94	43.24	40.64	155.38	88.50
PCA	5.33	48.31	45.67	139.95	88.77
AcPh	4.29	38.17	35.55	174.60	89.33
PMA	2.50	47.47	44.86	148.89	90.72
PMyA	2.30	30.07	27.45	206.10	90.93

A constancy in free energy of activation, $\Delta F^{\#}$ (~ 90 KJ mol^{-1}) in all acetophenones studied suggests that probably a similar mechanism prevails. This is further confirmed by the linear plot of $\Delta H^{\#}$ vs $\Delta S^{\#}$ (Fig. 4.1.16). The isokinetic temperature was evaluated by use of the isokinetic relationship suggested by Leffler and Grunwald[248], $\Delta H^{\#} = C + \beta \Delta S^{\#}$. The isokinetic temperature calculated (β = 271.9) was found to be less than the experimental range of temperature (308-323 K) indicating that the reaction is enthalpy controlled. Exner's plot of log k_{obs} (50^0) vs log k_{obs} (35^0) (Fig. 4.1.17) was also linear showing the existence of isokinetic relationship (β =255.05).

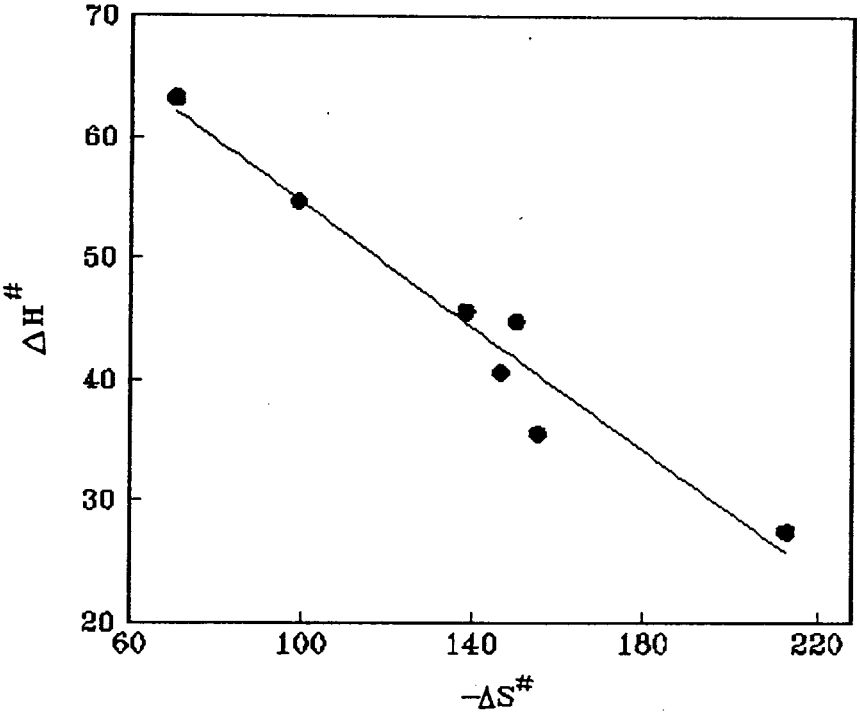


Fig. 4.1.16 Isokinetic plot for the oxdn. of AcPh in 50% aq. HOAc.

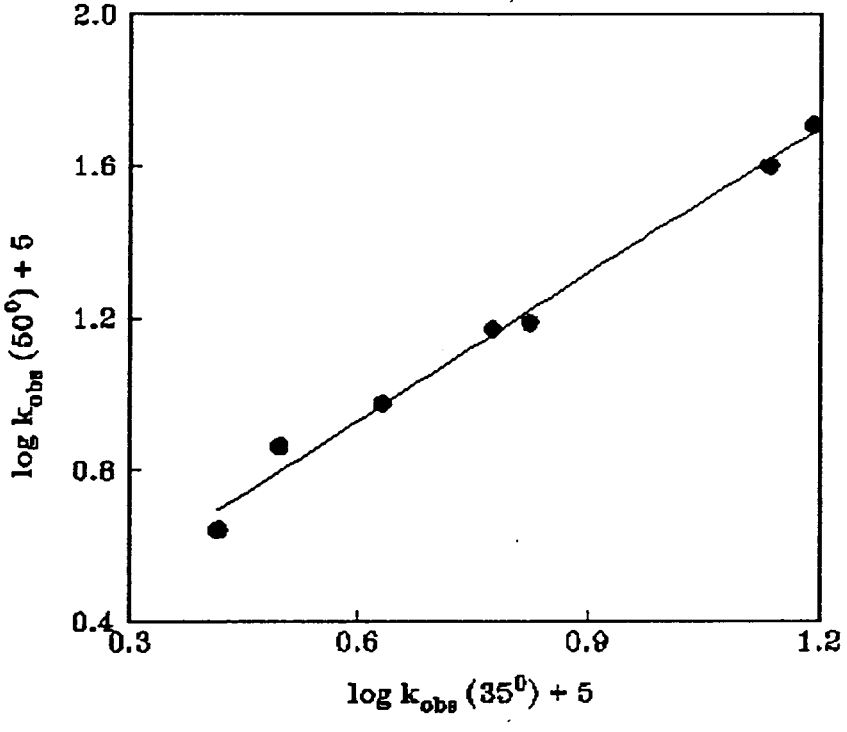


Fig.4.1.17 Exner's plot for the oxdn. of AcPh in 50% aq. HOAc.

Effect of Product concentration on the rate of oxidation

The influence of product on the rate of oxidation was studied by adding known concentrations of the product *i.e.* benzoic acid (0 to 2.0 x 10^{-2} mol dm^{-3}) directly to the reaction mixture (Table 4.1.10). The negligible effect on the rate indicates that it is not involved in a pre-equilibrium to the rate limiting step.

Table 4.1.10 Effect of [Benzoic Acid] on the oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} , [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3} , Temp. = 308 K

$[C_6H_5COOH]$ x 10^2 mol dm^{-3}	0.0	1.0	1.5	2.0
k_{obs} x 10^5 sec^{-1}	4.29	4.38	4.41	4.40
Correlation Coefficient	0.9977	0.9987	0.9992	0.9984

4.1.3 Effect of Addition of Acrylonitrile to the Reaction Mixture

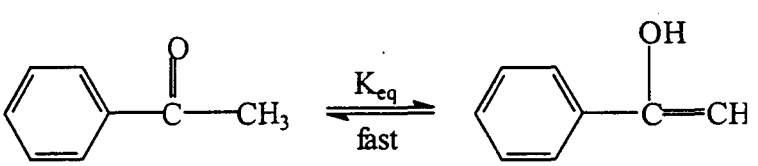
To the reaction mixture containing 1.0 x 10^{-2} mol dm^{-3} Acph, 1.0 x 10^{-3} mol dm^{-3} MnO_4^- in 50% aqueous acetic acid system, 5 ml of acrylonitrile was added and kept overnight in the dark. The absence of a white precipitate shows absence of polymerization reaction, indicating the absence of any free radical formation during the course of the reaction.

4.1.4 Mechanism and Rate law

Studies regarding the mechanism of a reaction are conveniently made by the following the quantitative variation of the rate under the influence of varying conditions of concentration and temperature.

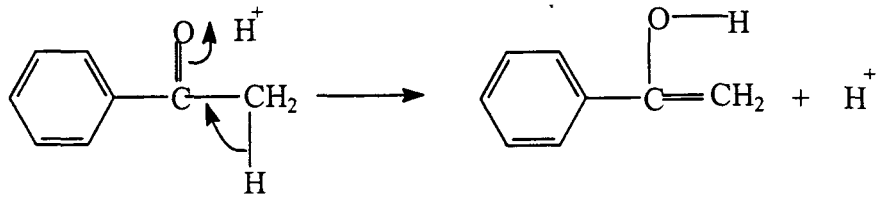
For reactions in solution, the mechanism is formulated by the determination of different kinetic parameters, the most important being the order of the reaction with respect to the different reactants, catalytic effect of additives, effect of ionic strength[249], solvent[250], dielectric constant[251] of the medium *etc.* and temperature on the reaction rate. Determination of the stoichiometry of the reaction, detection and estimation of products and effects of substrate structure on the reaction rate are also valuable factors which throw light on the mechanism of the reaction to confirm the rate-determining step.

Mechanism of oxidation of acetophenone with two electron oxidants differ from that of one electron oxidants mainly in the involvement of enol or keto form of the substrate. Litter and Waters[252] suggest that two electron oxidants attack the enol form rather than the keto form. Potassium permanganate behave as a two electron oxidant, hence the enol form of the substrate is believed to be taking part in the reaction.



Keto form Enol form

Acetophenone being a weak base, protonation and consequent enolisation is likely to take place.



This is supported by the effect of acid concentration on the reaction rate (Table 4.1.3). The plot of log k_{obs} vs log $[H^+]$ (Fig. 4.1.6) is linear with a fractional order dependence. This shows that H^+ is not directly involved in the rate-determining step but it accelerates the rate because it increases the rate of formation of enol form of the substrate, which is taking part in the rate-determining step. Thus it is an acid catalysed reaction.

Solvent effects provide some important information regarding 1) the nature of the reacting species in the rate-determining step and 2) structure of activated complex. The rate was found to decrease with increasing concentration of acetic acid *i.e.* decreasing dielectric constant. A plot between log k vs 1/D (Amis plot) (Fig. 4.1.10) was found to be linear with negative slope suggesting thereby that the rate-determining step was a reaction between a dipole and an anion in accordance with Amis treatment of rate data[250]. This anion is permanganate ion in the present study. This was confirmed by the addition of $MnSO_4$ which decreases the rate of oxidation showing that MnO_4^- is the active oxidizing species of the oxidant.

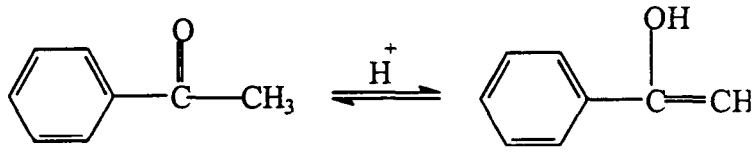
Added salts had no effect on the k_{obs}, thus confirming the reaction to be ion-dipole type.

The linear plot of $1/k_{obs}$ vs 1/[AcPh] (Fig. 4.1.4) passing through the origin indicates that no complex is formed or the complex formed is of transient nature. In the present case the reaction is assumed to proceed *via* the transition state involving the enol form of the substrate and MnO_4^- and that the intermediate formed in the slow step got consumed in a subsequent fast step[253].

Moreover the increase in the polarity of the medium decreases the rate (Table 4.1.6) suggesting charge dispersal in the transition state or suggesting that probably the transition state is more polarised than the reactants in the initial state.

The magnitude of the entropy of activation gives a rough knowledge about the nature of reacting species and the structural compactness of the transition state. A large negative value of entropy of activation observed (Table 4.1.9) is suggestive of the formation of a charged and rigid transition state[254] as compared to the ground state. This causes a restriction on the translational and rotational freedom thus reducing the entropy of the system. Further a large negative entropies of activation are expected for a bimolecular reaction with high polar transition state

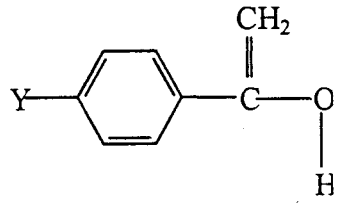
Though the rate of oxidation of acetophenone decreased with increase in percentage of acetic acid, the plot of log k_{obs} vs 1/D (Fig. 4.1.10) is not linear but curved. This may be due to the two competing reactions. Increase in percentage of acetic acid decreases the dielectric constant of the medium, which in turn decreases the rate of the reaction involving an anion and a dipole. But the enolization of ketones is catalyzed by acetic acid, which in turn increases the rate.



From the magnitude of the rate constants (Table 4.1.7) the reactivity trend observed for the substituted acetophenones is *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > Acph > *p*-CH_3 > *p*-OCH_3. Thus in the present study electron-withdrawing substituents exhibiting +I and –M effects are found to accelerate the reaction while electron-releasing retard the reaction.

Further the ρ value obtained from the Hammett plot (Fig. 4.1.12) is positive (+0.7210) indicating that electron-withdrawing substituents increase the rate of oxidation and electron-releasing substituents decrease the rate.

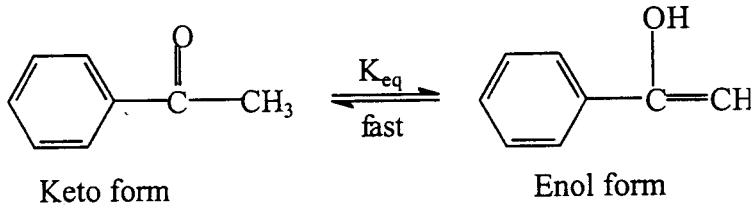
These adds support to present mechanism as the presence of electron-withdrawing groups in the phenyl ring facilitate the ease of removal of proton in the slow step.



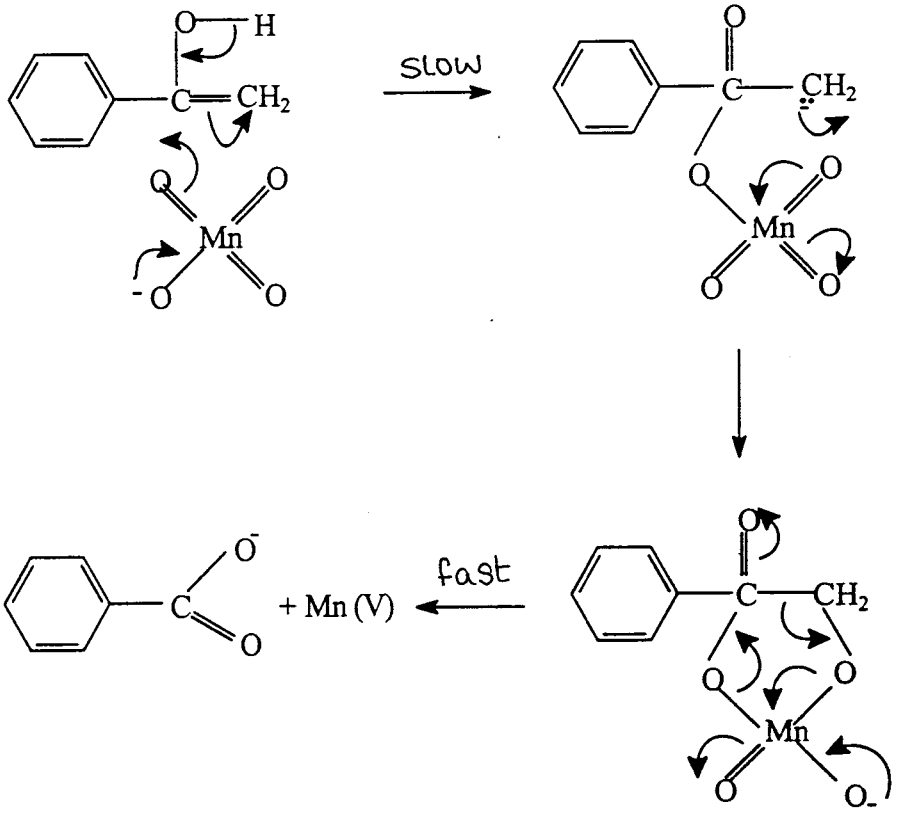
Addition of corresponding reaction product, benzoic acid to the reaction mixture had a negligible effect on the rate (Table 4.1.10), indicating that it is not involved in a pre-equilibrium to the rate-determining step.

In the light of all the experimental results obtained in the present investigation and the evidences from other investigation the following mechanistic steps has been proposed for the oxidation of acetophenone using $KMnO_4$ in aqueous acetic acid medium (Scheme 1).

The mechanism given below explains the experimental observations excellently, namely the stoichiometry (1:1 AcPh : $KMnO_4$), ionic strength, influence of dielectric constant of the medium, activation parameters especially $\Delta S^{\#}$, substituent effects, effect of added mineral acid and the effect of the product of oxidation. The mechanism proposed doesn't involve any free radicals, which is endorsed by the non- polymerisation of added acrylonitrile.



Keto form Enol form



$$Mn(V) \longrightarrow Mn(III) + Mn(II)$$

$$2Mn(III) \longrightarrow Mn(IV) + Mn(II)$$

Scheme 1

Thus the reaction proceeds *via* enol form of the Acetophenone and the oxidant is permanganate ion. The rate-determining step involves a two electron transfer from the enol form of acetophenone, resulting in the formation of an intermediate, which in a fast step gives the products.

The oxidation of all acetophenones were studied at different temperatures and the activation parameters were evaluated. The free energy of activation, $\Delta G^{\#}$ is found to be nearly same for all acetophenones studied (~90 KJ mol^{-1}), suggests that a similar mechanism is operating in the series.

The isokinetic (Fig. 4.1.16) and Exner's plot (Fig. 4.1.17) are linear with γ =0.9974 and γ = 0.9849 respectively further support the operation of an identical mechanism for all the acetophenones studied.

Based on the proposed mechanism, the rate law has been deduced as follows

$$\frac{d[MnO_4^-]}{dt} = k_2 \left[C_6H_5-\overset{OH}{\overset{|}{C}}=CH_2 \right] [MnO_4^-]$$

where $\left[C_6H_5-\overset{OH}{\overset{|}{C}}=CH_2 \right] = K_{eq} \left[C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \right]$

$$\therefore \quad \frac{d[MnO_4^-]}{dt} = k_2 K_{eq} \left[C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \right] [MnO_4^-]$$

The above rate law expression is in agreement with the observed order *i.e.* second order kinetics being first order in each reactant, ionic strength, effect of dielectric constant of the medium *etc.*

4.2 OXIDATION OF BENZALDEHYDE USING POTASSIUM PERMANGANATE IN 50% AQUEOUS ACETIC ACID MEDIUM

The reaction with aldehydes has received some study as shown in the review part. Inspite of these investigations, the detailed nature of the rate-determining step still remained obscure.

The results of an investigation of the reaction between an aromatic aldehyde *i.e.* Benzaldehyde and Potassium permanganate are reported herein.

4.2.1 Stoichiometry and Product Analysis

The stoichiometry of the benzaldehyde oxidation by potassium permanganate was determined as in the case of acetophenone (section 4.1.1). It is found that 3 moles of aldehyde consumed 2 moles of $KMnO_4$ in accordance with the following equation, which has already been suggested by Wiberg and Stewart[192].

$$3\ C_6H_5CHO + 2\ MnO_4^- \longrightarrow 2\ C_6H_5COO^- + C_6H_5COOH + 2MnO_2 + H_2O$$

The product analysis was also done in a similar manner and the product was characterized as benzoic acid from the qualitative analysis including melting point and IR spectrum.

4.2.2 Kinetic Studies

The specific rates for the reaction of benzaldehyde and some of its substituents using potassium permanganate in 50% aqueous acetic acid determined under different experimental conditions *i.e.* by changing the concentration of the oxidant, substrate, mineral acid, solvent polarity, ionic strength, temperature *etc.* are given in detail.

Effect of [MnO_4^-] on the oxidation C_6H_5CHO in 50% aq. HOAc.

The experiments were carried out keeping the concentration of C_6H_5CHO in excess to that of $KMnO_4$ to maintain pseudo order conditions. Under the conditions [MnO_4^-] << [C_6H_5CHO], the plot of log k_{obs} vs time were linear (Fig.4.2.1) indicating that the order in MnO_4^- to be unity.

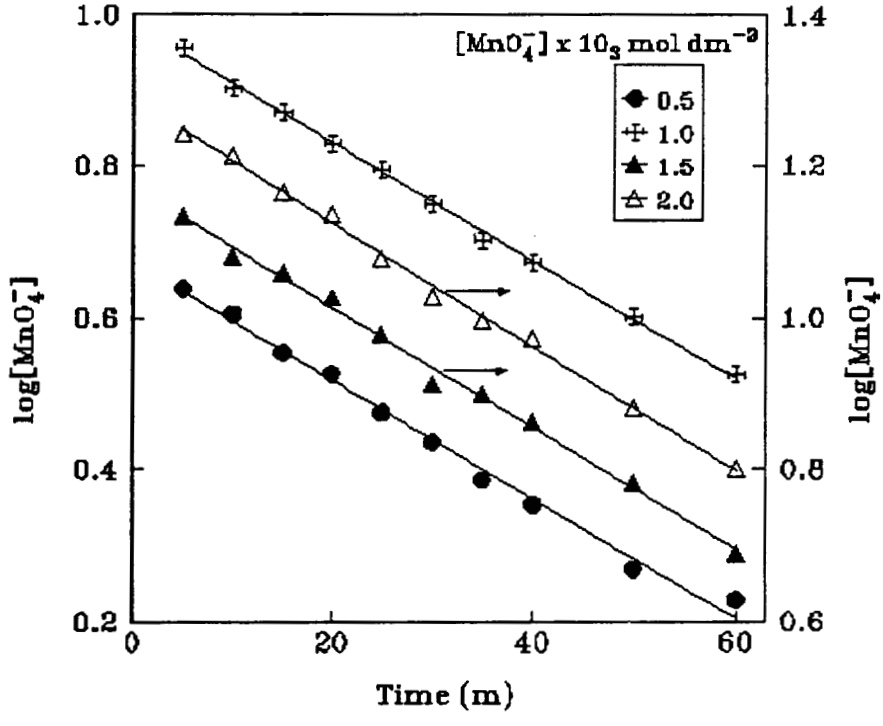


Fig. 4.2.1 Effect of [MnO_4^-] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Moreover the pseudo-first order rate constants calculated did not show any change by varying [MnO_4^-](Table 4.2.1).

Table 4.2.1 Effect of $[MnO_4^-]$ on the oxdn. of C_6H_5CHO in 50% aq.HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} Temp. = 308 K

$[MnO_4^-] \times 10^3$ mol dm^{-3}	0.5	1.00	1.50	2.0
$k_{obs} \times 10^4$ sec^{-1}	3.001	2.993	3.051	3.135
Correlation Coefficient	0.9963	0.9991	0.9973	0.9982

Effect of $[C_6H_5CHO]$

To study this effect, the concentration of C_6H_5CHO was varied by keeping all the other conditions the same. The first order rate constant increased with increasing concentration of the C_6H_5CHO (Fig.4.2.2 & Table 4.2.2) and consequently $k_2 = k_{obs}/ [C_6H_5CHO]$ remains constant showing the first order dependence on the substrate.

Table 4.2.2 Effect of $[C_6H_5CHO]$ on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[C_6H_5CHO] \times 10^2$ mol dm^{-3}	1.00	1.50	2.00	2.50
$k_{obs} \times 10^4$ sec^{-1}	2.993	3.907	5.642	6.882
$k_2 \times 10^2$ dm^3 mol^{-1} sec^{-1}	2.993	2.604	2.821	2.752
Correlation Coefficient	0.9991	0.9952	0.9975	0.9976

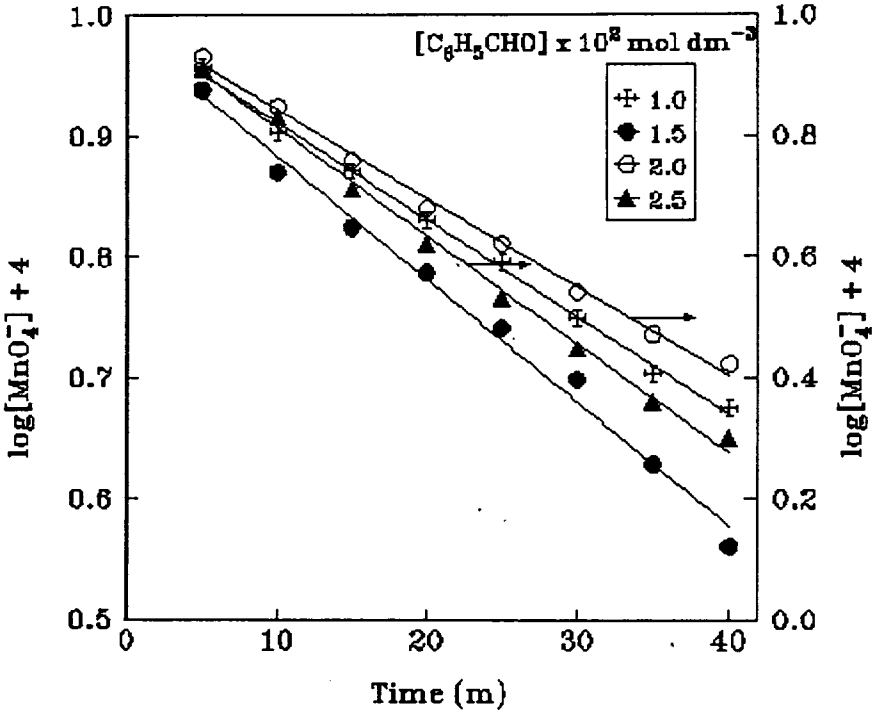


Fig. 4.2.2 Effect of [C_6H_5CHO] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

A plot of log k_{obs} vs log [C_6H_5CHO] (Fig.4.2.3) is linear with a slope equal to unity, further confirm the first order dependence of C_6H_5CHO. Lineweaver-Burke plot of $1/k_{obs}$ vs 1/[C_6H_5CHO] (Fig.4.2.4) is linear with positive intercept indicating the involvement of C_6H_5CHO in the formation of an intermediate before the formation of the product.

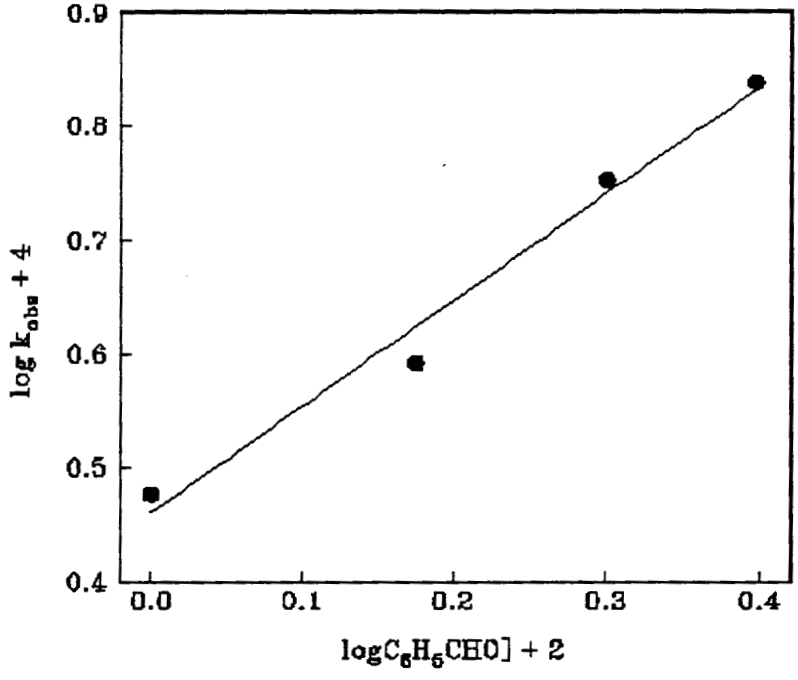


Fig. 4.2.3 Order with respect to Benzaldehyde

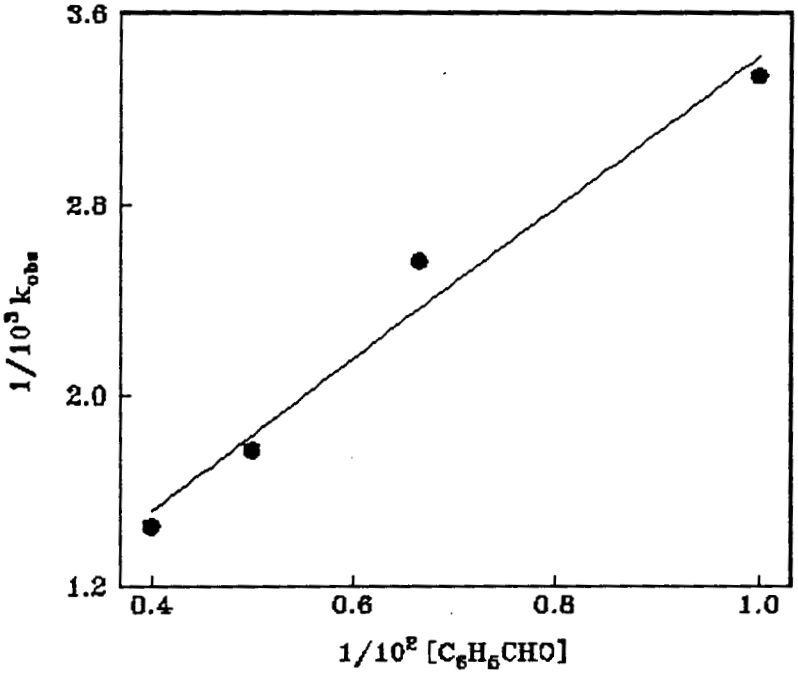


Fig. 4.2.4 Lineweaver – Burke Plot of $1/k_{obs}$ vs $1/[C_6H_5CHO]$

Effect of added mineral acid

The rate of the reaction was found to increase with $[H^+]$ (Fig.4.2.5 & Table 4.2.3). A plot of log k_{obs} vs log $[H^+]$ (Fig.4.2.6) is found to be linear with a slope almost equal to unity. Similarly, the ratio of specific rate to the first power of acid concentration was found to be unity. This substantiates the view that protonation of the substrate is one of the steps in the mechanism of the oxidation.

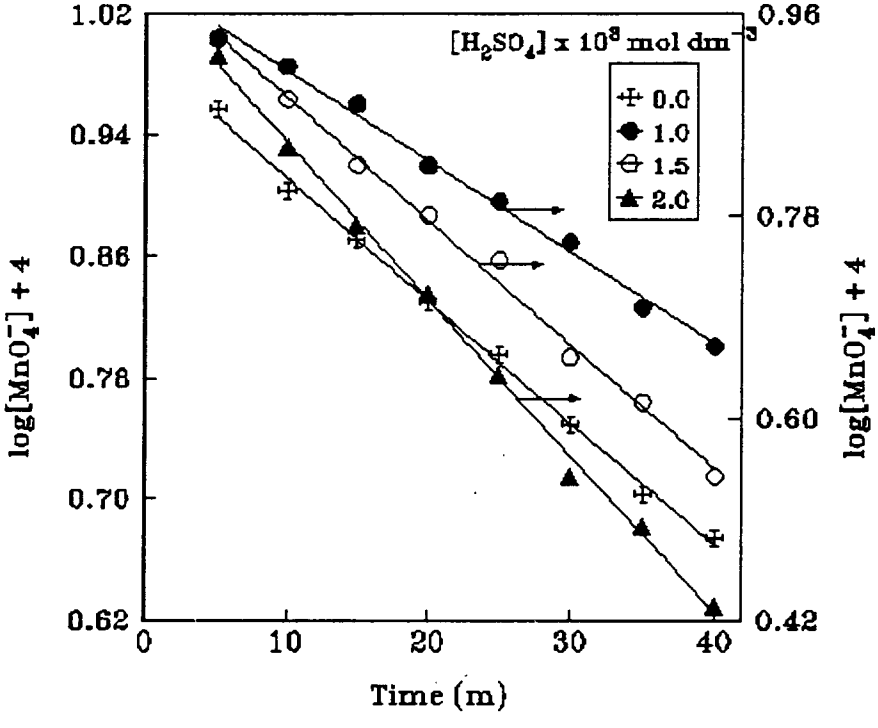


Fig. 4.2.5 Effect of $[H_2SO_4]$ on the oxdn. of C_6H_5CHO in 50% aq.HOAc

Table 4.2.3 Effect of $[H_2SO_4]$ on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Temp. = 308 K

$[H^+] \times 10^3$ mol dm^{-3}	0.0	1.0	1.5	2.0
$k_{obs} \times 10^4$ sec^{-1}	2.993	3.105	4.226	5.362
Correlation Coefficient	0.9991	0.9967	0.9974	0.9987

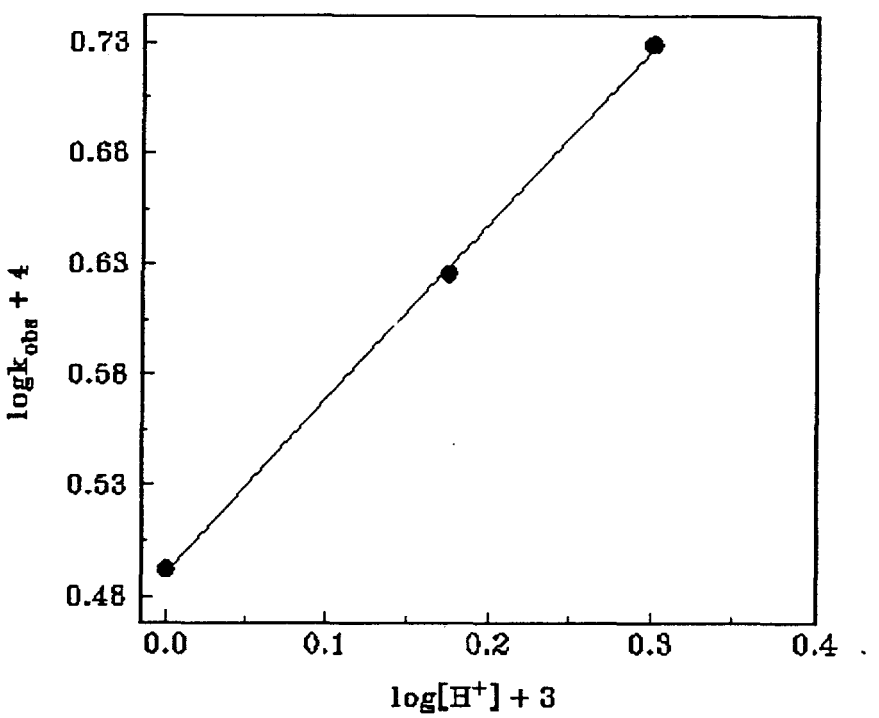


Fig. 4.2.6 Order with respect to Acid

Effect of added salts

An increase in ionic strength is found to have a small decrease in the rate. (Fig. 4.2.7 & Table 4.2.4).

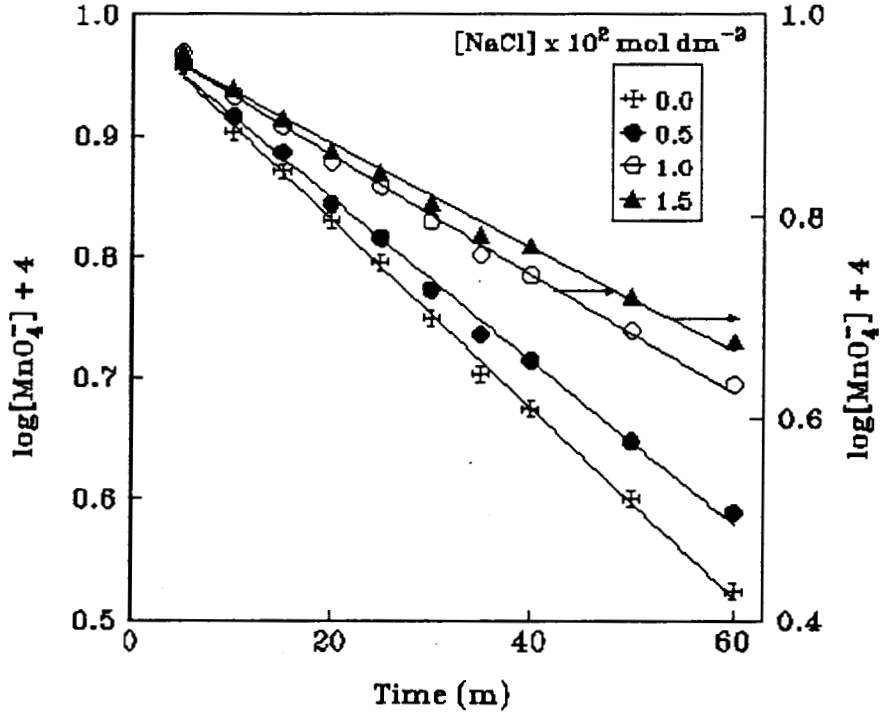


Fig. 4.2.7 Effect of [NaCl] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Table 4.2.4 Effect of [NaCl] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} , $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} , Temp. = 308 K

[NaCl] x 10^2 mol dm^{-3}	0.0	0.5	1.0	1.5
k_{obs} x 10^4 sec^{-1}	2.993	2.583	2.264	1.976
Correlation Coefficient	0.9971	0.9983	0.9978	0.9963

According to Bronsted[256], if the reaction involves unlike charges in the rate-determining step, the rate constant will decrease with increase in ionic strength. Since this decrease is very small, it is easily neglected.

In the present study also the addition of $MnSO_4$ decreases the rate of the reaction, thus showing that permanganate ion is the initial oxidizing species.

Table 4.2.5 Effect of [$MnSO_4$] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} , $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} , Temp. = 308 K

[$MnSO_4$] x 10^3 mol dm^{-3}	0.0	1.0	1.5	2.0
k_{obs} x 10^5 sec^{-1}	2.993	2.176	2.061	1.953
Correlation Coefficient	0.9991	0.9936	0.9893	0.9900

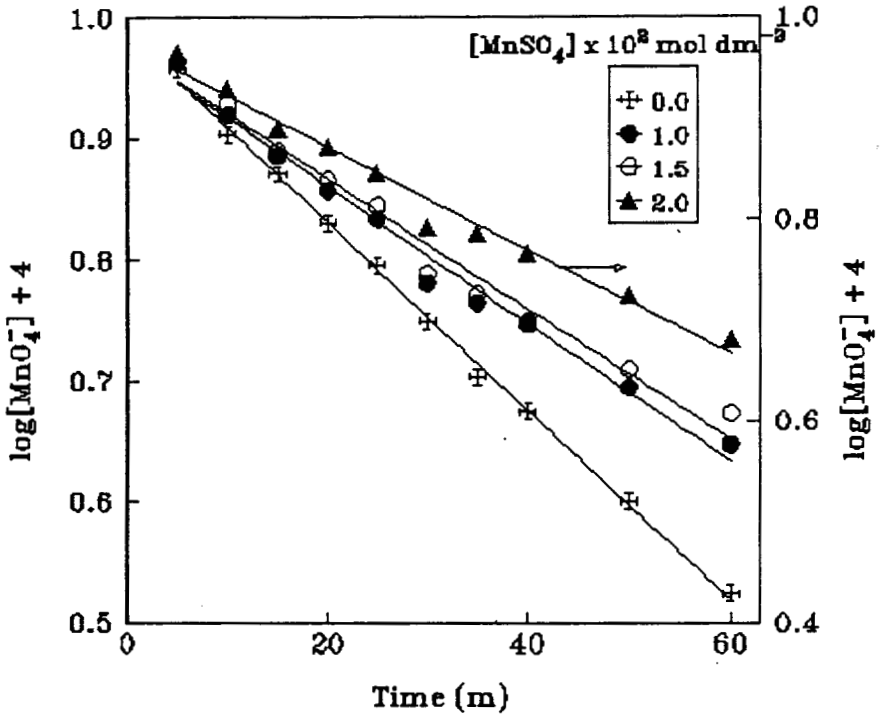


Fig. 4.2.8 Effect of [$MnSO_4$] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Effect of polarity of the solvent

The results obtained (Fig.4.2.9 & Table 4.2.6) show that the rate increases with increase in concentration of the acetic acid. Increase in acetic acid concentration of the solvent lowers the dielectric constant of the medium, which favors reactions involving protonation.

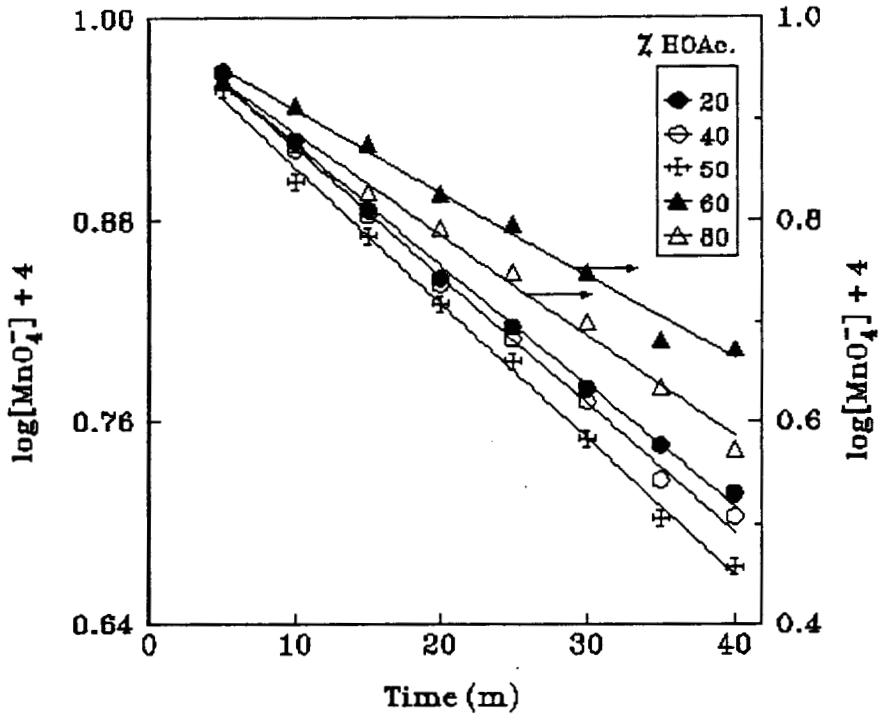


Fig. 4.2.9 Effect of solvent polarity on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Table 4.2.6 Effect of solvent polarity on the oxdn. of C_6H_5CHO in 50%aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Temp. = 308 K

HOAc %	20	40	50	60	80
Dielectric constant	61	47	39.8	32	17.5
$k_{obs} \times 10^4$ sec^{-1}	2.752	2.917	2.993	3.135	3.838
Correlation Coefficient	0.9983	0.9984	0.9971	0.9938	0.9965

Also the plot of log k_{obs} vs 1/D is found to be linear with a positive slope (Fig.4.2.10).

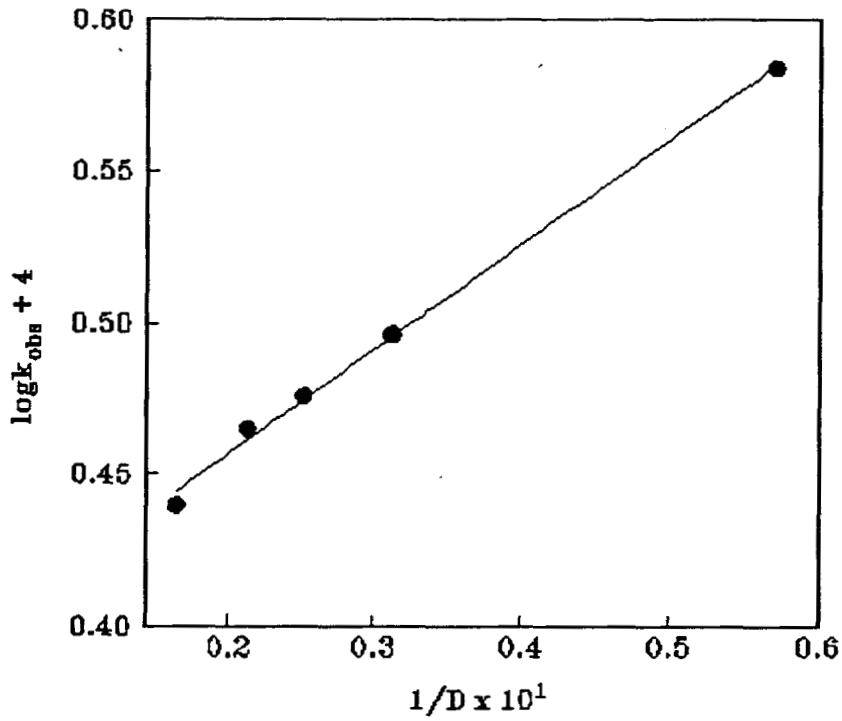


Fig. 4.2.10 Plot of log k_{obs} vs 1/D for the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Effect of substituents on the benzene ring of benzaldehyde

The substituent effect on the oxidation reaction was studied using *m*- nitro, *p*-nitro, *p*-chloro, *p*-methyl, *m*- methoxy and *p*-methoxy benzaldehydes. It is found that (Fig.4.2.11) the effect of substituents is fairly small.

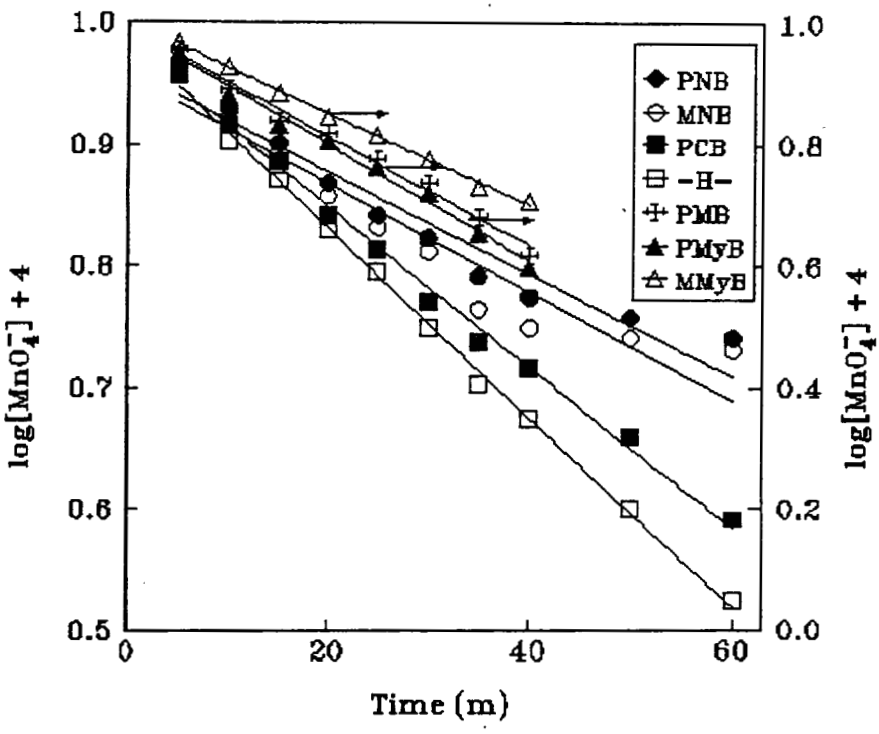


Fig.4.2.11 Effect of Substituents on the oxdn. of C_6H_5CHO in 50% aq.HOAc.

The order of reactivities of various substituted acetophenones were found to be *p*-NO_2 < *m*-NO_2 < *p*-Cl < *m* -OCH_3 < -H- < *p*-CH_3 < *p*-OCH_3 (Table 4.2.7).

Table 4.2.7 Effect of Substituents on the benzene ring on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Substrate	PNB	MNB	PCB	-H-	PMB	PMyB	MMyB
k_{obs} x 10^4 sec^{-1}	1.615	1.715	2.537	2.993	3.435	3.665	2.897
Corr. Coefficient	0.9691	0.9533	0.9973	0.9971	0.9936	0.9948	0.9987

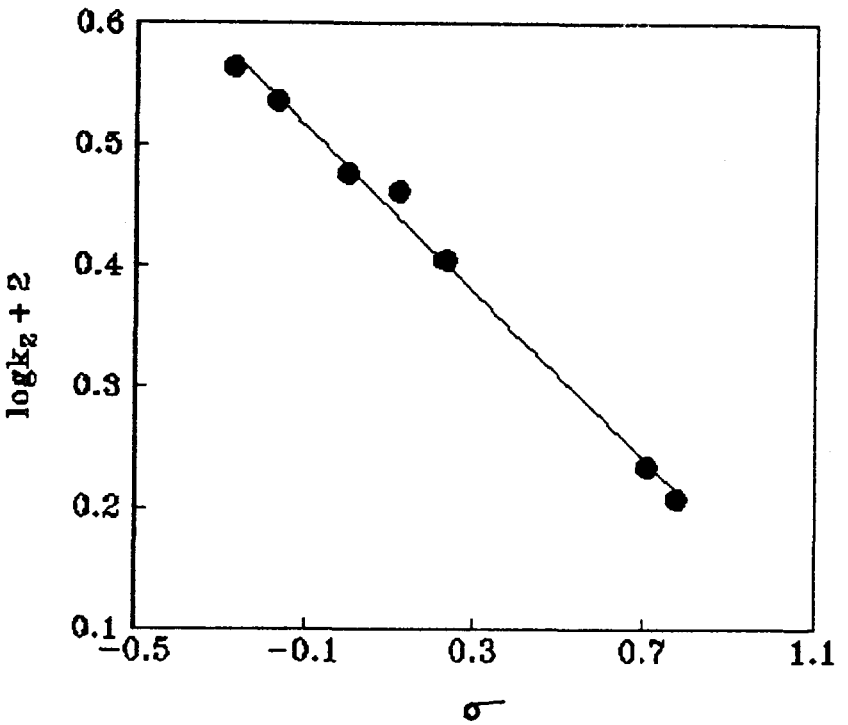


Fig. 4.2.12 Hammett plot for the oxdn. of C_6H_5CHO in 50% aq. HOAc

The reaction is slightly accelerated by the presence of electron-donating groups. The Hammett plot of log k_{obs} vs σ (Fig.4.2.12) was found to be linear with a slope of –0.3427. A similar value has been obtained in most reactions, which are considered to be acid catalysed[255].

Effect of Temperature on the rate of oxidation of C_6H_5CHO and evaluation of the thermodynamic parameters

The temperature coefficients of the reaction were studied for a range of 308-323K and are given below (Fig.4.2.13). The overall second order rate constants for the acetophenone and its derivatives were found to increase with increase in temperature (Table 4.2.8).

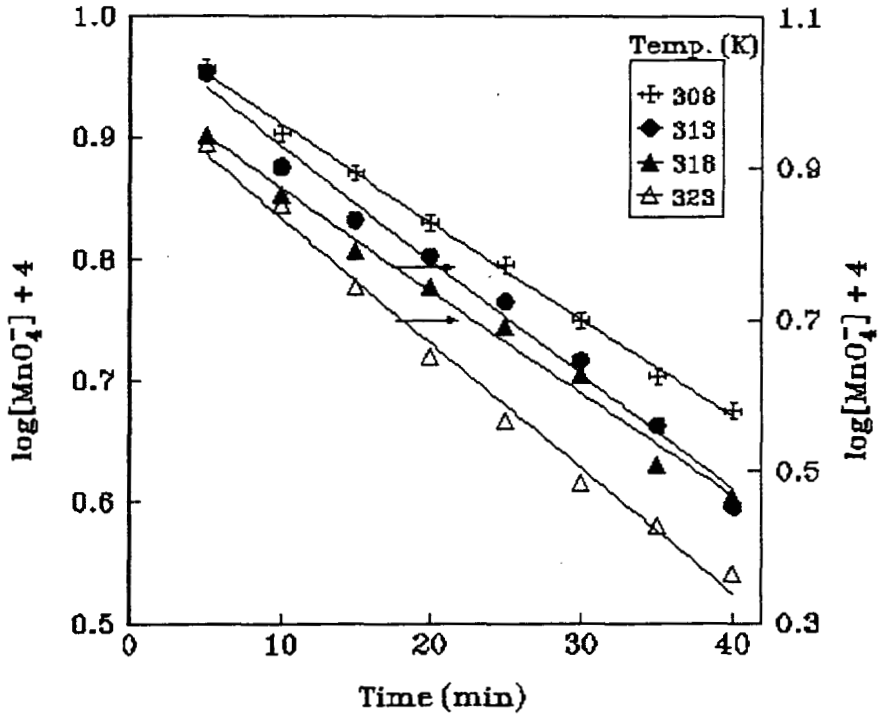


Fig. 4.2.13 (a) Effect of Temp. on the oxdn. of C_6H_5CHO in 50% aq. HOAc

Table 4.2.8 (a) Effect of Temp. on the oxdn. of C_6H_5CHO in 50% aq. HOAc

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}

Temperature (K)	308	313	318	323
$k_{obs} \times 10^4$ sec^{-1}	2.993	3.619	5.197	6.337
Correlation Coefficient	0.9986	0.9934	0.9948	0.9957

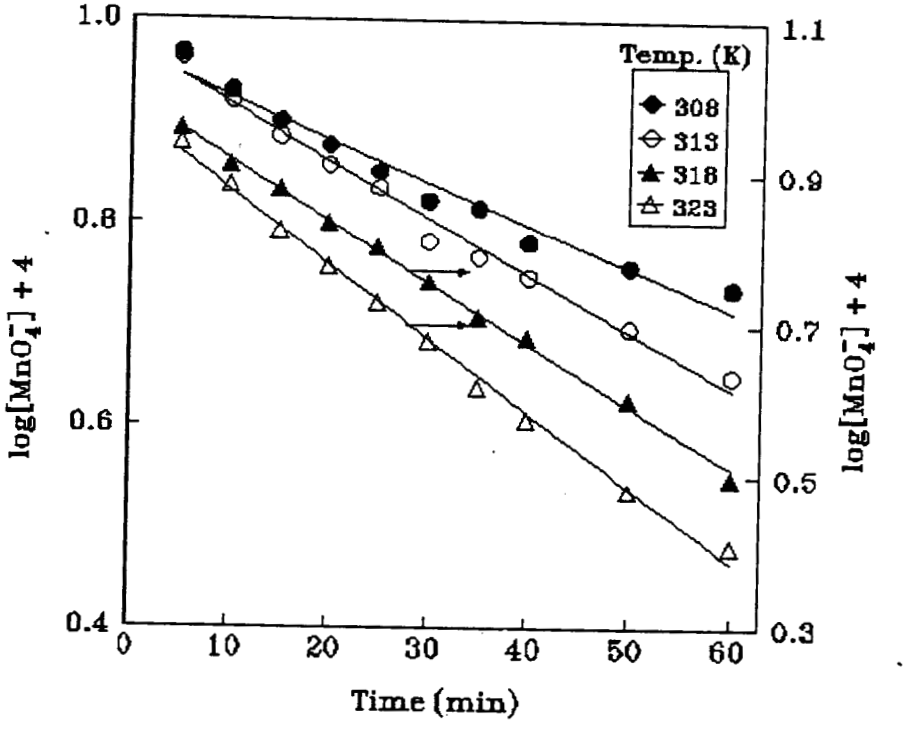


Fig. 4.2.13 (b) Effect of Temp. on the oxdn. of PNB in 50% aq. HOAc.

Table 4.2.8 (b) Effect of Temp. on the oxdn. of PNB in 50% aq. HOAc.

[PBA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	1.623	2.164	3.124	3.753
Correlation Coefficient	0.9832	0.9935	0.9989	0.9981

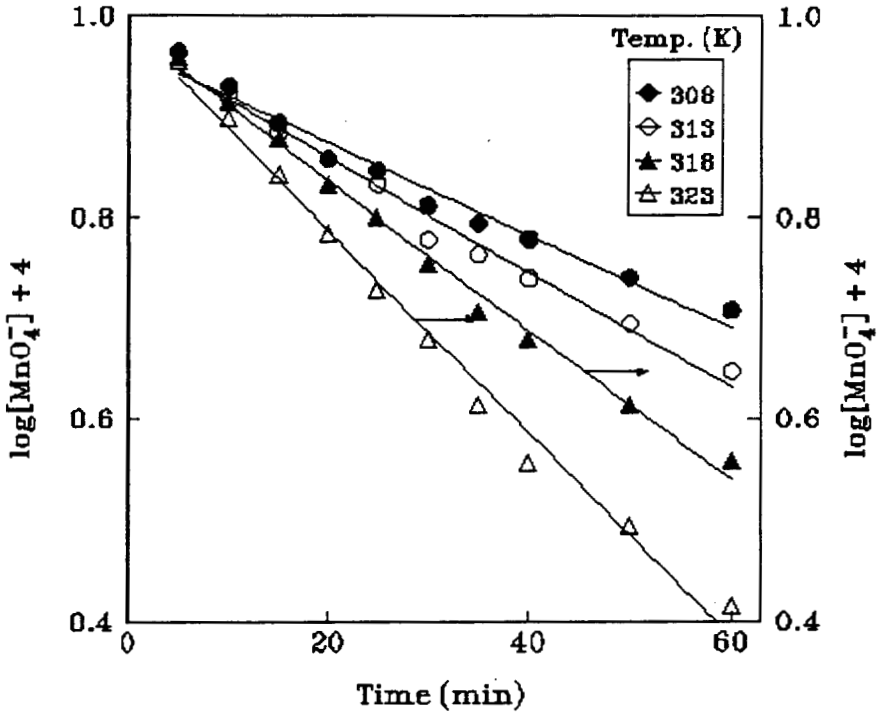


Fig. 4.2.13 (c) Effect of Temp. on the oxdn. of MNB in 50% aq. HOAc.

Table 4.2.8 (c) Effect of Temp. on the oxdn. of MNB in 50% aq. HOAc.

[MNB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	1.750	2.180	2.840	3.849
Correlation Coefficient	0.9865	0.9923	0.9968	0.9948

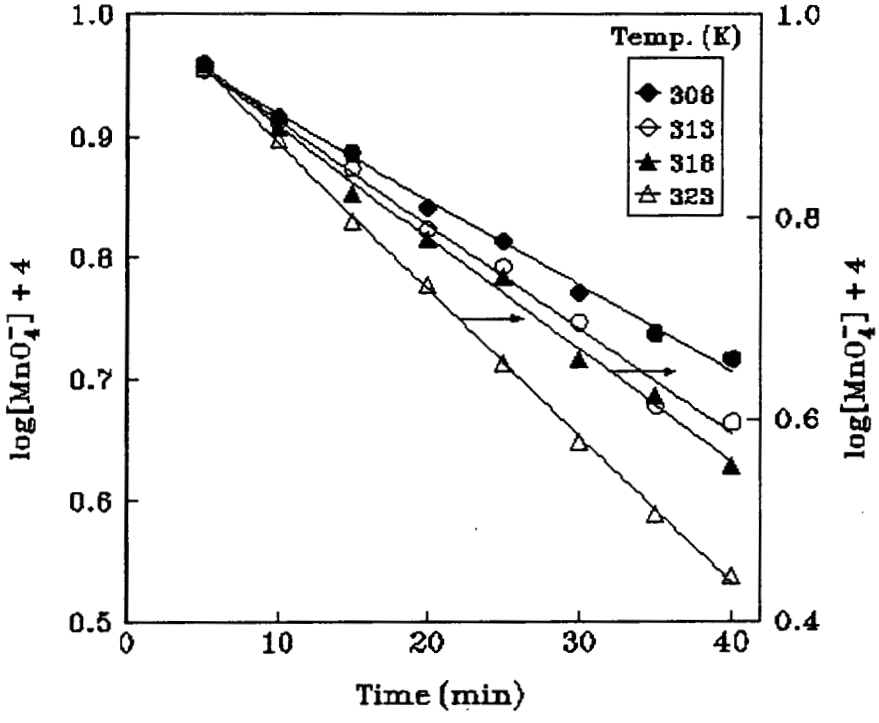


Fig. 4.2.13 (d) Effect of Temp. on the oxdn. of PCB in 50% aq. HOAc.

Table 4.2.8 (d) Effect of Temp. on the oxdn. of PCB in 50% aq. HOAc.

[PCB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	2.537	3.308	4.241	5.577
Correlation Coefficient	0.9976	0.9960	0.9977	0.9996

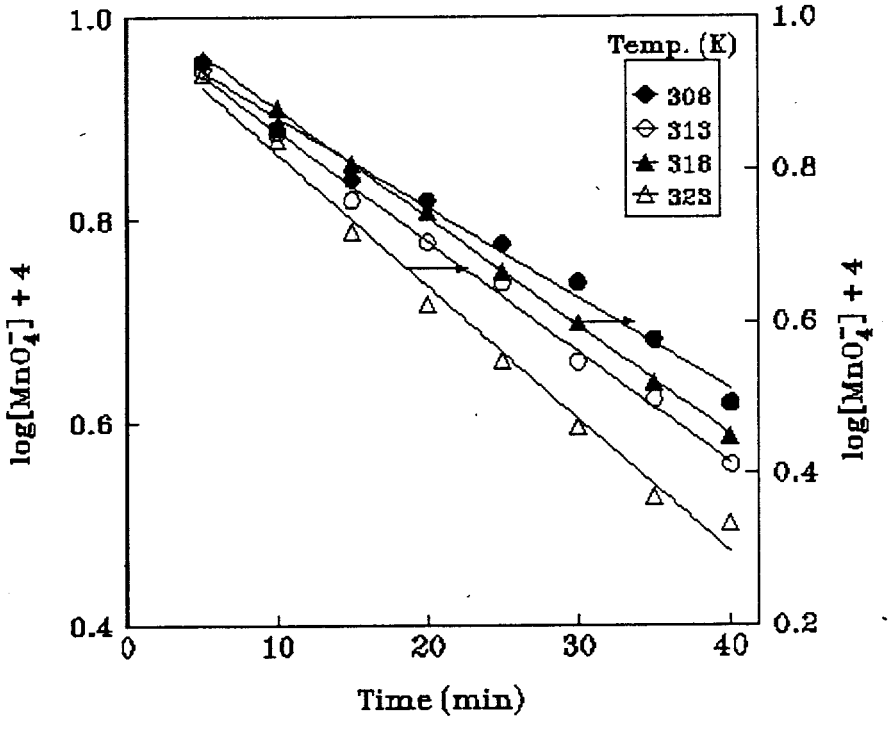


Fig. 4.2.13 (e) Effect of Temp. on the oxdn. of PMB in 50% aq. HOAc.

Table 4.2.8 (e) Effect of Temp. on the oxdn. of PMB in 50% aq. HOAc.

[PMB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	3.435	4.187	5.484	6.705
Correlation Coefficient	0.9936	0.9976	0.9997	0.9950

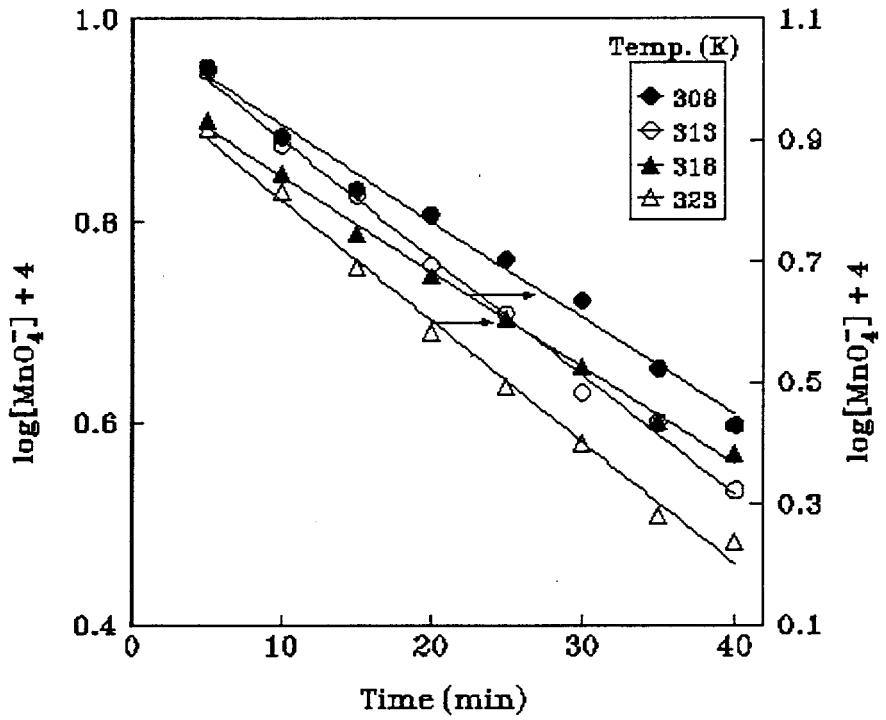


Fig. 4.2.13 (f) Effect of Temp. on the oxdn. of PMyB in 50% aq. HOAc.

Table 4.2.8 (f) Effect of Temp. on the oxdn. of PMyB in 50% aq. HOAc.

[PMyB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	3.665	4.49	6.068	7.676
Correlation Coefficient	0.9948	0.9978	0.9985	0.9966

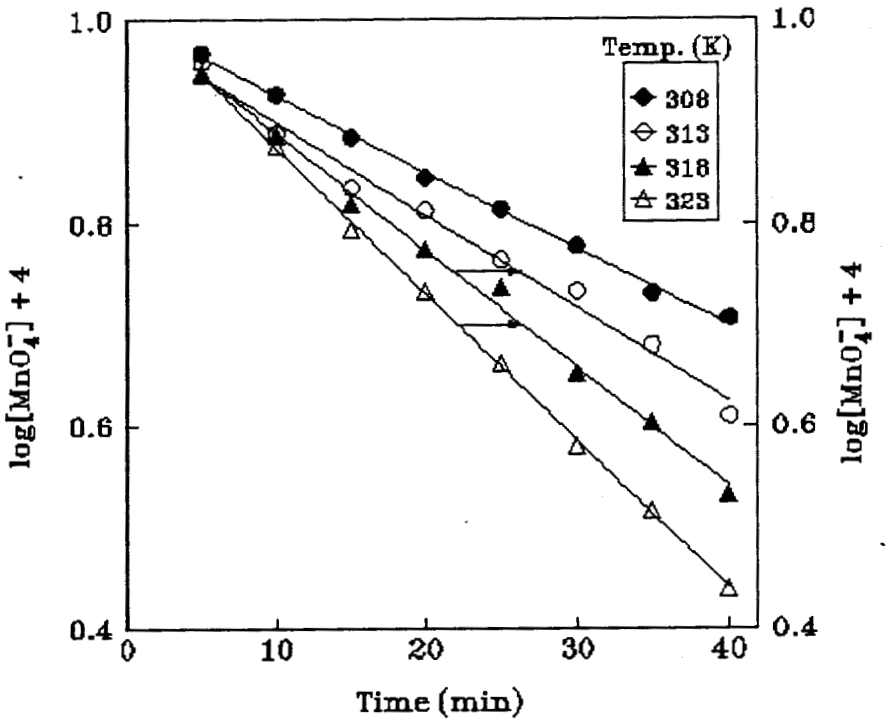


Fig. 4.2.14 (g) Effect of Temp. on the oxdn. of MMyB in 50% aq. HOAc.

Table 4.2.9 (g) Effect of Temp. on the oxdn. of MMyB in 50% aq. HOAc.

[MMyB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}

Temperature (K)	308	313	318	323
k_{obs} x 10^4 sec^{-1}	2.897	3.512	4.448	5.550
Correlation Coefficient	0.9987	0.9931	0.9975	0.9970

The various activation parameters were evaluated by plotting log k_2 vs 1/T (Fig.4.2.14) and log k_2/T vs 1/T (Fig.4.2.15) and are given in the Table 4.2.9.

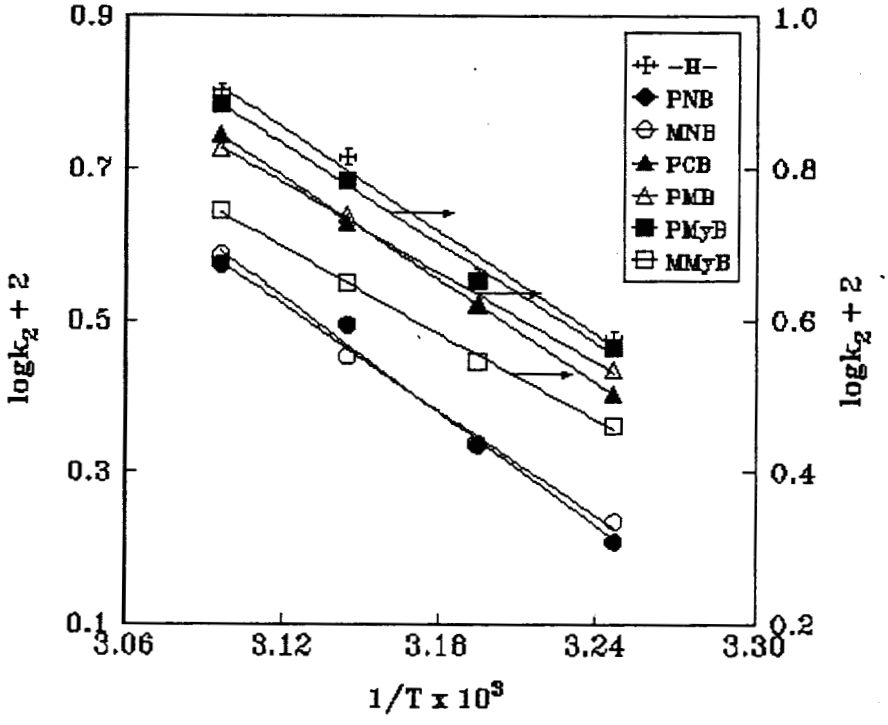


Fig. 4.2 14 Plot of log k_2 vs 1/T for the oxdn. of C_6H_5CHO in 50% aq. HOAc.

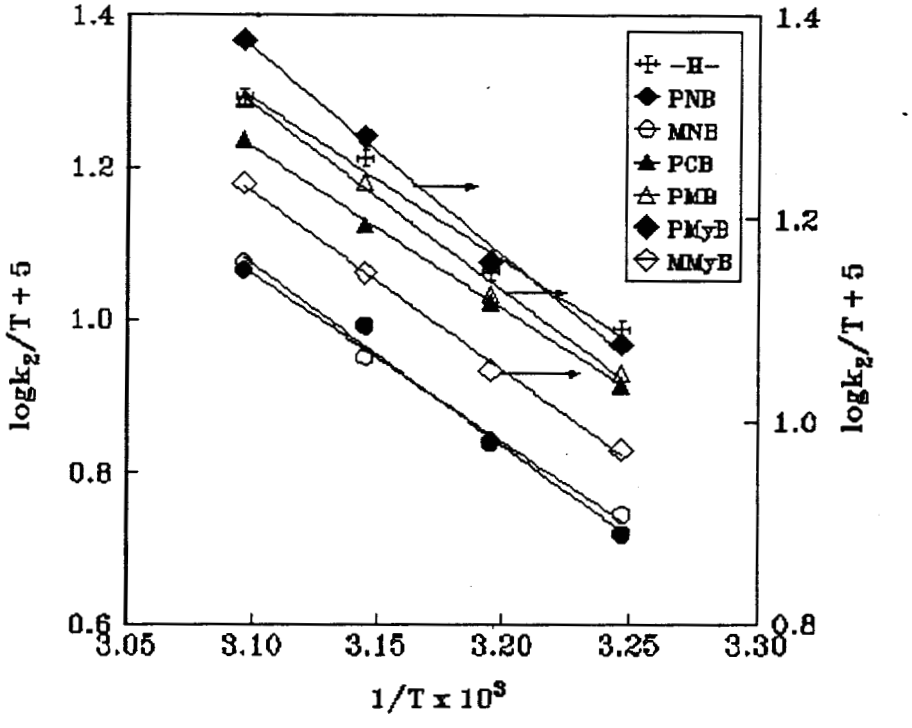


Fig. 4.2.15 Plot of log k_2/T vs 1/T on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Table 4.2.9 Activation Parameters for the oxdn. of C_6H_5CHO and its substituents in 50% aq. HOAc.

Substrate	k_{obs} x 10^4 sec^{-1}	E_a KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
PNB	1.623	47.92	45.32	131.94	85.957
MNB	1.715	44.41	41.79	142.91	85.806
PCB	2.537	43.16	40.52	143.77	84.801
-H-	2.993	43.16	4.056	142.27	84.379
PMB	3.435	37.62	35.07	158.94	84.023
PMyB	3.665	41.61	38.95	145.80	83.856
MMyB	2.897	36.14	33.51	165.43	84.462

The free energy of activation, $\Delta G^{\#}$ is nearly the same indicating that a similar mechanism is operating for all the benzaldehydes studied. Moreover the existence of a linear relationship (γ = 0.9864) of the isokinetic plot ($\Delta H^{\#}$ vs $\Delta S^{\#}$)(Fig.4.2.16) and the Exner's plot (γ = 0.9863) (Fig. 4.2.17) further support the above assumption.

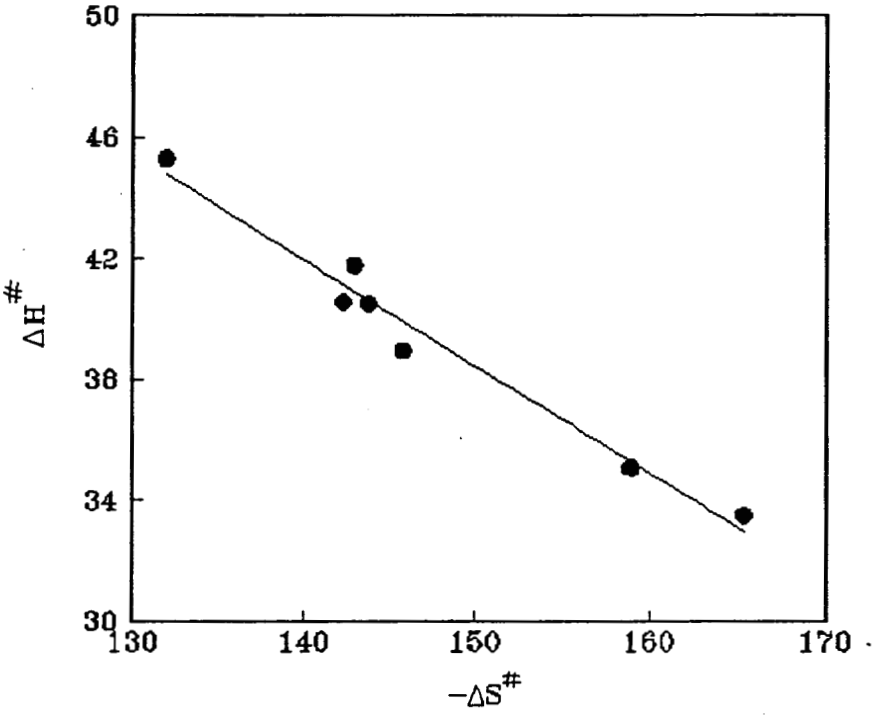


Fig. 4.2.16 Isokinetic plot for the oxdn. of C_6H_5CHO in 50% aq. HOAc.

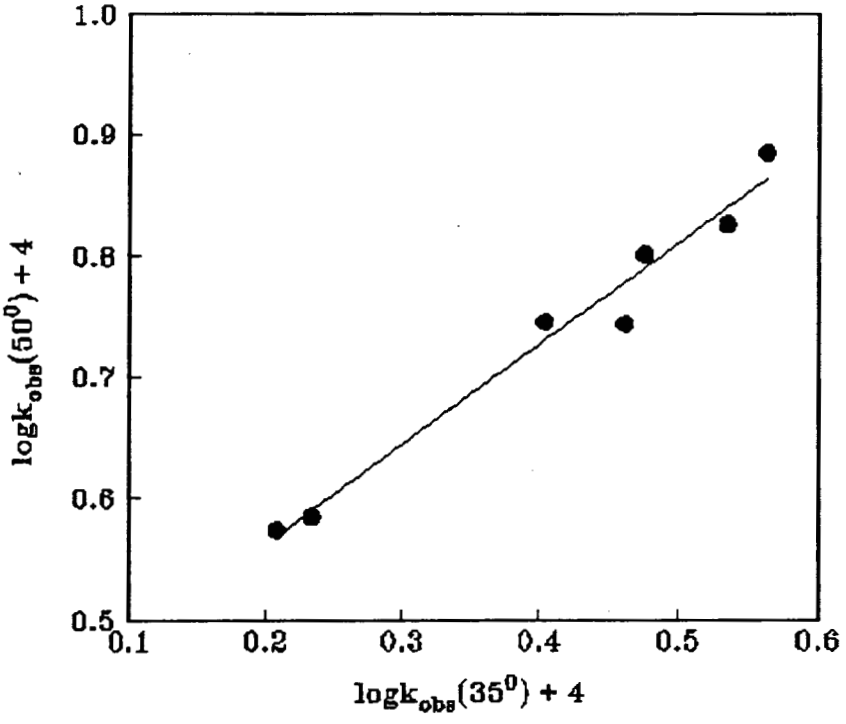


Fig.4.2.17 Exner's plot for the oxdn. of C_6H_5CHO in 50% aq. HOAc.

Effect of Product on the rate of oxidation

To study the influence of the reaction products on the rate, various concentrations of benzoic acid were added to the system and the kinetics were followed. The results obtained are presented in the Table 4.2.10. this shows that thew product is not involved in the pre-equilibrium step.

Table 4.2.10 Effect of [C_6H_5COOH] on the oxdn. of C_6H_5CHO in 50% aq.HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Temp. = 308 K

$[C_6H_5COOH] \times 10^2$ mol dm^{-3}	0.0	1.0	1.5	2.0
$k_{obs} \times 10^4$ s^{-1}	2.993	2.867	2.886	2.913
Correlation Coefficient	0.9991	0.9992	0.9984	0.9989

4.2.3 Effect of Addition of Acrylonitrile to the Reaction Mixture

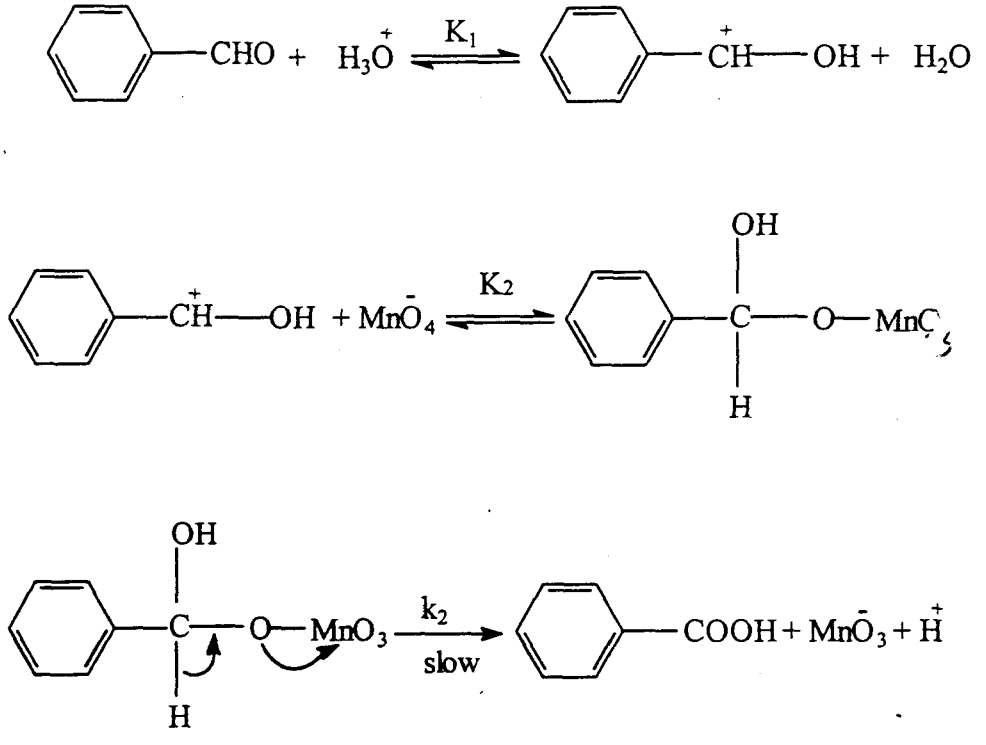
The non-involvement of free radicals in the reaction was ascertained using acrylonitrile as done in the oxidation of acetophenone. The absence of white precipitate even after keeping it overnight in the dark shows that the free radicals are not involved in the process.

4.2.4 Mechanism and Rate law

Aldehydes are easily oxidized to carboxylic acids than ketones. This difference is due to the difference in structure. An aldehyde has a hydrogen atom attached to the carbonyl carbon; this hydrogen is abstracted in oxidation either as a proton or as an atom.

By considering all the experimental observations and comparing it with similar observations, mainly the oxidation of isopropyl alcohol with chromic acid[256] in which an ester intermediate is postulated. In the chromic acid oxidation, the ester is formed by utilizing the oxygen of the alcohol whereas in this case it is expected that the oxygen of the oxidizing agent forms the ester bond.

The suggested mechanism is as follows (Scheme 2).



Thus the reaction is believed to involve the formation and subsequent decomposition of the permanganate ester. The intermediate ester is presumed to be in rapid equilibrium with the aldehyde and permanganate. The reaction is accompanied by transfer of oxygen from the permanganate to the aldehyde and that the rate-

determining step involves the abstraction of the proton of the aldehyde by a weak base followed by the cleavage of the oxygen-manganese bond. Thus the reaction is expected to proceed by the formation of an intermediate manganate ester, which can decompose to give oxidized products.

Though the mechanism suggested above could explain all the principal observations concerning the oxidation of C_6H_5CHO using $KMnO_4$ like

1) the rate of the reaction was found to be proportional to first powers of permanganate and benzaldehyde concentration

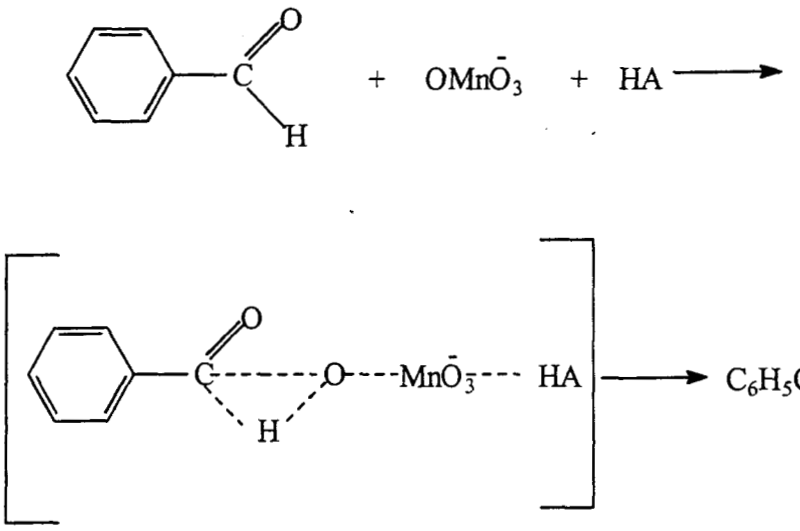
2) The reaction was acid catalyzed

3) The rate controlling step involves the cleavage of the aldehyde C-H bond

4) The oxygen introduced into the aldehyde was derived from the permanganate ion, indicating that a bond was formed between the benzaldehyde carbon and an oxygen of the permanganate *etc.*

But there is a slight drawback with the above mechanism. The electron-withdrawing substituents should actually facilitate both the pre-equilibrium step and the rate-determining step and hence should increase the rate. But a reverse effect is obtained actually.

Inorder to account for the rate of the electron-withdrawing groups, the following mechanism is also suggested.



Hydrogen bonding to the permanganate anion by an acid molecule would increase the electron-withdrawing character of the permanganate ion. This effect would also support the effect of acid on the reaction rate.

The above mechanism leads to the following rate law equation,

$$\frac{d[MnO_4^-]}{dt} = k_2\,[\text{Complex}]$$

$$[\text{Complex}] = K_2\,[MnO_4^-]\,[C_6H_5\overset{+}{C}HOH]$$

$$\text{but}\quad [C_6H_5\overset{+}{C}HOH] = K_1\,[C_6H_5CHO]\,[H^+]$$

$$\text{Rate} = K_1 K_2 k_2\,[C_6H_5CHO]\,[MnO_4^-]$$

The rate law in its final form accounts for the observed kinetics.

4.3 EXTRACTION OF PERMANGANATE ION INTO ORGANIC SOLVENTS USING PHASE TRANSFER CATALYSTS

The effectiveness of any phase transfer system will be dependent on the ability of that system to extract the permanganate ion from aqueous phase into organic phase. Hence in this particular section, a systematic study on the extraction of permanganate ion was carried out to find out the efficiency of extraction under different conditions like

1) the effect of time
2) the effect of structure and concentration of quaternary ammonium salt
3) the effect of solvent polarity
4) the effect of addition of salts to the aqueous phase,

and thus the optimum conditions required for the complete transference of permanganate ion from the aqueous phase was calculated.

The results obtained by the extraction of 10 ml of 0.01 mol dm^{-3} aqueous potassium permanganate with an equal volume of organic solvent containing phase transfer catalyst are given below. From this the percentage of MnO_4^- extracted into the organic phase,

$$\% \text{ of } MnO_4^- \text{ extracted into the organic phase} = \frac{[Q^+ MnO_4^-]_{org}}{[MnO_4^-]_{aqueous\ initially}} \times 100$$

and hence the efficiency of extraction has been calculated.

4.3.1 Effect of time on the extraction of MnO_4^- from the aqueous phase

In this particular section extractions were conducted to find out the optimum time needed for the extraction of MnO_4^- into the organic phase

Table 4.3.1 Effect of time on the extraction

[PTC] = 0.01 mol dm^{-3}, $[MnO_4^-]_{aq}$ = 0.01 mol dm^{-3}, Solvent - Benzene

Time (min)	% of MnO_4^- extracted into organic phase	
	TCMAC	TBAB
15	75	58
30	92	79
45	93	81
60	93	82

The results obtained clearly indicate that the extraction is almost steady after 30 minutes and there is only a slight increase in the percentage of extraction (Table 4.3.1 & Fig.4.3.1)

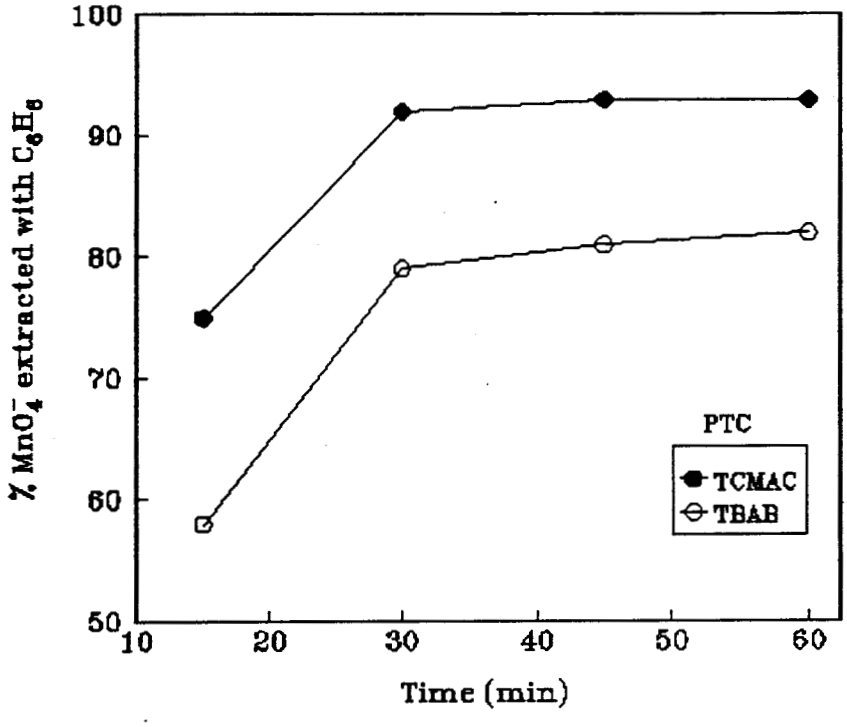


Fig.4.3.1 Effect of time on the extraction efficiency

Thus the optimum time required for the extraction under the given conditions is just 30 minutes. Hence in the rest of the experiments the extraction efficiency was calculated by stirring the mixture for half an hour using a magnetic stirrer.

4.3.2 Effect of Structure and Concentration of the Catalyst

Effect of structure of the cation on the extraction has been illustrated by the work of Gibson and Weatherburn[149], Okimoto and Swern[181], and Herriott and Picker[173], but in this present work an attempt has been made to find out the exact concentration of different catalysts needed to extract almost completely the MnO_4^- present in the aqueous phase (Table 4.3.2 & Fig. 4.3.2)

Table 4.3.2 Effect of Structure and Concentration of the Catalyst

Time – 30 minutes, $[MnO_4^-] = 0.01$ mol dm^{-3}, Solvent - Benzene

[PTC]	% of MnO_4^- extracted into organic phase	
	TCMAC	TBAB
0.005	61	52
0.01	92	79
0.015	98	94
0.02	100	97

The TCMAC catalyst was found to extract MnO_4^- more effectively than the TBAB catalyst. The results obtained indicate that the size of the quaternary ammonium cation is an important factor in the extraction. The greater effectiveness of TCMAC is due to the high organophilicity imparted by the three large alkyl groups combined with a small methyl group, which could allow the MnO_4^- to be more closely associated with the positive nitrogen[156]. Thus there is a relation between the cation size and extraction efficiency.

The extraction power of the catalyst is probably the most important factor in the permanganate oxidations. It is found that a moderate excess of lipophilic quaternary salts can extract MnO_4^- almost quantitatively into the organic phase.

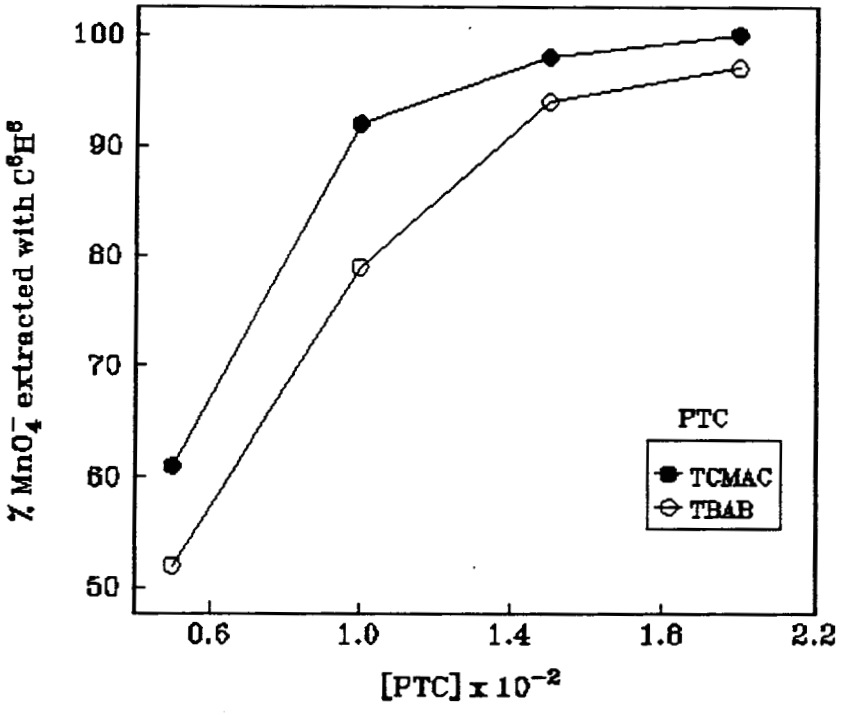


Fig. 4.3.2 Effect of Structure and concentration of PTC on extraction efficiency

4.3.3 Effect of Solvent Polarity

It is well known that potassium permanganate exists in an ionic form when dissolved in water. However, when a quaternary ammonium permanganate salt dissolves in an organic solvent it exists predominantly as an ion-pair[180, 156]. According to Brandstrom[156], the point at which ion-pair formation occurs is inversely dependent on the dielectric constant of the solvent. This means that ion-pairing is much likely to

occur in non-polar solvents with low dielectric constants. Hence in this particular work the extraction efficiency of some solvents with low dielectric constants has been carried out.

Table 4.3.3 Effect of Solvent Polarity

[PTC] = 0.01 mol dm^{-3} , [MnO_4^-] = 0.01 mol dm^{-3} , Time = 30 minutes

Organic Solvent	C_6H_6	$C_6H_5CH_3$	CH_2Cl_2	$CHCl_3$	CCl_4	$CH_3COOC_2H_5$	$C_2H_5OC_2H_5$
Dielectric Constant	2.27	2.40	8.90	4.70	2.22	6.0	4.2
TCMAC	92	90	86	88	90	81	74
TBAB	79	76	89	86	75	63	52

The effect of the solvent on the extraction is found to be quite small (Table 4.3.3). A very little correlation is found between the extracting ability and the dielectric constant of the solvent. In this the extraction of MnO_4^- into six different solvents have been carried out. From this it is clear that for TBAB, methylene chloride is found to be the best solvent of choice, but TCMAC were found to be effective PT agents for all the solvents used especially for the used especially for the use in the less polar solvents such as benzene and carbontetrachloride.

4.3.4 Effect of Inorganic salts in the aqueous phase

The effects of inorganic salts were found out by varying the concentration of permanganate ion in the aqueous phase and also by varying the amount of some foreign salts (NaCl).

Table 4.3.4 (a) Effect of initial concentration of MnO_4^-

Time – 30 minutes , [PTC] = 0.01 mol dm^{-3} , Solvent - Benzene

$[MnO_4^-]$	% of MnO_4^- extracted into organic phase	
	TCMAC	TBAB
0.01	92	79
0.015	95	87
0.02	96	89
0.025	96	90

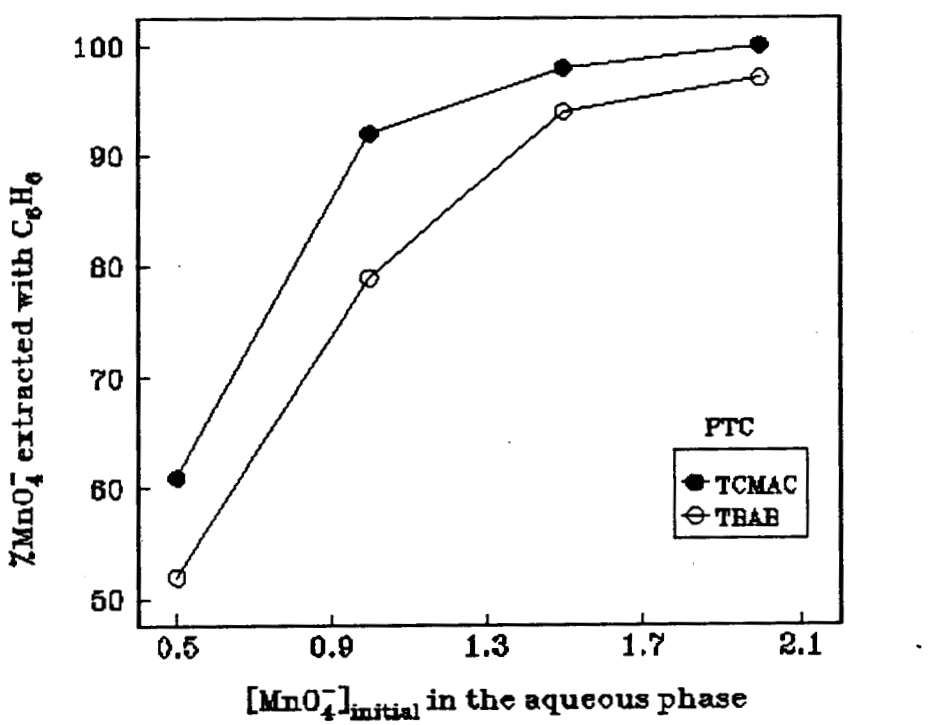


Fig. 4.3.4 Effect of $[MnO_4^-]_{initial}$ in the aqueous phase on the extraction efficiency

From the results (Table 4.3.4(a) & Fig. 4.3.4(a)) it is understood that by increasing the concentration of MnO_4^- in the aqueous phase, increases the extraction efficiency. This may be due to the salting out effect. Increasing the concentration of inorganic salts in the aqueous phase tends to salt out organic salts, pushing them into the organic phase. Moreover increasing concentration of inorganic salts concentration also ties up additional water of hydration, reducing the amount of water available for anion hydration, providing for easier transfer of the anions into the organic phase.

This effect was further confirmed by the addition of a foreign salt like NaCl(Table 4.3.4(b) & Fig. 4.3.4(b)).

Table 4.3.4 (b) Effect of addition of NaCl

Time – 30 minutes , [PTC] = 0.01 mol dm^{-3} , Solvent - Benzene

[NaCl]	% of MnO_4^- extracted into organic phase	
	TCMAC	TBAB
0.0	92	79
0.005	93	85
0.01	95	87
0.02	96	87

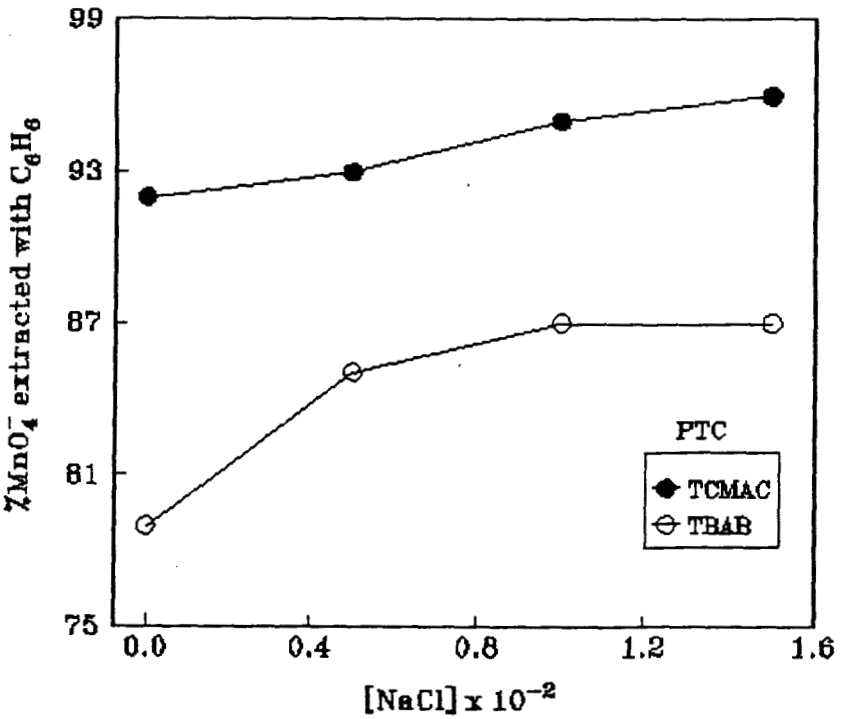


Fig. 4.3.4(b) Effect of [NaCl] on the extraction efficiency

The above experiments predicts that the concentration of quaternary ammonium permanganate ion-pair in the organic phase is affected by time, organic structure of the quaternary ammonium cation, polarity of the solvent and concentration of inorganic salts in the aqueous phase.

4.4 STABILITY OF PERMANGANATE ION IN ORGANIC SOLVENTS

Although potassium permanganate has been widely used as oxidant under phase transfer conditions[129], only little attention has been paid to the investigation of the stability of its solutions in organic solvents[15,172]. Permanganate attacks to some degree all organic solvents in which it is soluble.

In this particular section the stability of the MnO_4^- in various solvents *viz.* benzene, toluene, chloroform, methylene chloride and carbontetrachloride in the presence of phase transfer catalysts *viz.* TCMAC and TBAB was studied. These solutions were prepared by shaking a 10 ml of 0.01 mol dm^{-3} aqueous solution of permanganate with an equal volume of organic solvent containing 0.02 mol dm^{-3} PTC. The solution thus obtained was separated, dried and its stability determined. The decomposition of MnO_4^- was found out by measuring the absorbance of MnO_4^- spectrophotometrically in known intervals of time.

The absorbance spectrum of MnO_4^- in organic solvents is similar to that in water (Fig. 4.4.1).

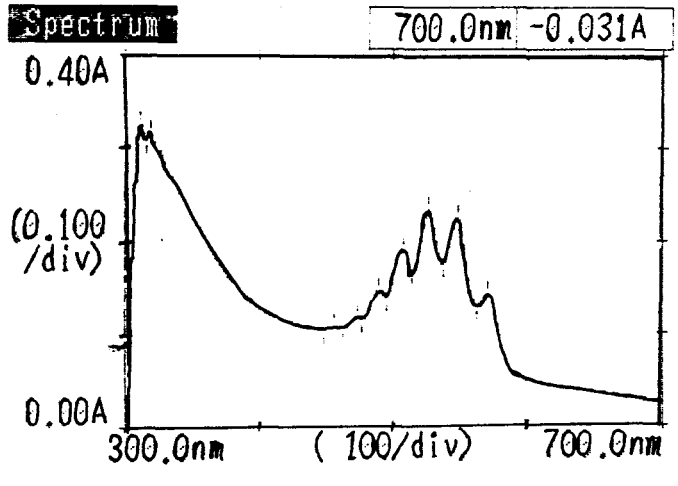


Fig. 4.4.1 Absorbance Spectrum of $Q^+MnO_4^-$ (1.0×10^{-4} mol dm^{-3}) in C_6H_6 extracted with TCMAC

Thus in general we could say that $Q^+ MnO_4^-$ behaves like MnO_4^- in neutral aqueous solution, being reduced in the presence of a suitable reductant to manganese dioxide.

It was found that the absorption of the most intense peak of MnO_4^- (~ 526 nm) in these solvents were found to decrease slightly and percentage of MnO_4^- decomposed in different solvents were found out.

Table 4.4.1 Percentage decrease of MnO_4^- in various organic solvents

$[MnO_4^-]$ = 0.01 mol dm^{-3} [PTC] = 0.02 mol dm^{-3}

Organic Solvent	C_6H_6	$C_6H_5CH_3$	CH_2Cl_2	$CHCl_3$	CCl_4
TCMAC	2.01	2.74	3.14	2.74	2.11
TBAB	1.77	2.41	2.81	2.25	2.01

From the above experiments, we have arrived at the following conclusions.

1) The loss of permanganate ion extracted into organic solvents with both the catalysts were found to be less than 3% for a period of one hour, indicating that these solutions are stable enough to carry out the kinetics of oxidation of organic substrates.

2) The most stable solution are those prepared with TBAB as PTC in benzene solvent

The permanganate solutions thus prepared above are fairly stable, and are very convenient for carrying out the oxidation reactions under anhydrous conditions.

4.5 OXIDATION OF ACETOPHENONE USING QUATERNARY AMMONIUM PERMANGANATE

Oxidation of organic substrates with water-soluble oxidants such as permanganate, dichromate, hypochlorite *etc.* can be conveniently carried out in organic media by the use of phase transfer technique[129].

In this present work an attempt has been made to carry out the kinetics of oxidation of acetophenone and some of its derivatives using the permanganate solutions prepared in organic solvents using quaternary ammonium salts as phase transfer catalysts (section 4.3).

4.5.1 Stoichiometry and Product Analysis

Stoichiometry of the reaction has been investigated by equilibrating known amounts of acetophenone and quaternary ammonium permanganate at room temperature.

The results obtained shows that PTC did not alter the stoichiometry , [AcPh] : $[Q^+MnO_4^-] = 1:1$, nor the major product (benzoic acid) of the reaction.

4.5.2 Kinetic Studies

The kinetic profile of the reaction has been investigated as a function of variables such as the concentration of the oxidant, concentration of the substrate, structure and concentration of the catalyst, solvent polarity, substituents and temperature.

In all the experiments the catalyst concentration was double the concentration of the permanganate ion unless otherwise mentioned. The dependence of the rate on the [$Q^+MnO_4^-$] and [AcPh] was investigated using benzene as solvent and TCMAC and TBAB as phase transfer catalysts.

Effect of [$Q^+MnO_4^-$] on the rate of oxidation

Despite the complexities of the reaction using [$Q^+MnO_4^-$] as oxidant, the plot of log[MnO_4^-] vs time (Fig. 4.5.1(a) & (b)) were linear.

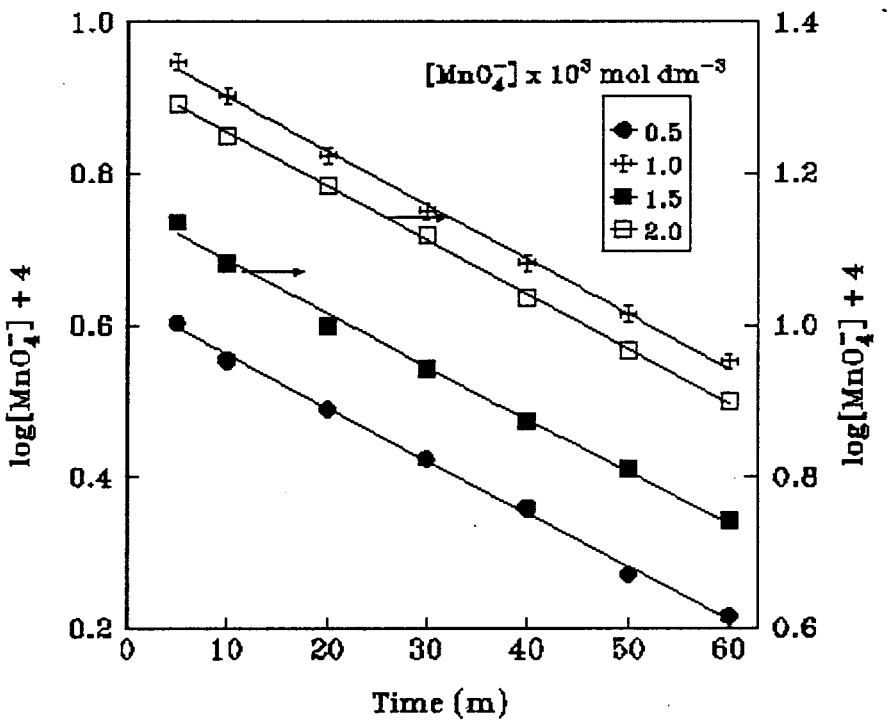


Fig. 4.5.1 (a) Effect of [$Q^+MnO_4^-$] on the oxdn. of AcPh in Benzene (TCMAC)

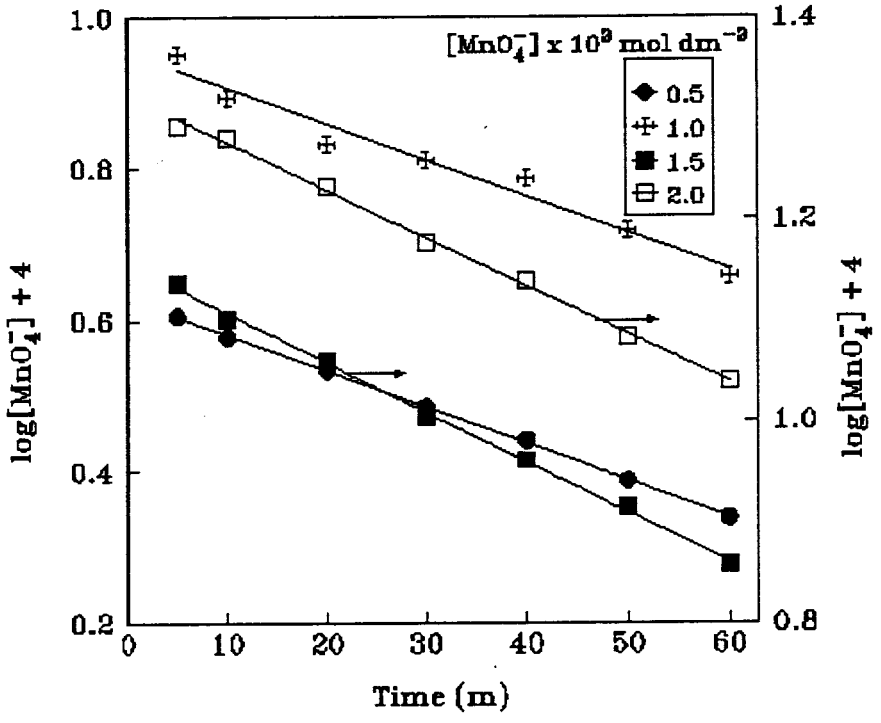


Fig. 4.5.1 (b) Effect of $[Q^+MnO_4^-]$ on the oxdn. of AcPh in Benzene (TBAB)

Moreover by varying the concentration of $Q^+MnO_4^-$, there was no much difference in the rate constant (Table 4.5.1), which once again supports the first order dependence of the permanganate ion.

Table 4.5.1 Effect of $[Q^+MnO_4^-]$ on the oxdn. of AcPh in Organic solvents

Solvent – Benzene Temp. – 303 K

$[Q^+MnO_4^-] \times 10^3$ mol dm^{-3}	TCMAC		TBAB	
	$k_{obs} \times 10^4$ s^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ s^{-1}	Corr. Coeff.
0.5	2.694	0.9989	1.846	0.9997
1.0	2.755	0.9988	1.850	0.9848
1.5	2.663	0.9978	1.896	0.9990
2.0	2.740	0.9997	1.811	0.9981

Effect of [AcPh] on the oxdn. of AcPh in organic solvents

The effect of varying the concentration of AcPh was also studied for a range of 1.0 – 2.5 x 10^{-2} mol dm^{-3}, keeping all the other conditions the same. Here also the plots of log[MnO_4^-] vs time were linear (Fig. 4.5.2 (a) & (b)), but the evaluated k_{obs} values were found to be dependent on the concentration of AcPh (Table 4.5.2)

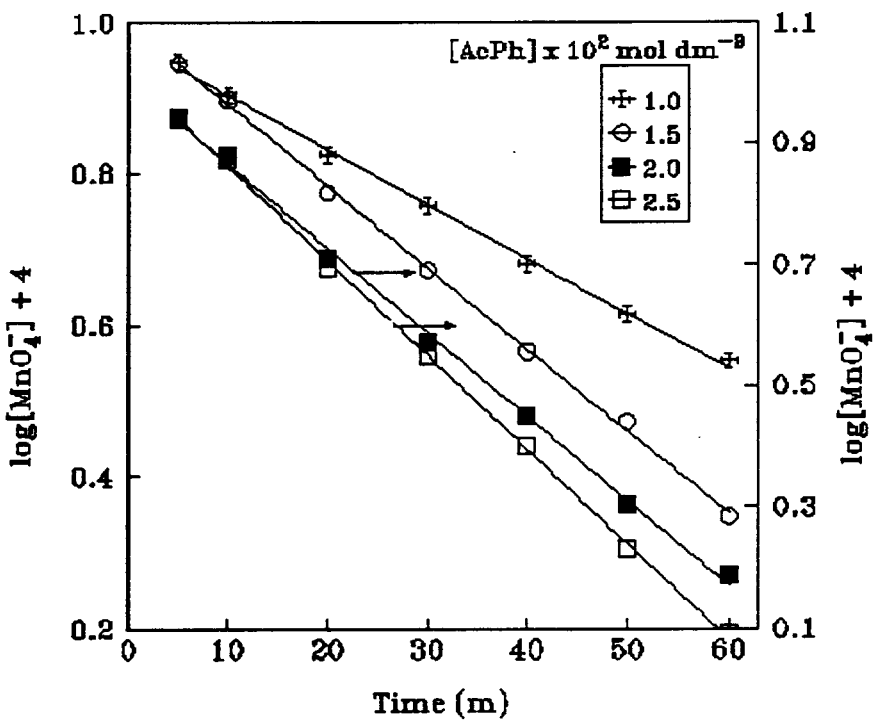


Fig. 4.5.2 (a) Effect of [AcPh] on the oxdn. of AcPh in Benzene (TCMAC)

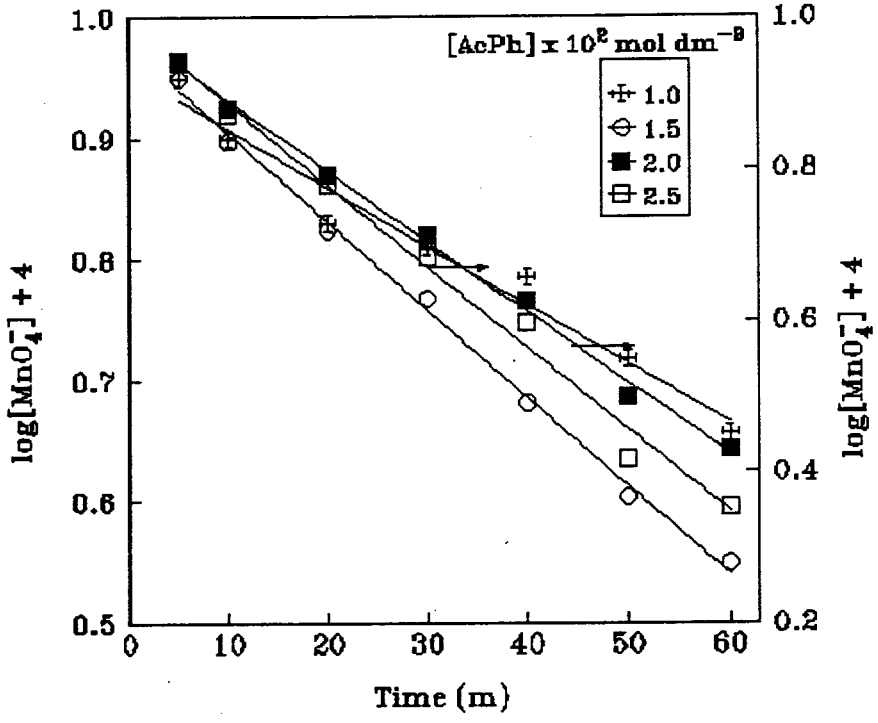


Fig. 4.5.2 (b) Effect of [AcPh] on the oxdn. of AcPh in Benzene (TBAB)

Table 4.5.2 Effect of [AcPh] on the rate of oxdn. of Acph in Organic solvents

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} , Temp. – 303 K , Solvent – Benzene

[AcPh] x 10^2 mol dm^{-3}		1.0	1.5	2.0	2.5
TCMAC	k_{obs} x 10^4 sec^{-1}	2.759	4.133	5.323	5.964
	k_{obs}/[AcPh] x $10^2 dm^3 mol^{-1} sec^{-1}$	2.759	2.755	2.662	2.386
	Corr. Coeff.	0.9991	0.9995	0.9989	0.9997
TBAB	k_{obs} x 10^4 sec^{-1}	1.850	2.790	3.573	4.118
	k_{obs}/[AcPh] x 10^2 $dm^3 mol^{-1} sec^{-1}$	1.850	1.860	1.787	1.647
	Corr. Coeff.	0.9848	0.9984	0.9981	0.9948

The second order rate constants (k_2) obtained are found to be identical, which indicates the first order dependence with respect of AcPh (Table 4.5.2). More over the plot of $logk_{obs}$ vs log [AcPh] (Fig. 4.5.3) were linear with almost unit slope confirming that the order with respect to AcPh is one.

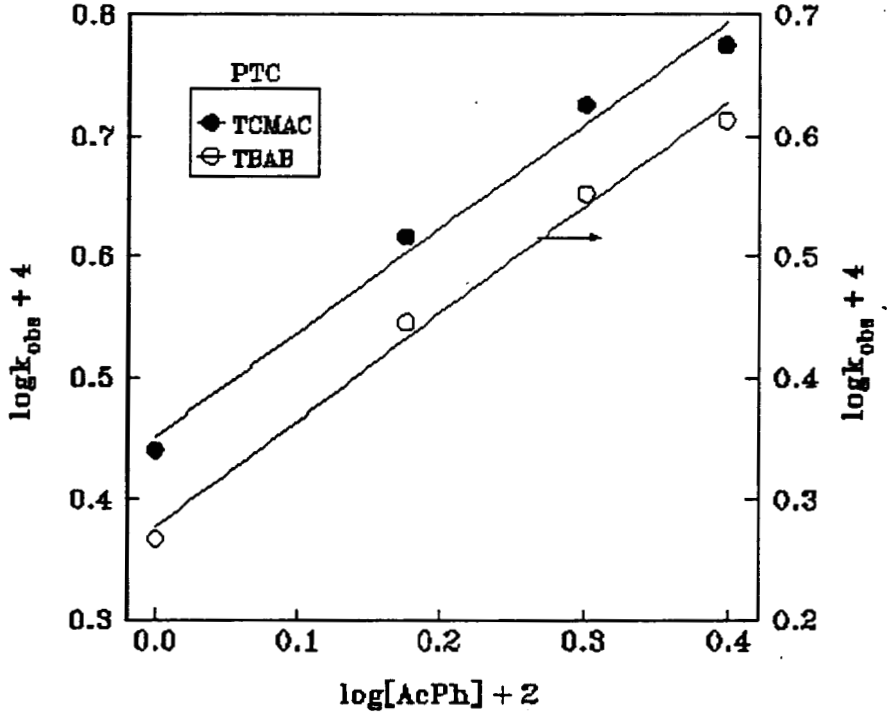


Fig. 4.5.3 Order with respect to Acetophenone

Thus the reaction orders of both the quaternary ammonium permanganate ion pairs and acetophenone for the oxidation of acetophenone in the benzene solvent were found to be equal to one using both the catalysts.

Effect of [PTC] on the rate of oxidation of AcPh in Organic Solvents

The effect of [PTC] was studied using the two quaternary ammonium salts *viz.*TCMAC and TBAB. The rate constant of the reaction was found to be dependent on the concentration of the catalyst (Table 4.5.3, Fig. 4.5.4 (a) & (b)).

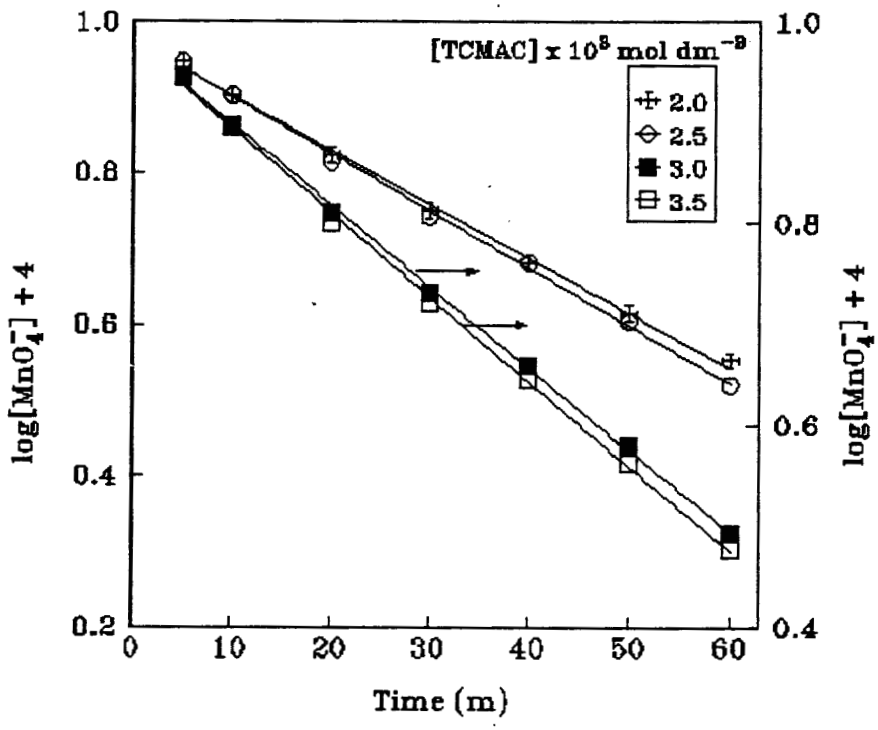


Fig. 4.5.4 (a) Effect of [TCMAC] on the oxdn. of AcPh in Benzene

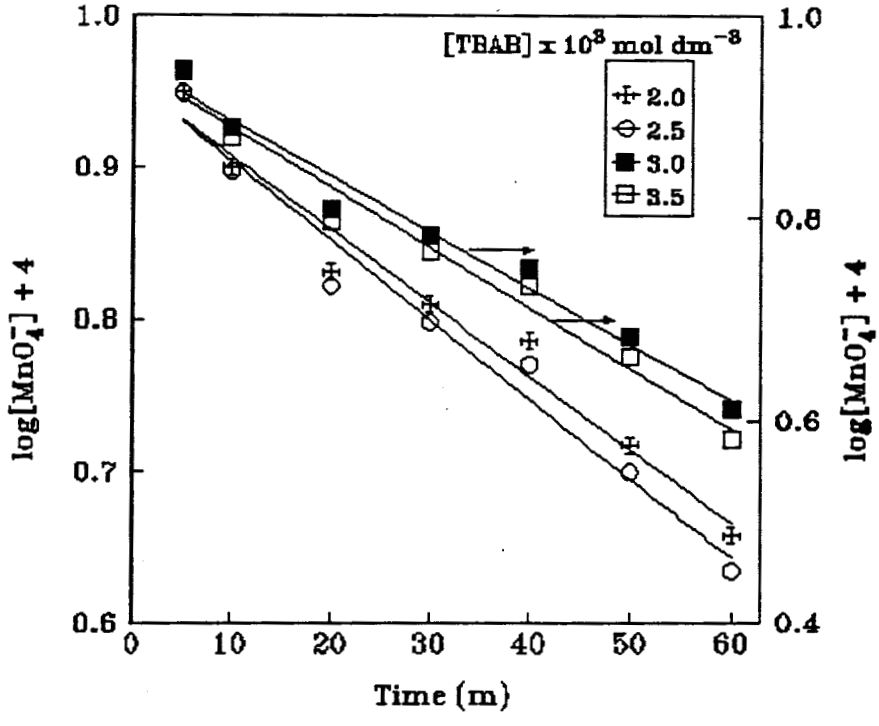


Fig. 4.5.4 (b) Effect of [TBAB] on the oxdn. of AcPh in Benzene

Table 4.5.3 Effect of [PTC] on the oxdn. of AcPh in Organic solvent

Solvent – Benzene Temp. – 303 K

[PTC] x 10^3 mol dm^{-3}	TCMAC		TBAB	
	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.
2.0	2.755	0.9988	1.850	0.9848
2.5	2.909	0.9989	2.003	0.9861
3.0	3.101	0.9994	2.118	0.9859
3.5	3.216	0.9995	2.279	0.9854

A plot of log k_{obs} vs log [PTC] (Fig. 4.5.5) was linear with a fractional order dependence.

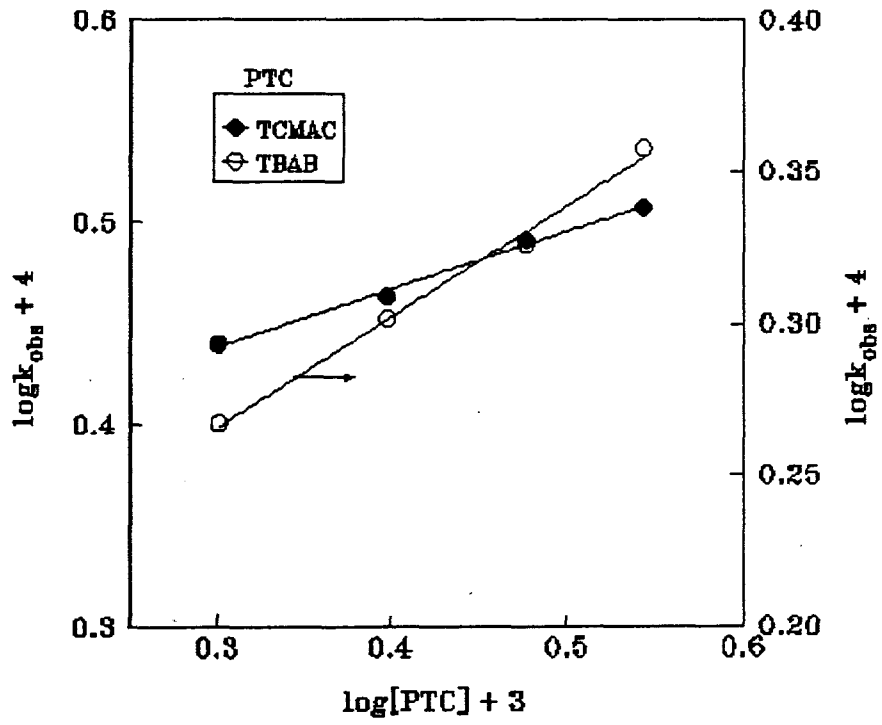


Fig. 4.5.5 Order with respect to PTC

This project has also tried to focus the effect of catalyst structure on the rate of oxidation. The rate constants obtained (Table 4.5.3) shows the influence of the structure of the quaternary ammonium cation on the rate constant. TCMAC, $(C_{10}H_{21})_3 N^+CH_3 Cl^-$ has been found to be a better catalyst than TBAB, $(C_4H_9)_4 N^+ Br^-$. This may be due to the greater organophilicity of TCMAC compared to TBAB.

Effect of Solvent Polarity

Changes in the organic solvents had some pronounced effects on the rate constants as indicated in the Table 4.5.4 and Fig. 4.5.6 (a) & (b). The rate constants obtained were in the order benzene > toluene > carbontetrachloride > dichloromethylene > chloroform. The lower rate of oxidation in polar solvents may be because the active oxidizing species, MnO_4^- in $Q^+MnO_4^-$ ion pair is more strongly solvated through the ion dipole interaction in a polar solvent. However, the rate of rection in chloroform and dichloromethane were found to be in the reverse order.

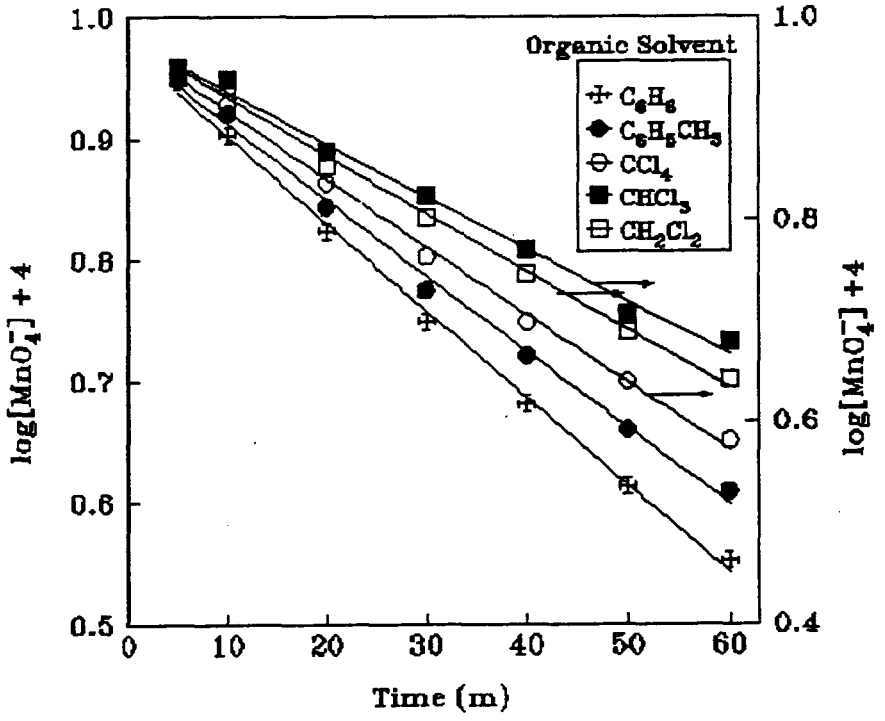


Fig. 4.5.6 (a) Effect of Solvent Polarity on the oxdn. of AcPh in Org. solvents (TCMAC)

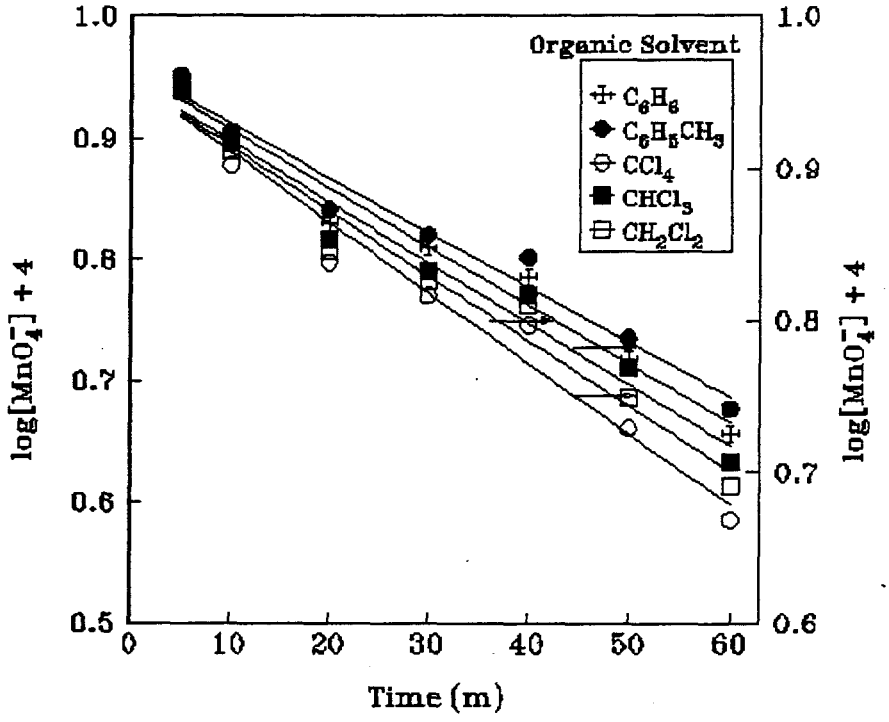


Fig. 4.5.6 (b) Effect of Solvent Polarity on the oxdn. of AcPh in Org. solvents (TBAB)

Table 4.5.4 Effect of Solvent Polarity on the oxdn. of AcPh in Organic solvents

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, [AcPh] = 1.0×10^{-2} mol dm^{-3}, Temp. – 303 K

Organic Solvent	Intrinsic Dielectric Constant	TCMAC		TBAB	
		$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
Benzene	2.27	2.755	0.9988	1.850	0.9848
Toluene	2.40	2.406	0.9980	1.731	0.9835
Carbontetrachloride	2.22	2.575	0.9987	1.784	0.9834
Chloroform	4.70	1.992	0.9965	1.539	0.9831
Dichloromethane	8.90	2.203	0.9982	1.638	0.9823

Effect of Substituents on the oxdn of AcPh in Organic solvents

It was found that PTC did not affect the general order of reactivities *ie.* Slow reactions still remained slow (Table 4.5.5 and Fig. 4.5.7 (a) & (b)).

The rate constants obtained for the oxidation of various substituted acetophenones are found to be in the order to be *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > Acph > *p*-CH_3 > *p*-OCH_3 (Table 4.5.5). The log k_2 values for the various substituted acetophenones were found to correlate well (Fig. 4.5.8) with the Hammett's σ values and a reaction constant of + 0.8451 and + 0.9208 were obtained for the TCMAC and TBAB respectively. The positive values indicates that the electron withdrawing groups accelerate the process.

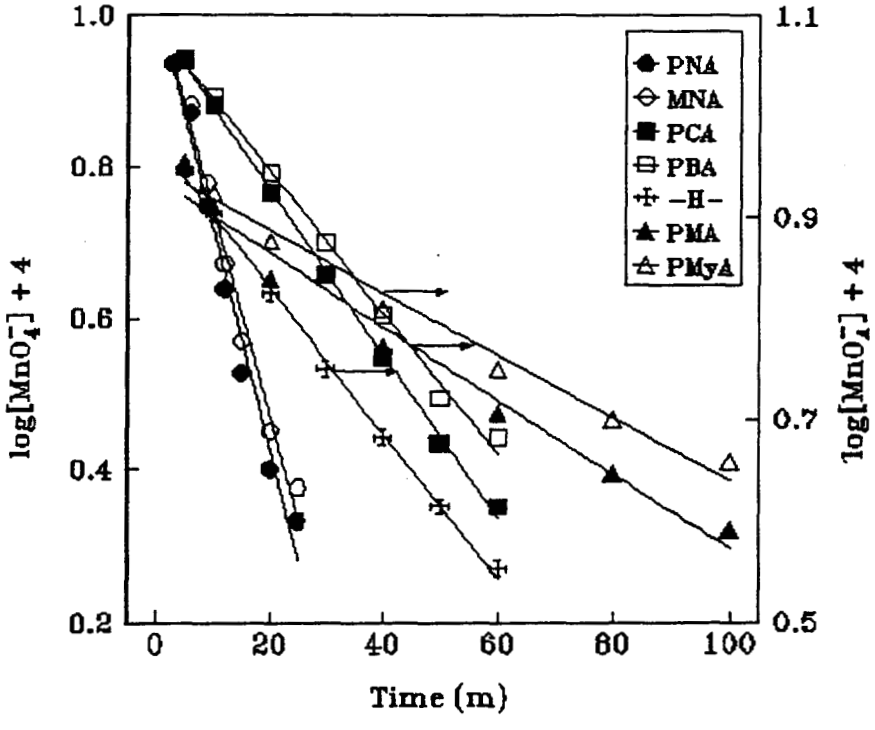


Fig. 4.5.7 (a) Effect of Substituents on the oxdn. of AcPh in Benzene (TCMAC)

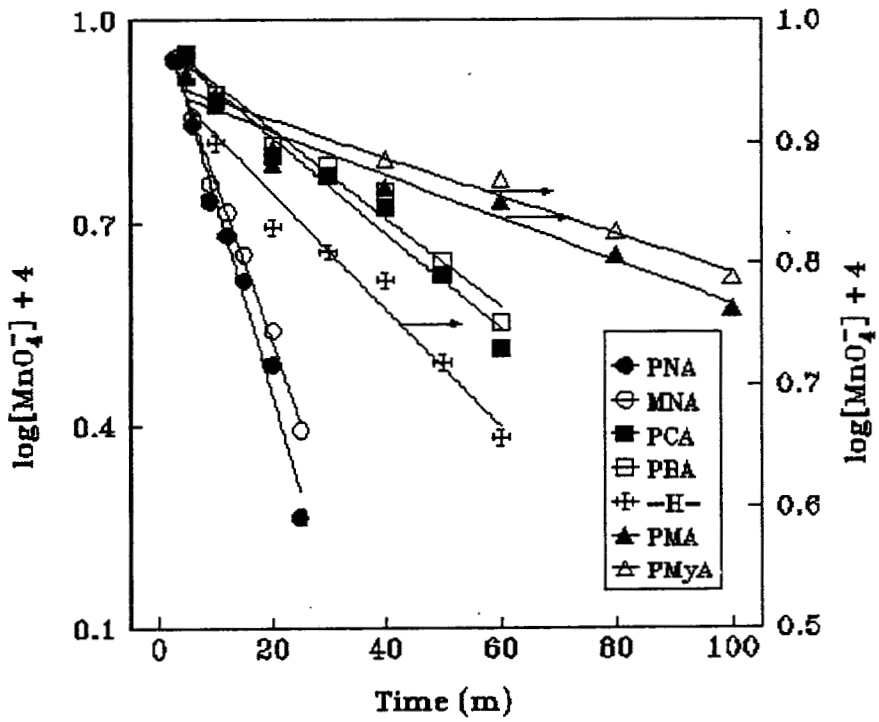


Fig. 4.5.7 (b) Effect of Substituents on the oxdn. of AcPh in Benzene (TBAB)

Table 4.5.5 Effect of Substituents on the oxdn. of Acph in Organic solvents

$[Q^+MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}
[Substrate] = 1.0 x 10^{-2} mol dm^{-3}

Solvent - Benzene
Temp. – 303 K

Substrate	TCMAC		TBAB	
	k_{obs} x 10^4 s^{-1}	Corr. Coeff.	k_{obs} x 10^4 s^{-1}	Corr. Coeff.
PNA	11.215	0.9884	11.062	0.9922
MNA	10.432	0.9915	9.181	0.9966
PCA	4.153	0.9993	2.729	0.9851
PBA	3.703	0.9974	2.533	0.9855
AcPh	2.755	0.9988	1.850	0.9848
PMA	1.400	0.9878	.6870	0.9751
PMyA	1.182	0.9909	.6060	0.9763

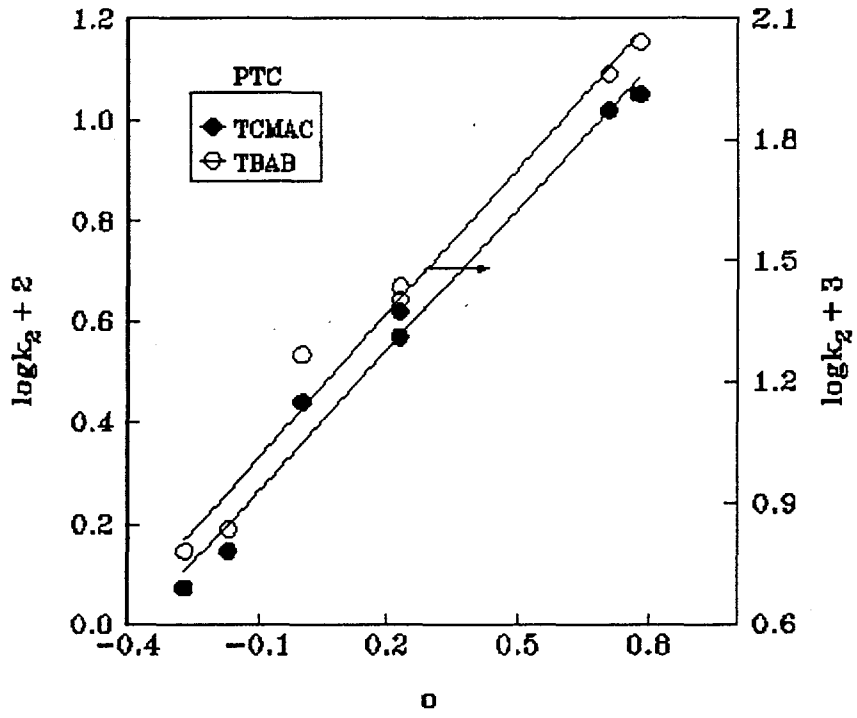


Fig. 4.5.8 Hammett plot for the oxdn. of AcPh in Benzene

Effect of Temp. on the oxdn. of AcPh in Organic solvent

The temperature co-efficient of AcPh and some of its derivatives were determined in the temperature range of 303-313 K (Table 4.5.6 –Table 4.5.12, and Fig. 4.5.9 (a) & (b)) – Fig. 4.5.15 (a) & (b)).

Table 4.5.6 Effect of Temp. on the oxdn. of AcPh in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Solvent – Benzene
[AcPh] = 1.0×10^{-2} mol dm^{-3}, Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	2.755	0.9988	1.850	0.9848
308	3.055	0.9987	2.222	0.9827
313	3.638	0.9959	2.544	0.9841

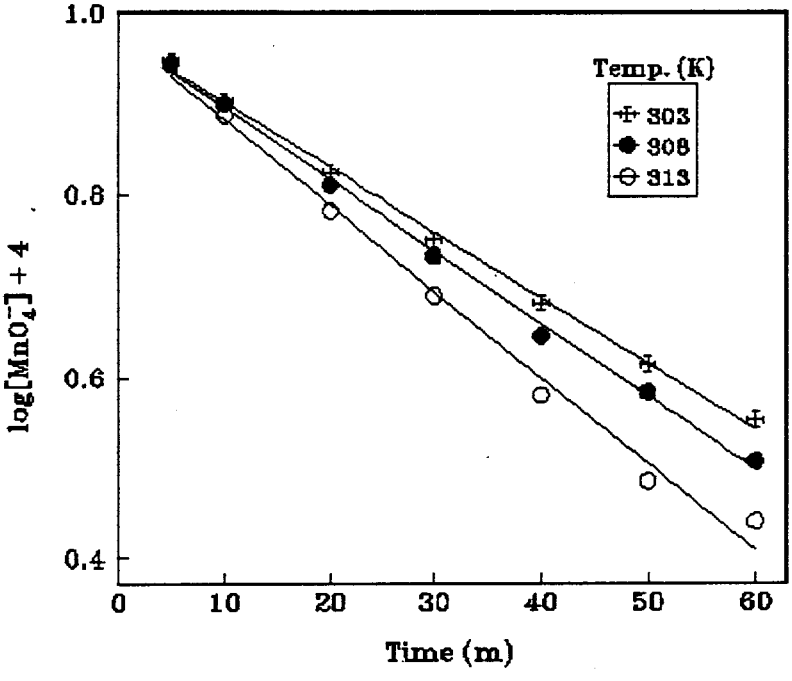


Fig. 4.5.9 (a) Effect of Temp. on the oxdn. of AcPh in Benzene (TCMAC)

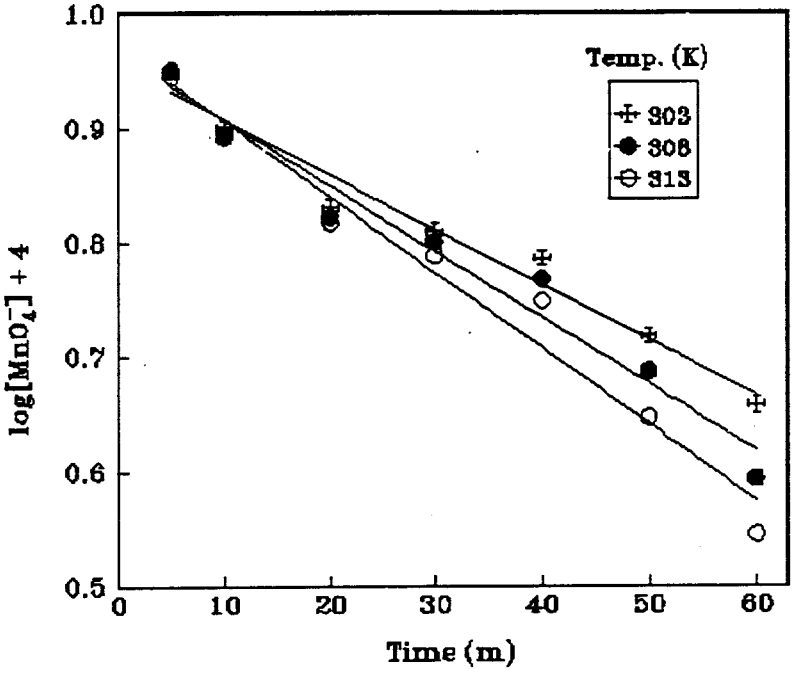


Fig. 4.5.9 (b) Effect of Temp. on the oxdn. of AcPh in Benzene

Table 4.5.7 Effect of Temp. on the oxdn. of PNA in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Solvent – Benzene
[PNA] = 1.0×10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	11.215	0.9884	11.062	0.9922
308	15.720	0.9962	15.210	0.9963
313	17.480	0.9931	16.62	0.9904

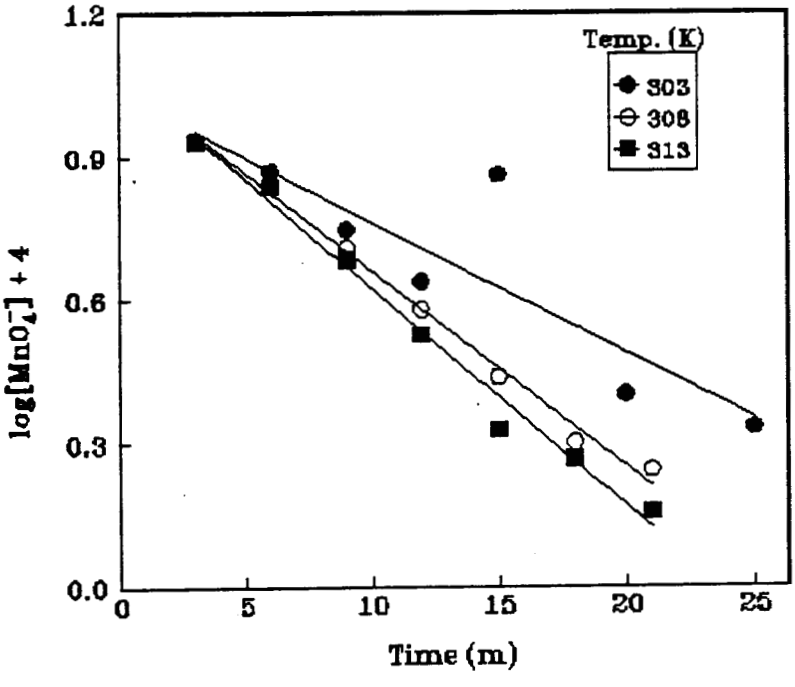


Fig. 4.5.10 (a) Effect of Temp. on the oxdn. of PNA in Benzene (TCMAC)

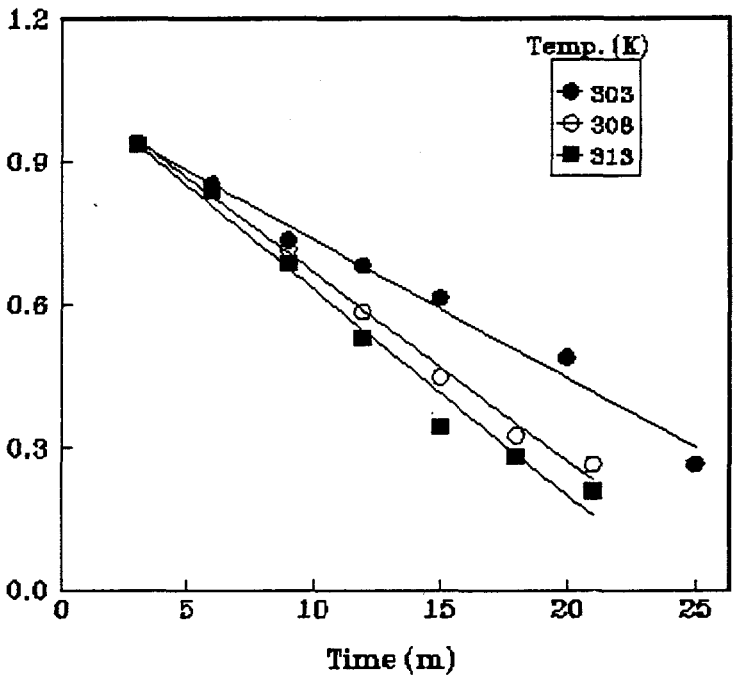


Fig. 4.5.10 (b) Effect of Temp. on the oxdn. of PNA in Benzene (TBAB)

Table 4.5.8 Effect of Temp. on the oxdn. of MNA in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Solvent – Benzene
[MNA] = 1.0×10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	10.432	0.9915	9.181	0.9966
308	13.070	0.9983	11.380	0.9906
313	15.16	0.9969	13.360	0.9919

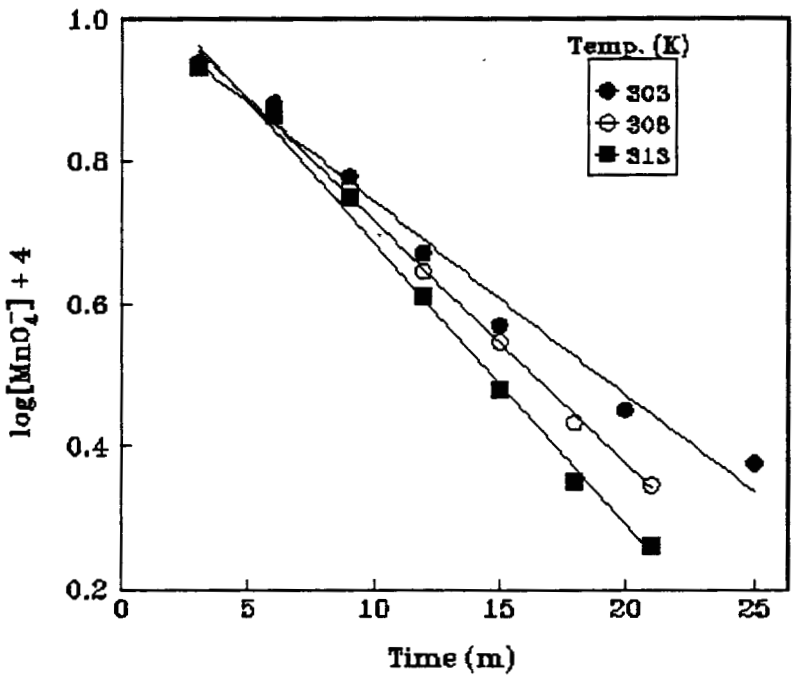


Fig. 4.5.11 (a) Effect of Temp. on the oxdn. of MNA in Benzene (TCMAC)

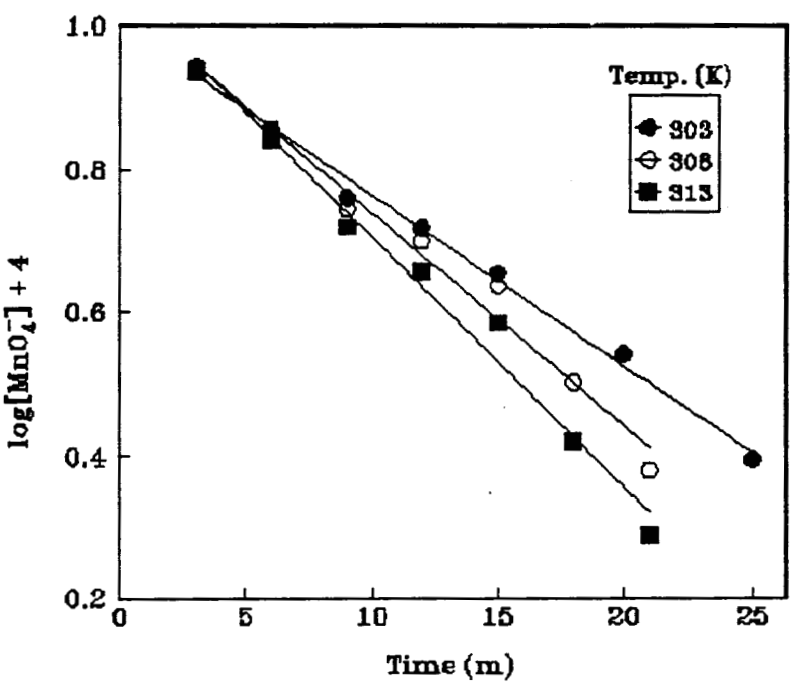


Fig. 4.5.11 (b) Effect of Temp. on the oxdn. of MNA in Benzene (TBAB)

Table 4.5.9 Effect of Temp. on the oxdn. of PCA in Organic solvent

$[Q^+MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Solvent – Benzene
[PCA] = 1.0 x 10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.	k_{obs} x 10^4 sec^{-1}	Corr. Coèff.
303	4.153	0.9993	2.729	0.9851
308	5.392	0.9888	3.700	0.9884
313	6.252	0.9909	3.861	0.9884

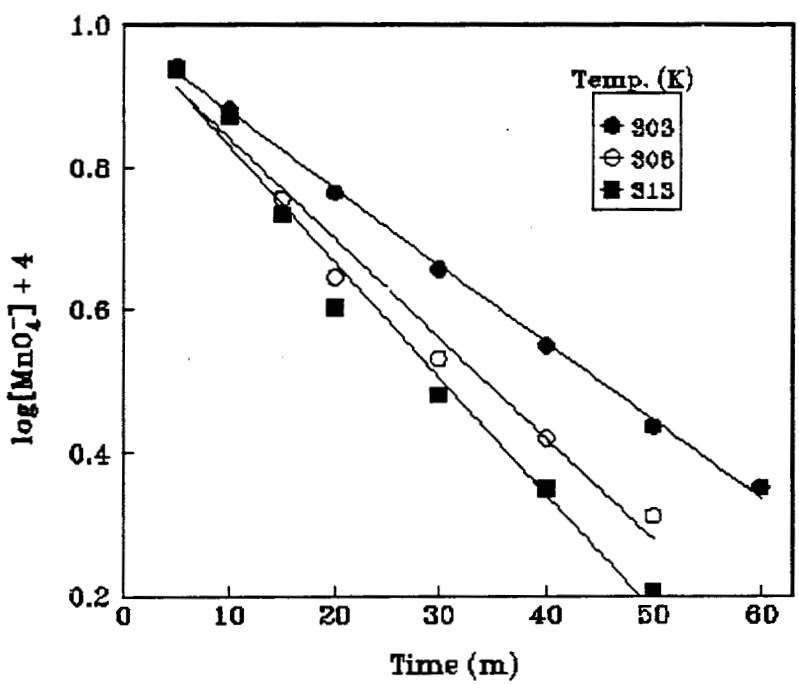


Fig. 4.5.12 (a) Effect of Temp. on the oxdn. of PCA in Benzene (TCMAC)

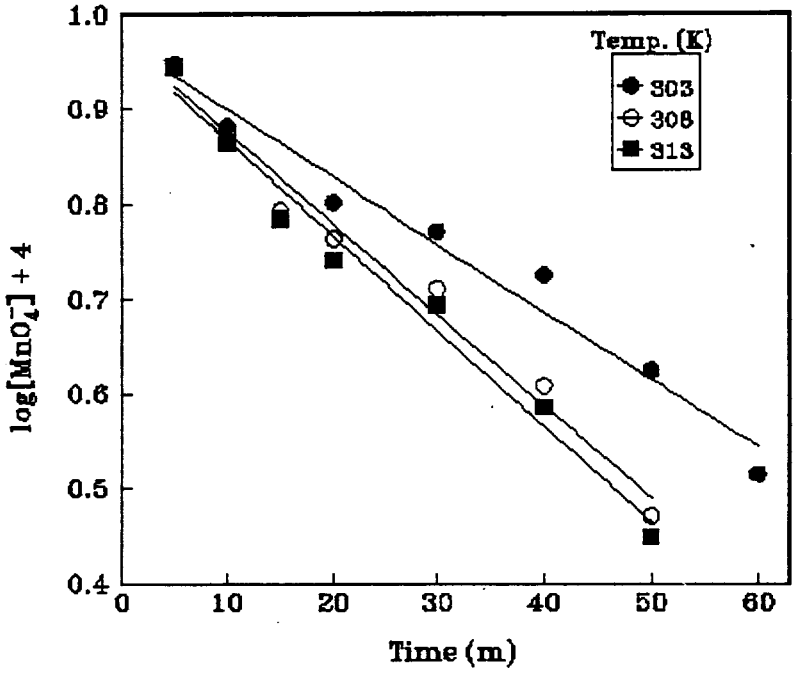


Fig. 4.5.12 (b) Effect of Temp. on the oxdn. of PCA in Benzene (TBAB)

Table 4.5.10 Effect of Temp. on the oxdn. of PBA in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Solvent – Benzene
[PBA] = 1.0×10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	3.703	0.9974	2.533	0.9855
308	4.932	0.9846	3.058	0.9825
313	5.239	0.9888	3.588	0.9838

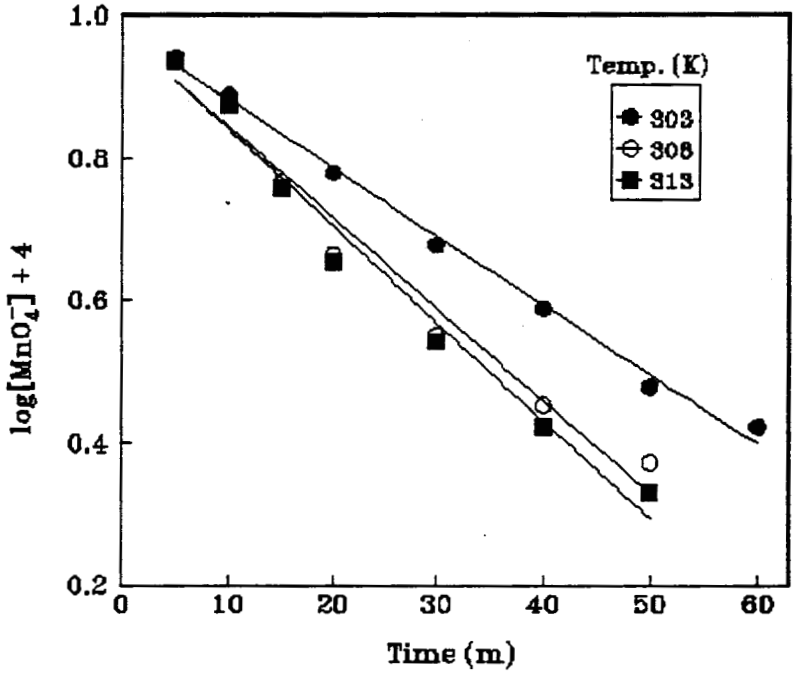


Fig. 4.5.13 (a) Effect of Temp. on the oxdn. of PBA in Benzene

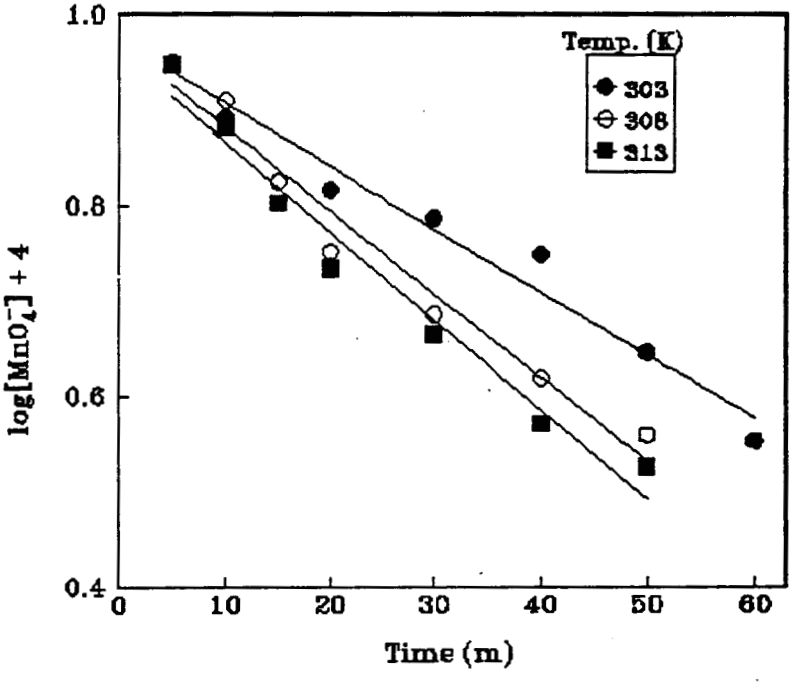


Fig. 4.5.13 (b) Effect of Temp. on the oxdn. of PBA in Benzene (TBAB)

Table 4.5.11 Effect of Temp. on the oxdn. of PMA in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Solvent – Benzene
[PMA] = 1.0×10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	1.400	0.9878	0.6870	0.9751
308	1.800	0.9843	1.017	0.9655
313	1.907	0.9832	1.090	0.9716

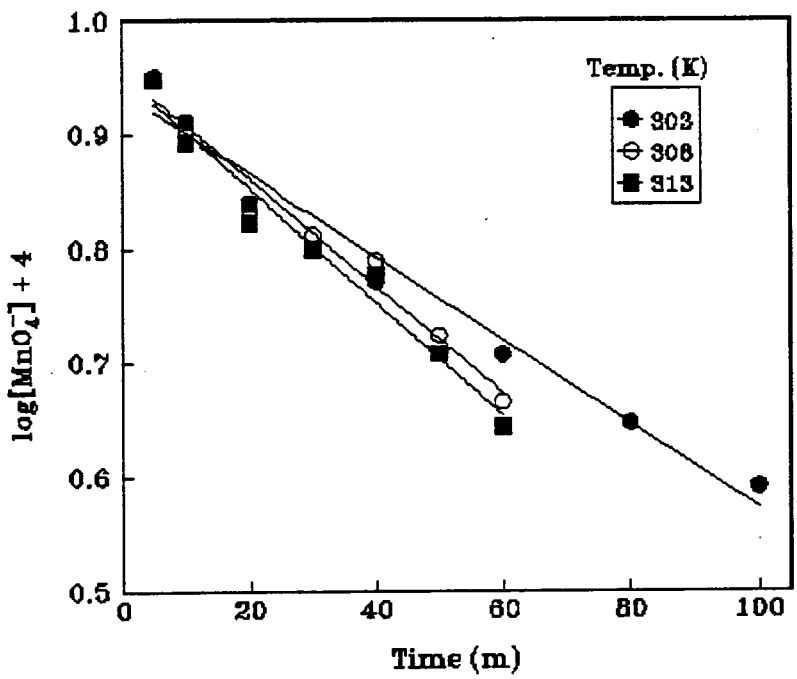


Fig. 4.5.14 (a) Effect of Temp. on the oxdn. of PMA in Benzene (TCMAC)

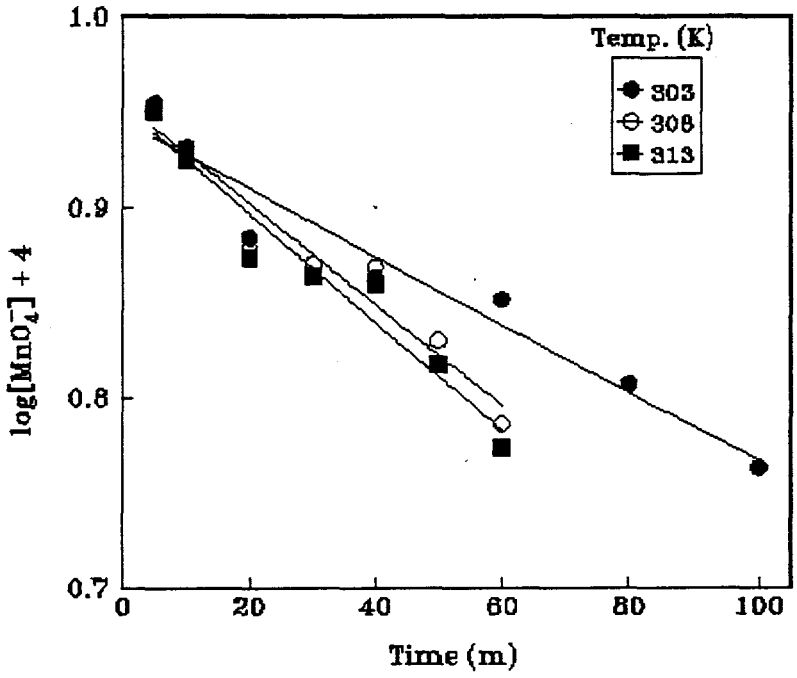


Fig. 4.5.14 (b) Effect of Temp. on the oxdn. of PMA in Benzene (TBAB)

Table 4.5.12 Effect of Temp. on the oxdn. of PMyA in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Solvent – Benzene
[PMyA] = 1.0×10^{-2} mol dm^{-3} Temp. – 303 K

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	1.182	0.9909	0.6060	0.9763
308	1.462	0.9959	0.8820	0.9737
313	1.658	0.9969	.9940	0.9786

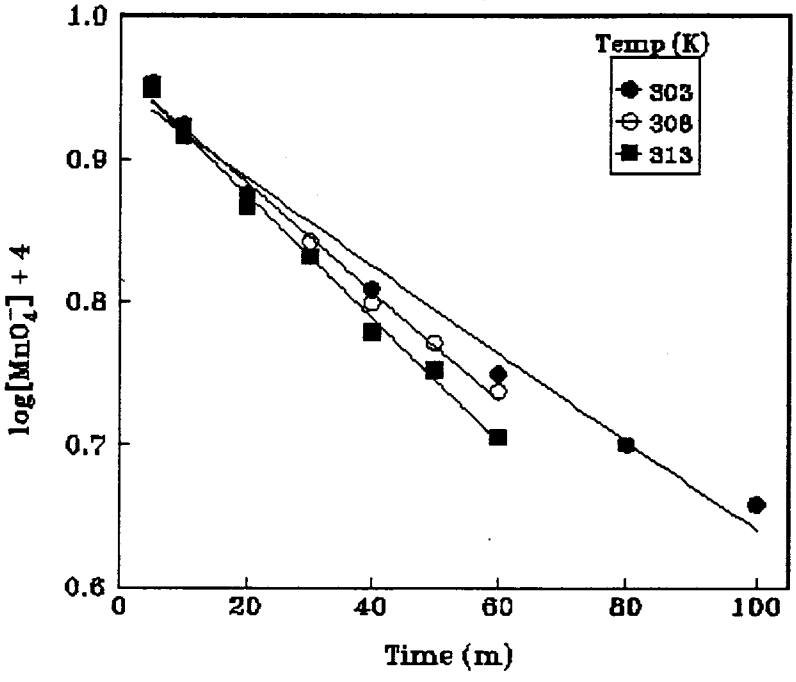


Fig. 4.5.15 (a) Effect of Temp. on the oxdn. of PMyA in Benzene (TCMAC)

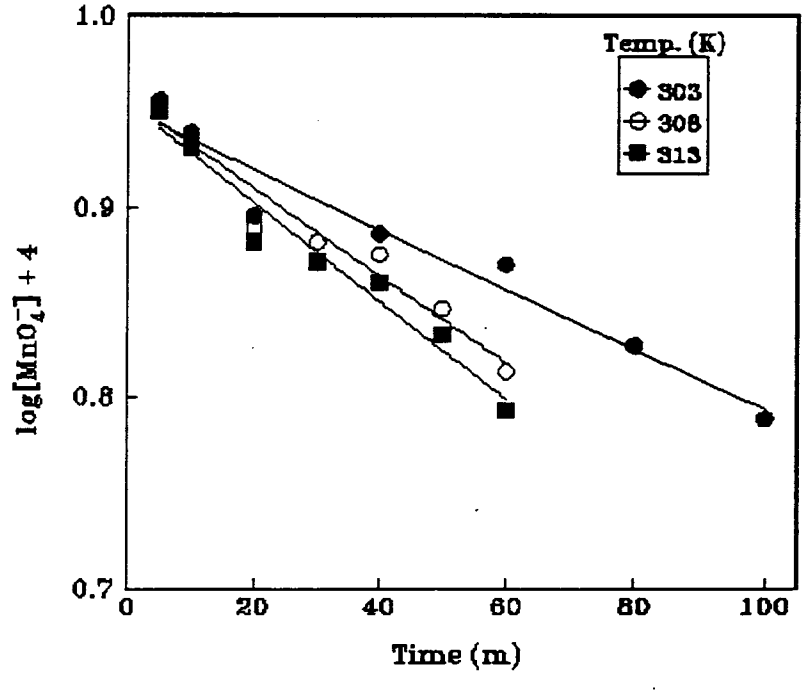


Fig. 4.5.15 (b) Effect of Temp. on the oxdn. of PMyA in Benzene (TBAB)

The values of various thermodynamic parameters calculated from the plot of log k_2 vs 1/T (Fig. 4.5.16 (a) & (b)) and from the plot of log k_2/T vs 1/T (Fig. 4.5.17 (a) & (b)) are given in the Table 4.5.13. A constancy in the free energy of activation, $\Delta G^{\#}$ in all the acetophenones studied suggests operation of similar mechanism in all the cases. This is further confirmed by the linear plot of $\Delta H^{\#}$ vs $\Delta S^{\#}$ (Fig. 4.5.18).

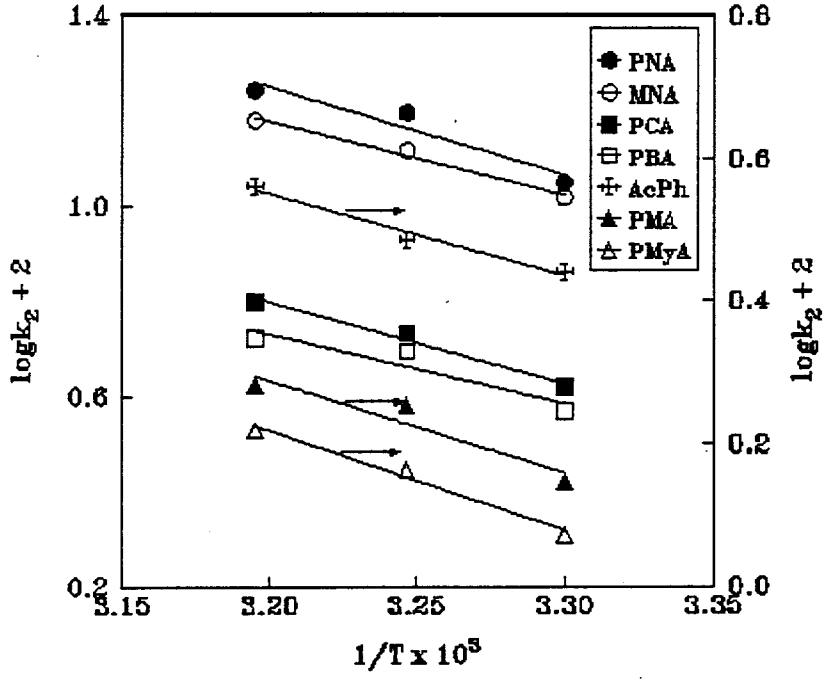


Fig. 4.5.16 (a) Plot of log k_2 vs 1/T for the oxdn. of AcPh in Benzene (TCMAC)

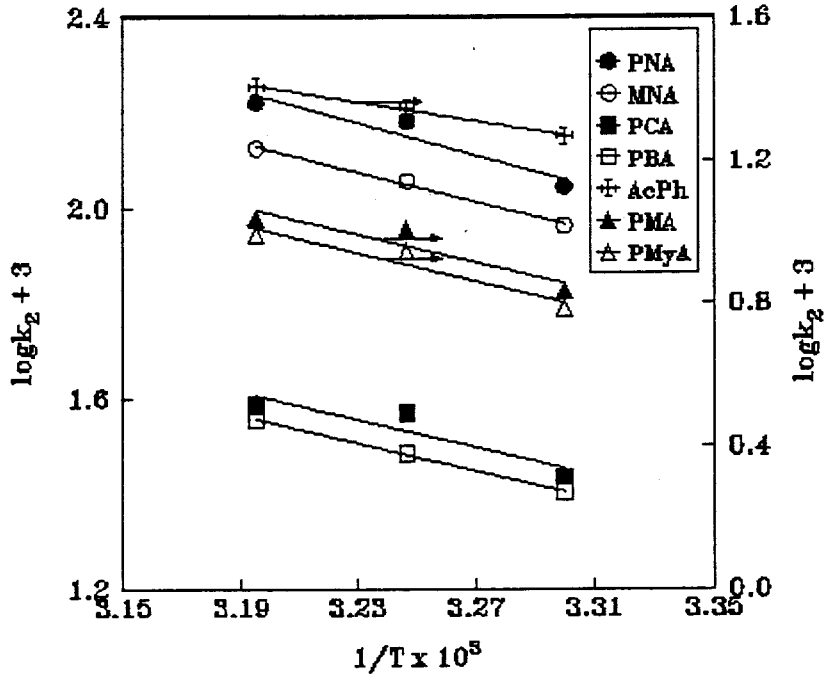


Fig. 4.5.16 (b) Plot of log k_2 vs 1/T for the oxdn. of AcPh in Benzene (TBAB)

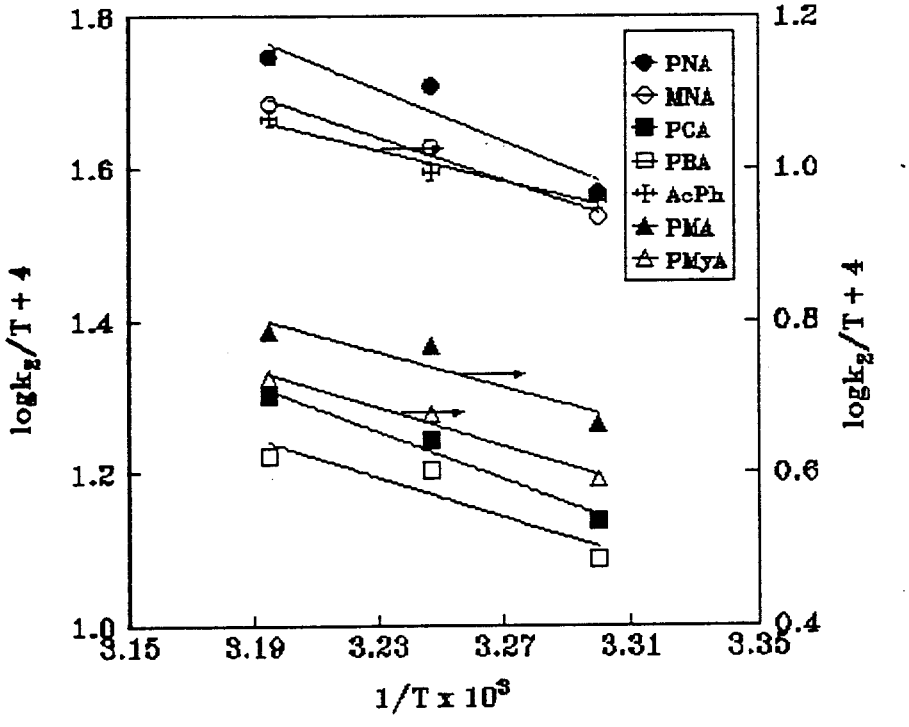


Fig. 4.5.17 (a) Plot of log k_2/T vs 1/T for the oxdn. of AcPh in Benzene (TCMAC)

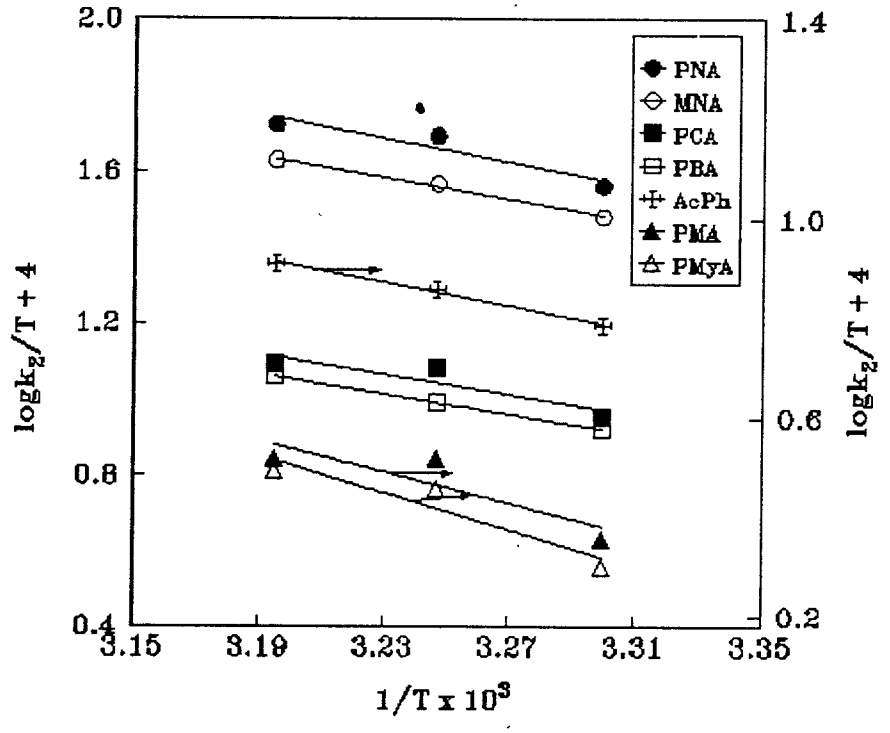


Fig. 4.5.17 (b) Plot of log k_2/T vs 1/T for the oxdn. of AcPh in Benzene (TBAB)

Table 4.5.13 (a) Activation Parameters for the oxdn. of AcPh and its substituents in Organic solvents

Solvent - Benzene PTC - TCMAC

Substrate	k_{obs} x 10^4 sec^{-1}	E_a KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
PNA	11.215	32.25	32.62	146.49	79.64
MNA	10.432	29.56	27.01	166.13	79.70
PCA	4.153	32.41	29.84	164.14	82.14
PBA	3.703	27.52	24.86	181.22	82.43
AcPh	2.755	22.01	19.42	201.83	83.16
PMA	1.400	24.54	21.95	199.15	84.88
PmyA	1.182	26.83	24.24	192.99	85.31

Table 4.5.13 (b) Activation Parameters for the oxdn. of AcPh and its substituents in Organic solvents

Solvent - Benzene PTC - TBAB

Substrate	$k_{obs} \times 10^4$ sec^{-1}	E_a KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
PNA	11.062	32.33	29.78	157.20	79.96
MNA	9.181	29.75	27.19	166.30	80.13
PCA	2.729	27.54	24.94	183.69	83.19
PBA	2.533	27.58	24.90	184.17	83.38
AcPh	1.850	25.23	22.68	194.55	84.17
PMA	.6870	37.37	30.12	162.72	86.67
PmyA	.6060	38.03	35.46	160.78	86.74

4.5.3 Mechanism of the oxidation of Acph using Quaternary ammonium permanganate

Sequential scans obtained during the oxidation of acetophenone by $Q^+MnO_4^-$ in benzene at 303 K are shown in the Fig. 4.5.17.

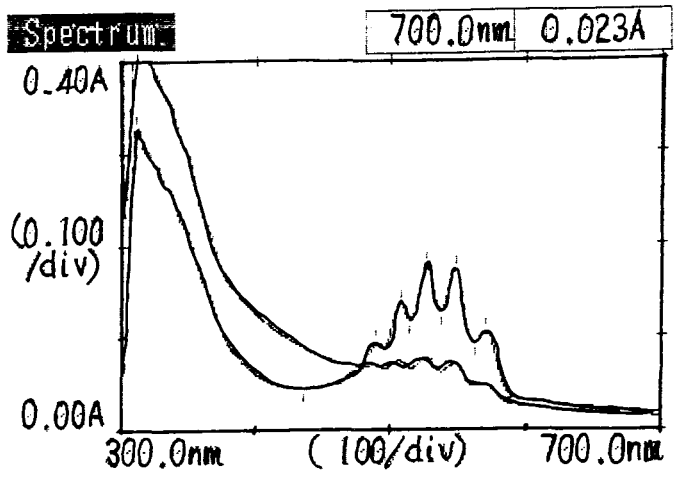
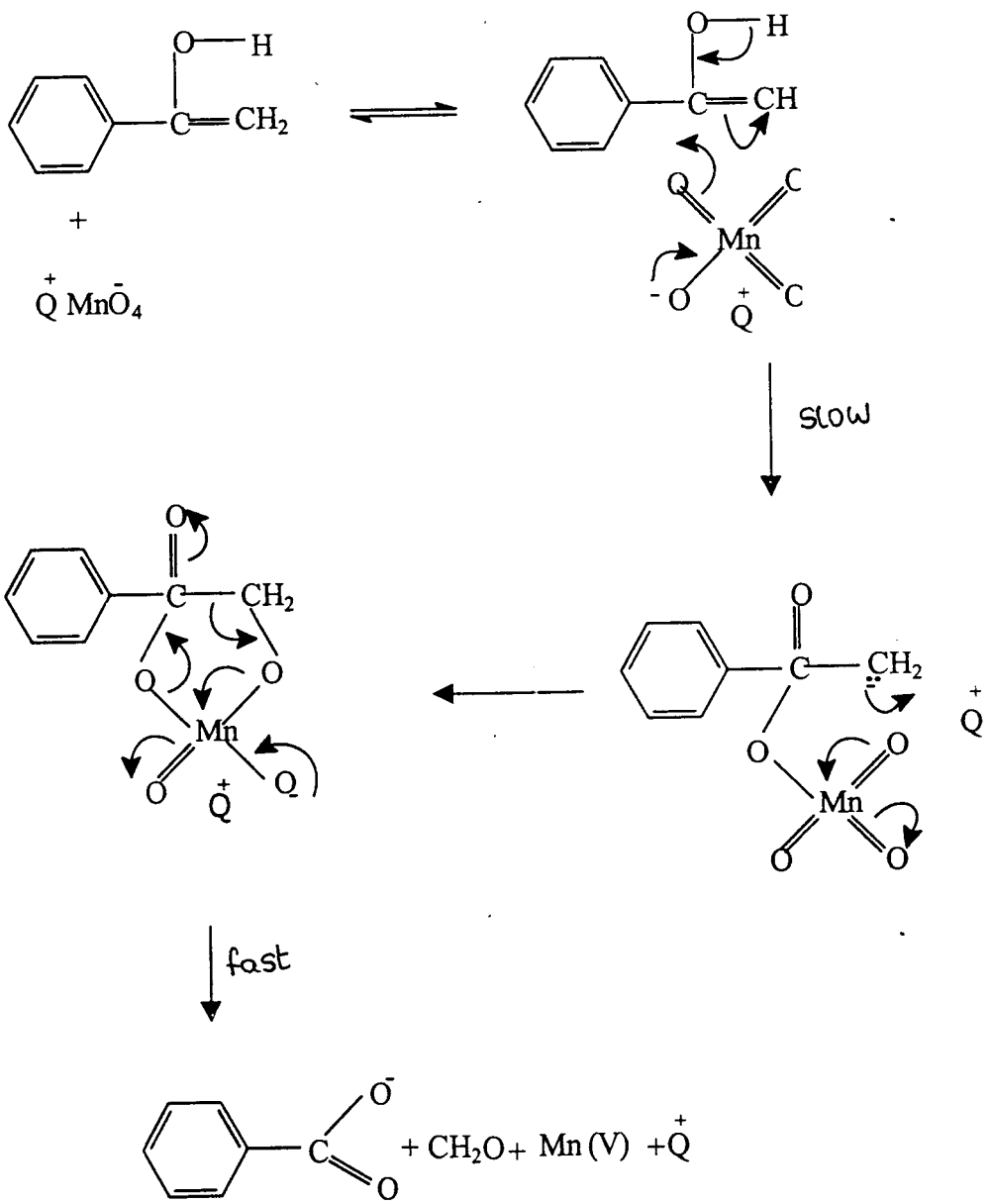


Fig. 4.5.11 Successive UV – Vis characteristic spectra for the oxdn. of AcPh in Benzene using TCMAC (Scan interval – 20 minutes)

The isobestic points at only 494 nm suggests that the reaction does not involve a complicated sequence of events.

The effects such as effect of substrate, oxidant, substituents are almost same for the oxidation of acetophenone in aqueous acetic acid medium (section 4.1) and in organic solvents with PTC. Hence a similar type of mechanism is suggested .



Scheme 3

The emergence of a peak at 474 nm during the oxidation process corresponds to the peak characteristic of Mn (III). MnO_2^- *ie.* Mn (V) is found to be the reduced form of manganese. The collodial MnO_2 obtained after keeping the reaction mixture for some hours, is the result of the following disproportional.

$$\text{Mn (V)} \longrightarrow \text{Mn (IV)} + \text{Mn (III)}$$

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

The mechanism suggested involves a negatively charged transition state. The greater activity in polar solvents can be easily explained with this mechanism. The proximity of the quaternary ammonium ion increases the stability of the transition state in non-polar solvents, which is less pronounced in more polar solvents due to greater separation of both the ion by solvation of the cation.

The rate law is therefore

$$\frac{d[\bar{MnO}_4]}{dt} = k_2 \left[C_6H_5 - \underset{\displaystyle OH}{\underset{|}{C}} = CH_2 \right]^a \left[\bar{Q}^+ \bar{MnO}_4 \right]^b$$

Where a and b are the order of $C_6H_5COCH_3$ and Quaternary ammonium permangante ion-pair in the organic solvent. The values of a and b are obtained to be unity.

The kinetic investigation carried out thus for the oxidation of AcPh using potassium permanganate in the presence of PTC can be shown to proceed as per the following steps.

During extraction, the quaternary cation replaces its anion with the permanganate ion in the aqueous phase,

$$Q^+X^-_{(aq)} + KMnO_{4\,(aq)} \longrightarrow Q^+MnO_4^-{}_{(aq)} + K^+X^-_{(aq)}$$

which is transferred into the organic layer in the form of ion-pairs.

$$Q^+MnO_4^-{}_{(aq)} \rightleftharpoons Q^+MnO_4^-{}_{(org)}$$

This phase transferred permanganate ion in the organic solvent containing the substrate (acetophenone) helps the oxidation in the organic phase.

$$Q^+MnO_4^-{}_{(org)} + C_6H_5COCH_{3\,(org)} \xrightarrow{k_2} C_6H_5COOH_{(org)}$$

4.6 OXIDATION OF BENZALDEHYDE USING QUATERNARY AMMONIUM PERMANGANATE

The oxidation of Benzaldehyde and some of its derivatives were carried out in the same way as that of Acetophenone (see section 4.5) and the results obtained are presented in this section.

4.6.1 Stoichiometry and Product Analysis

Stoichiometry and product analysis of the oxidation of PhCHO with quaternary ammonium permanganate was found to be almost same to that calculated in aqueous acetic acid medium. [PhCHO] : $[Q^+MnO_4^-]$ = 2:3 and the product obtained was carboxylic acid which was identified as benzoic acid.

4.6.2 Kinetic Studies

The kinetic profile of this reaction has also been investigated to find out the effect of the following variables for the oxidation of benzaldehyde using quaternary ammonium permanganate. 1) the concentration of the oxidant 2) the concentration of the substrate 3) the structure and concentration of the phase transfer catalyst 4) solvent polarity 5) substituents and 6) temperature.

In all the experiments the catalyst concentration was double the concentration of the permanganate ion unless otherwise mentioned. The dependence of the rate on the $[Q^+MnO_4^-]$ and [PhCHO] was investigated using benzene as solvent and TCMAC and TBAB as phase transfer catalysts.

Effect of $[Q^+MnO_4^-]$ on the rate of oxidation

Under the conditions of $[Q^+MnO_4^-] << [PhCHO]$, the plot of log $[MnO_4^-]$ vs time were linear (Fig. 4.6.1(a) & (b)) indicating that the order in $[Q^+MnO_4^-]$ to be unity.

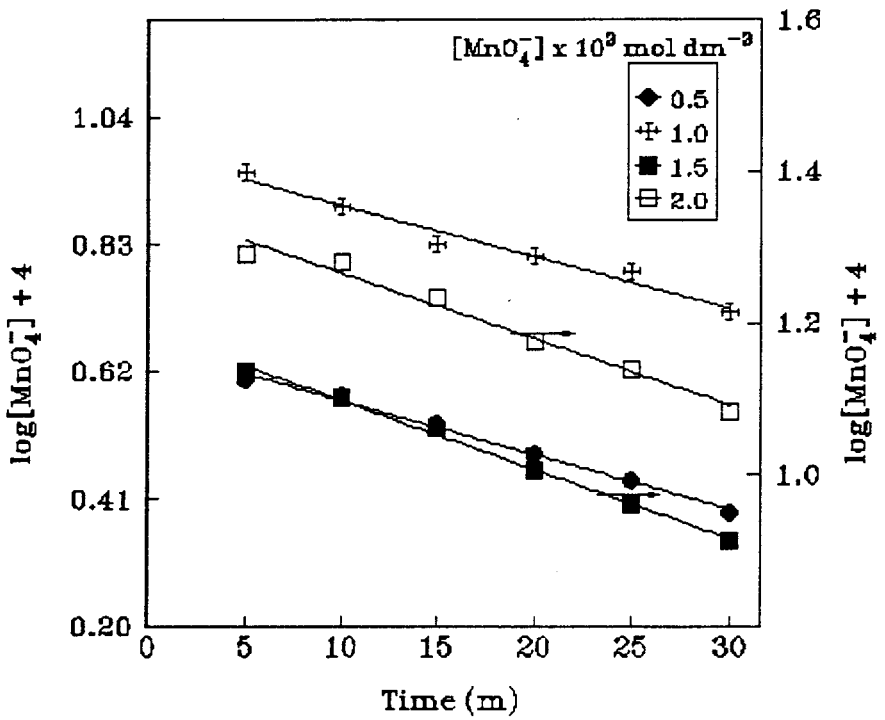


Fig. 4.6.1 (a) Effect of $[Q^+MnO_4^-]$ on the oxdn. of PhCHO in Benzene (TCMAC)

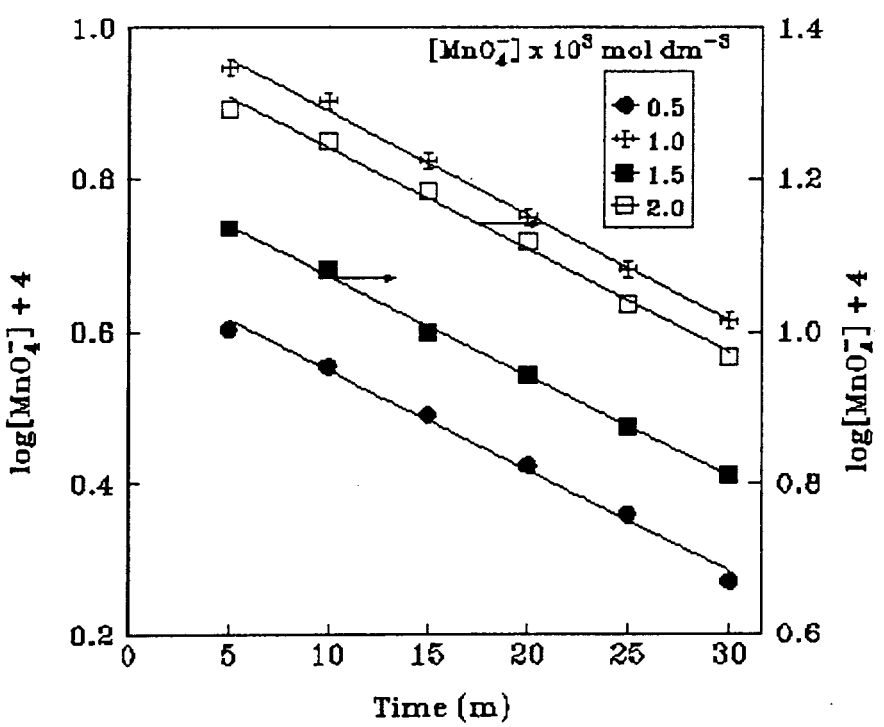


Fig. 4.6.1 (b) Effect of $[Q^+MnO_4^-]$ on the oxdn. of PhCHO in Benzene (TBAB)

Moreover the pseudo-first order rate constants calculated did not show any changes by varying the concentration of $Q^+MnO_4^-$ (Table 4.6.1), which once again supports the first order dependence of the permanganate ion.

Table 4.6.1 Effect of $[Q^+MnO_4^-]$ on the oxdn. of PhCHO in organic solvents

Solvent – Benzene Temp. – 303 K

$[Q^+MnO_4^-] \times 10^3$ mol dm^{-3}	TCMAC		TBAB	
	$k_{obs} \times 10^3$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
0.5	5.079	0.9964	3.393	0.9967
1.0	5.289	0.9981	3.343	0.9850
1.5	5.039	0.9989	3.469	0.9983
2.0	5.135	0.9961	3.354	0.9895

Effect of [PhCHO] on the oxdn. of PhCHO in organic solvents

The rate constants of PhCHO increased from 5.289 to 11.177 sec^{-1} for TCMAC, from 3.343 to 7.730 s^{-1} for TBAB, when the concentration of PhCHO was increased from 1.0 – 2.5 x 10^{-2} mol dm^{-3}, keeping all the other conditions the same (Fig. 4.6.2 (a) & (b) and Table 4.6.2)

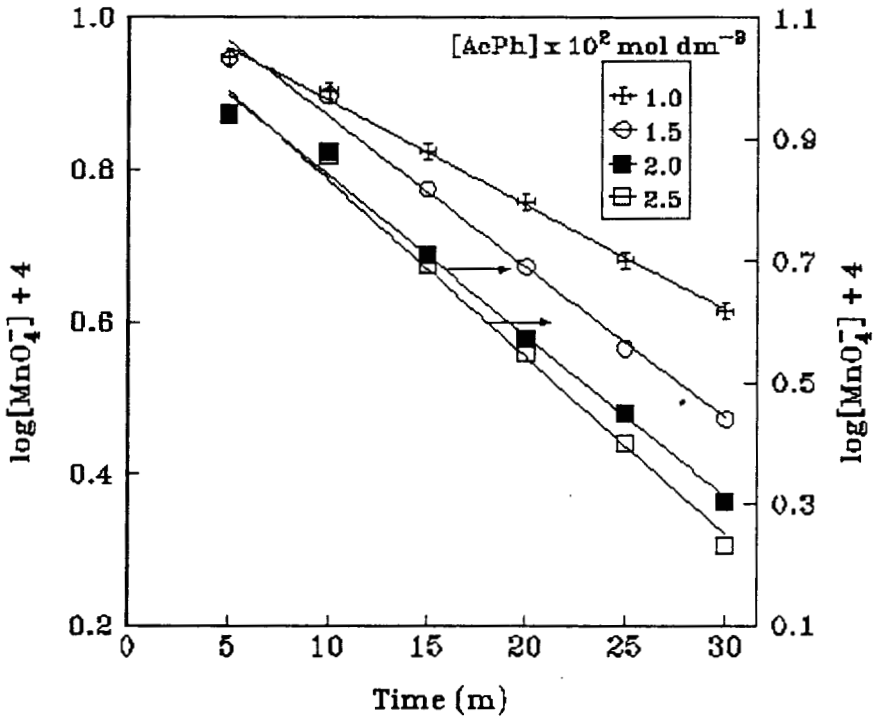


Fig. 4.6.2 (a) Effect of [PhCHO] on the oxdn. of PhCHO in Benzene (TCMAC)

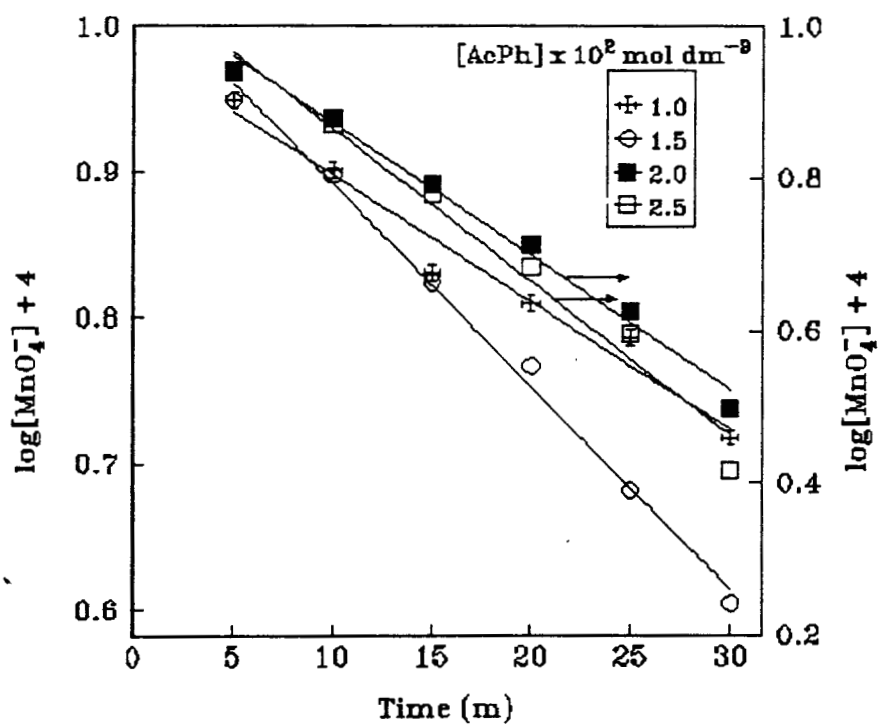


Fig. 4.6.2 (b) Effect of [PhCHO] on the oxdn. of PhCHO in Benzene (TBAB)

Table 4.6.2 Effect of [PhCHO] on the rate of oxdn. of PhCHO in Org. solvents

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} , Temp. – 303 K , Solvent – Benzene

[PhCHO] x 10^2 mol dm^{-3}		1.0	1.5	2.0	2.5
TCMAC	k_{obs} x 10^4 s^{-1}	5.289	7.588	10.150	11.177
	k_{obs}/[PhCHO] x 10^2 dm^3 mol^{-1} s^{-1}	5.289	5.058	5.075	4.470
	Corr. Coeff.	0.9981	0.9962	0.9961	0.9954
TBAB	k_{obs} x 10^4 sec^{-1}	3.343	5.335	6.724	7.730
	k_{obs}/[PhCHO] x 10^2 dm^3 mol^{-1} s^{-1}	3.343	3.556	3.362	3.092
	Corr. Coeff.	0.9850	0.9972	0.9949	0.9875

The second order rate constants (k_2) remains constant showing the first order dependence with respect of PhCHO (Table 4.6.2). The plot of log k_{obs} vs log [PhCHO] (Fig. 4.6.3) yielded a straight line with a slope of 0.8451 (γ =0.9933) and 0.9208 (γ =0.9913) for TCMAC and TBAB respectively confirming the order with respect to PhCHO is one.

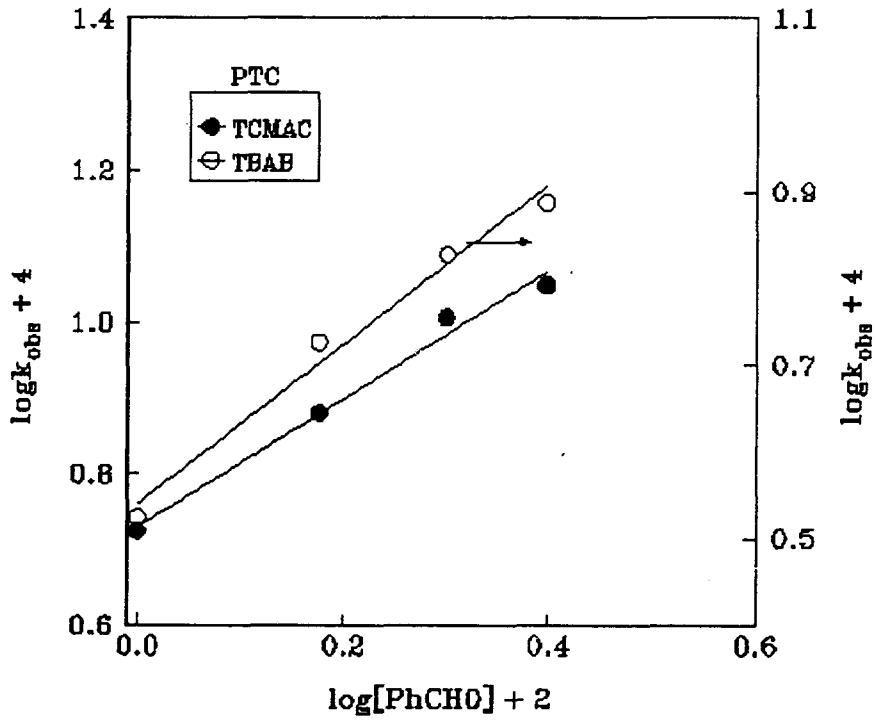


Fig. 4.6.3 Order with respect to Benzaldehyde

Thus the reaction orders of both the PhCHO and quaternary ammonium permanganate ion pairs for the oxidation of PhCHO in the benzene solvent were found to be equal to one using both the catalysts.

Effect of [PTC] on the rate of oxidation of PhCHO in organic Solvents

The effect of [PTC] was studied using the two quaternary ammonium salts *viz.*TCMAC andTBAB. With an increase of PTC from 2.0 to 3.5 mol dm^{-3}, the rate constant of the reaction was found to increase from 5.289 to 6.022 s^{-1} for the TCMAC and from 3.343 to 4.126 s^{-1} for TBAB (Table 4.6.3, Fig. 4.6.4 (a) & (b)).

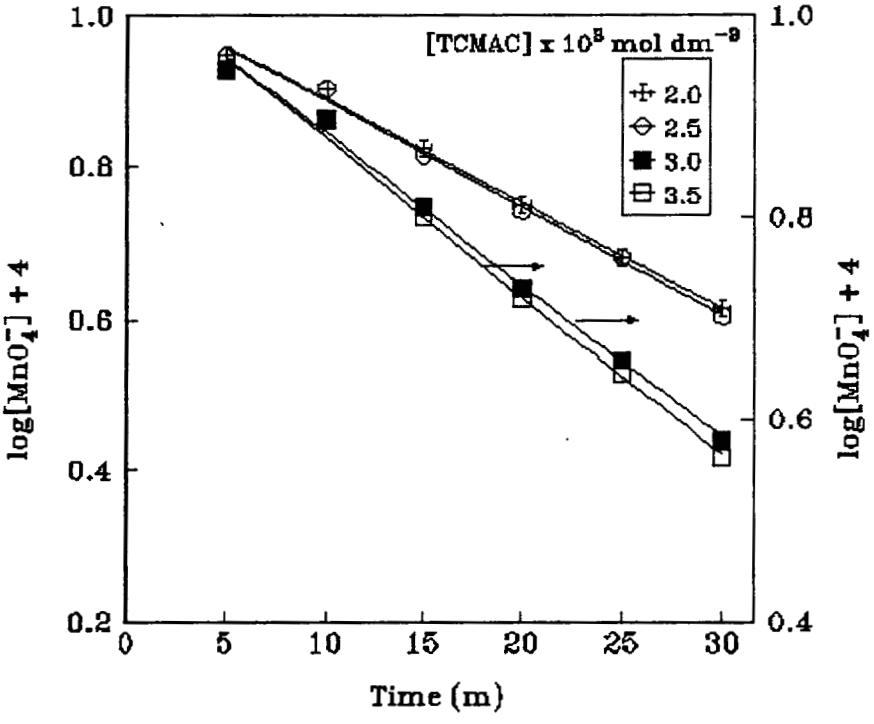


Fig. 4.6.4 (a) Effect of [TCMAC] on the oxdn of PhCHO in Benzene

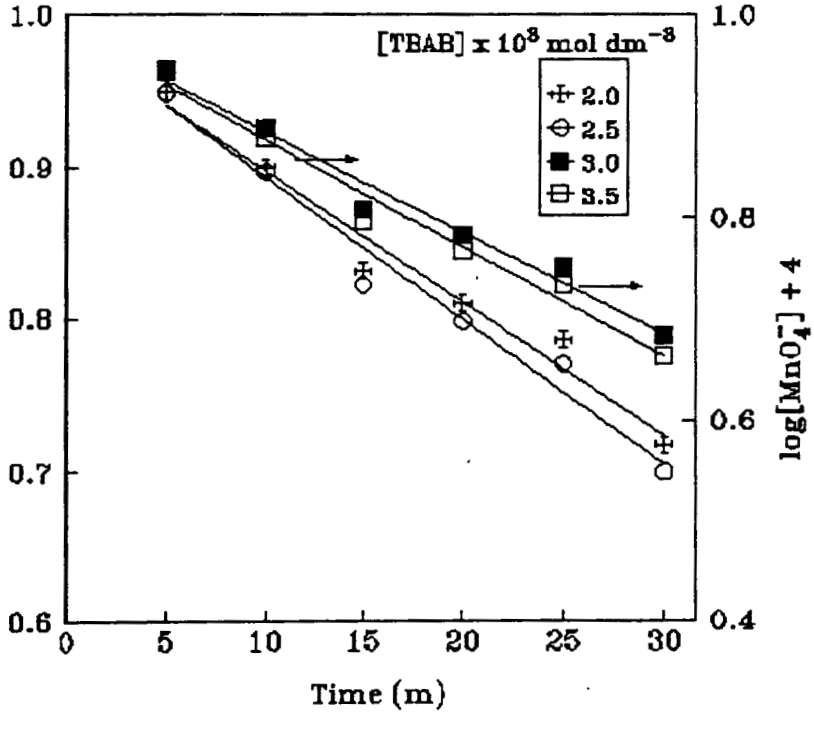


Fig. 4.6.4 (b) Effect of [TBAB] on the oxdn. of PhCHO in Benzene

Table 4.6.3 Effect of [PTC] on the oxdn. of PhCHO in organic solvent

Solvent – Benzene Temp. – 303 K

[PTC] x 10^3 mol dm^{-3}	TCMAC		TBAB	
	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.
2.0	5.289	0.9981	3.343	0.9850
2.5	5.392	0.9976	3.623	0.9868
3.0	5.761	0.9981	3.865	0.9872
3.5	6.022	0.9981	4.126	0.9878

A plot of log k_{obs} vs log [PTC] (Fig. 4.6.5) was found to be linear with a fractional order dependence.

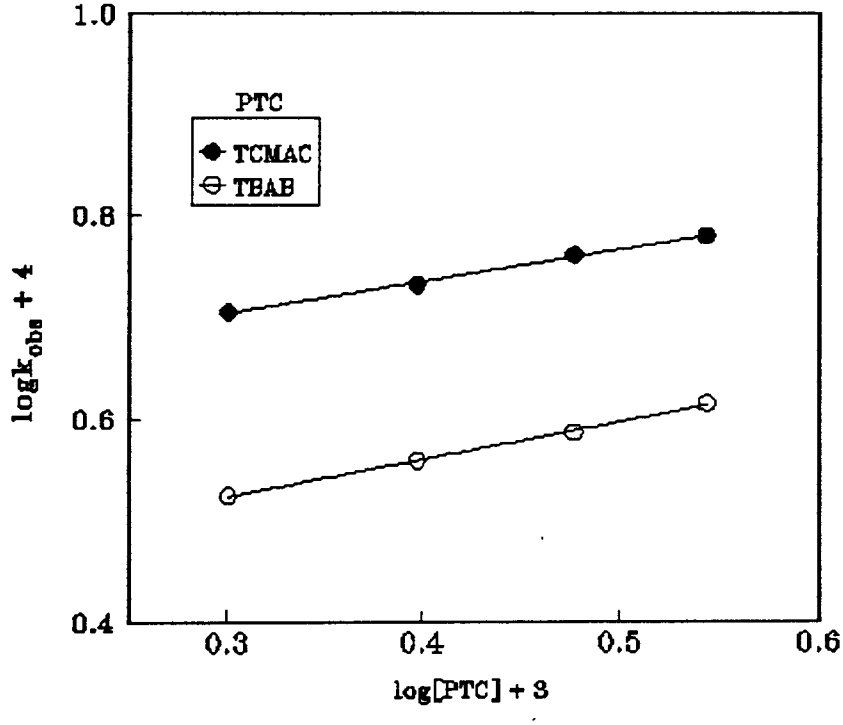


Fig. 4.6.5 Order with respect to PTC

The examination of the specific rates obtained with the two catalysts (Table 4.6.3) reveals the influence of the structure of the quaternary ammonium cation on the rate constant. TCMAC, $(C_{10}H_{21})_3\ N^+CH_3\ Cl^-$, which has a larger quaternary ammonium cation is found to be a more effective than TBAB, $(C_4H_9)_4\ N^+\ Br^-$ (Fig. 4.6.5).

Effect of Solvent Polarity

There was some connection found between the rate constants for the oxidation of PhCHO and the polarity of the organic solvent (Table 4.6.4 and Fig. 4.6.6 (a) & (b)). The order of rate constants obtained were as follows; benzene > toluene > carbontetrachloride > chloroform > dichloromethane. This order was just opposite of the dielectric constant of the organic solvent used. The organic solvent with a lower dielectric constant was found to have a higher value.

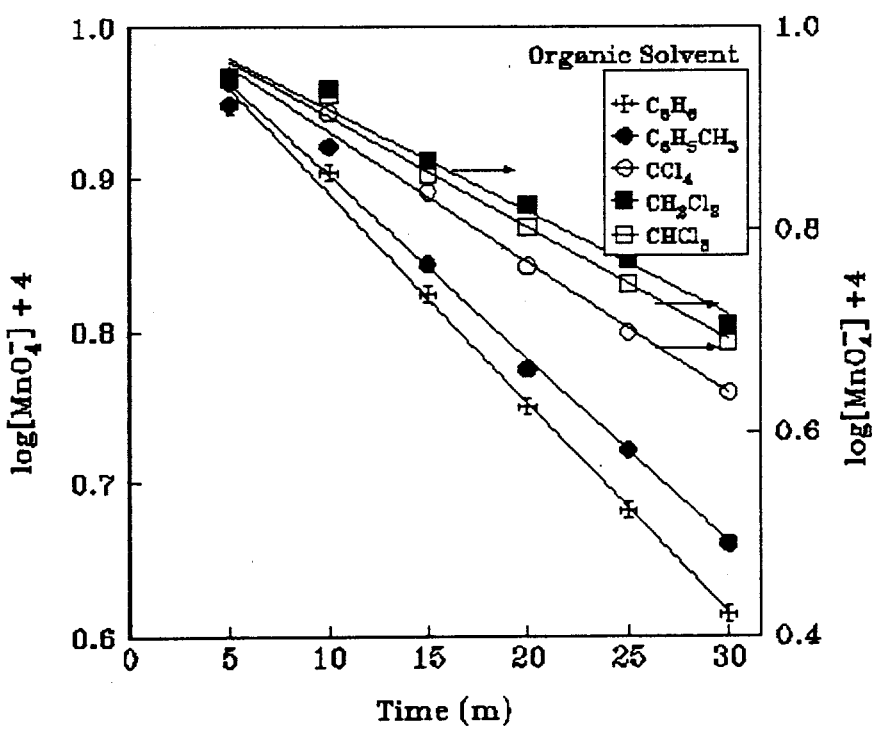


Fig. 4.5.7 (a) Effect of Solvent Polarity on the oxdn of PhCHO in Org. solvents (TCMAC)

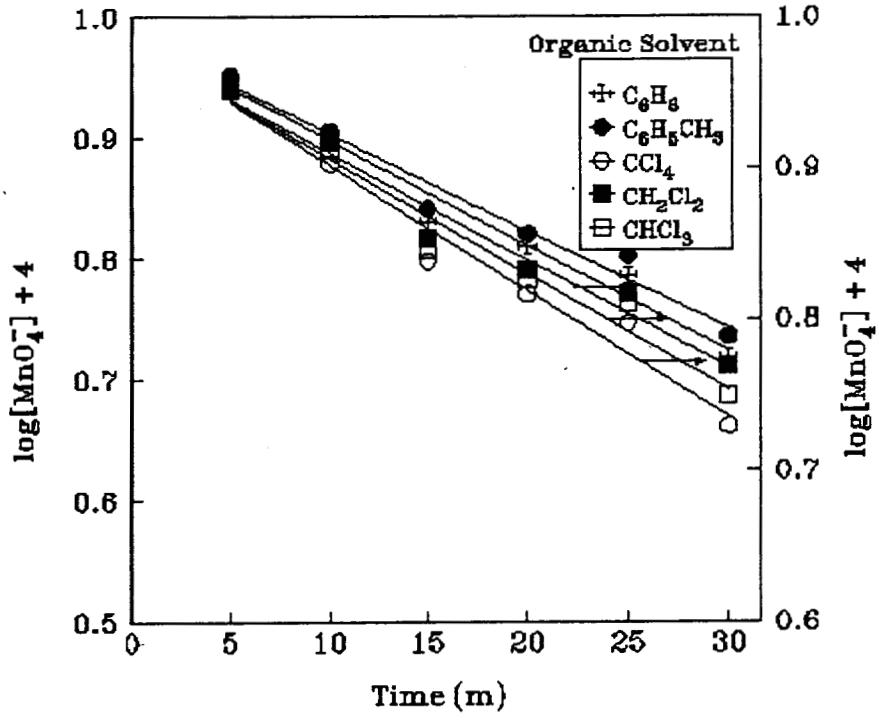


Fig. 4.6.6 (b) Effect of Solvent Polarity on the oxdn of PhCHO in Org. solvents (TBAB)

Table 4.6.4 Effect of Solvent Polarity on the oxdn. of PhCHO in Org. solvents

$[Q^+MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}, [PhCHO] = 1.0 x 10^{-2} mol dm^{-3}, Temp. – 303 K

Organic Solvent	Intrinsic Dielectric Constant	TCMAC		TBAB	
		k_{obs} x 10^4 sec^{-1}	Corr. Coeff.	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.
Benzene	2.27	5.289	0.9981	3.343	0.9850
Toluene	2.40	4.636	0.9954	3.097	0.9833
Carbontetrachloride	2.22	4.928	0.9957	3.189	0.9838
Chloroform	4.70	3.869	0.9901	2.928	0.9812
Dichloromethane	8.90	2.203	0.9982	2.721	0.9838

Effect of Substituents on the oxdn of PhCHO in Organic solvents

There was a slight change in the order of reactivities of PhCHO when compared to that in the aqueous acetic acid medium (Table 4.6.5 and Fig. 4.6.7 (a) & (b)).

The rate constants obtained for the oxidation of various substituted Benzaldehydes are found to be in the order to be PCB > MNB > PNB> PMA > -H- > PMyB > MMyB (Table 4.6.5). Here also the Hammett plot is found to have a positive ρ value of + 0.2915 and +0.5733 for the TCMAC and TBAB respectively. The positive values indicates that the electron withdrawing groups accelerate the reaction.

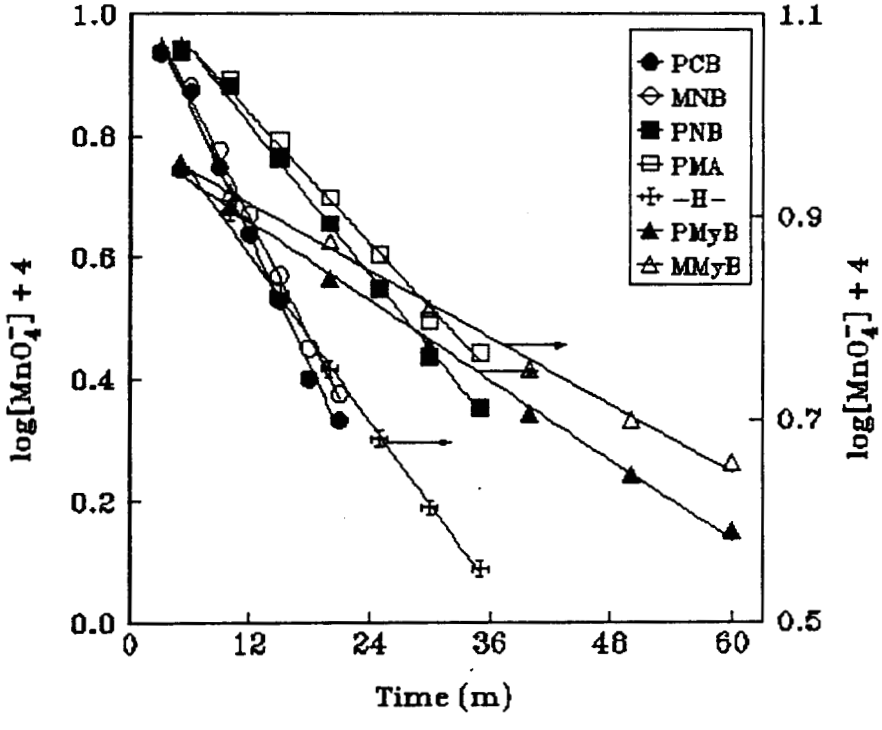


Fig. 4.6.7 (a) Effect of Substituents on the oxdn of PhCHO in Benzene (TCMAC)

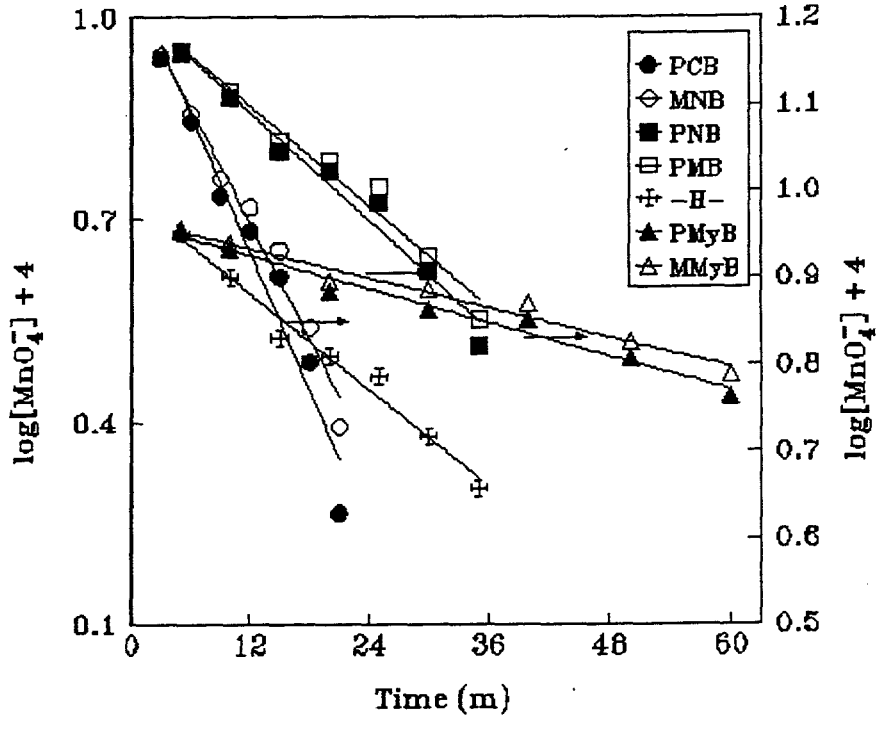


Fig. 4.6.7 (b) Effect of Substituents on the oxdn of PhCHO in Benzene (TBAB)

Table 4.6.5 Effect of Substituents on the oxdn of PhCHO in Organic solvents

$[Q^+MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}, Solvent - Benzene
[Substrate] = 1.0 x 10^{-2} mol dm^{-3}, Temp. – 303 K

Substrate	TCMAC		TBAB	
	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.	k_{obs} x 10^4 sec^{-1}	Corr. Coeff.
PCB	13.57	0.9973	13.06	0.9765
MNB	12.58	0.9972	10.91	0.9872
PNB	7.872	0.9979	5.181	0.9856
PMB	6.805	0.9964	4.805	0.9857
PhCHO	5.289	0.9980	3.343	0.9850
PMyB	3.703	0.9973	1.235	0.9878
MMyB	2.510	0.9951	1.082	0.9856

Effect of Temp. on the oxdn. of PhCHO in Organic solvent

The reaction rate constant of the oxidation of PhCHO was studied in the temperature range of 303-313 K (Table 4.6.6). The rate constant increase from 5.289 to 7.254 sec^{-1} for TCMAC and from 3.343 to 6.5444 sec^{-1} in the temperature range 303 to 313K.

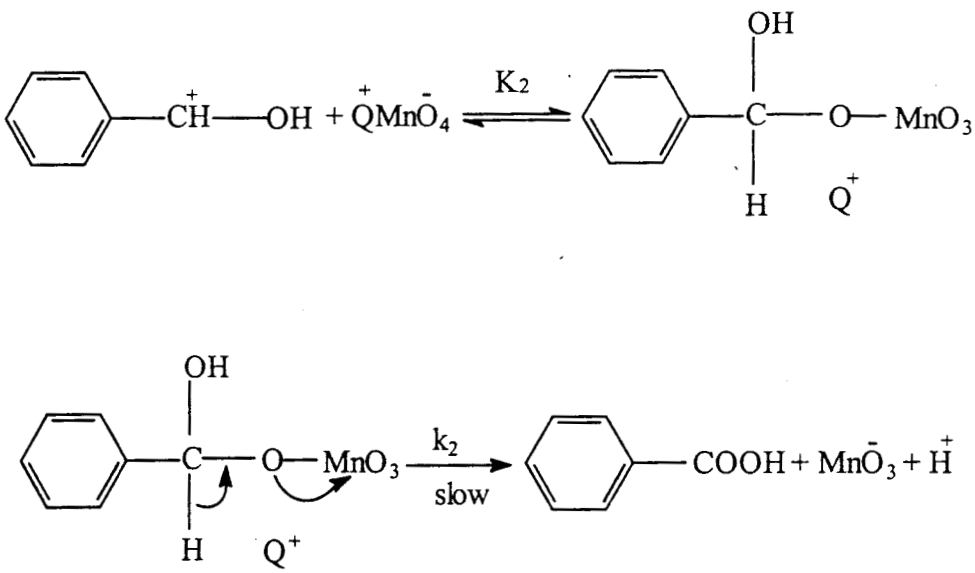
Table 4.6.6 Effect of Temp. on the oxdn. of PhCHO in Organic solvent

$[Q^+MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Solvent – Benzene
$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3}

Temp. (K)	TCMAC		TBAB	
	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.	$k_{obs} \times 10^4$ sec^{-1}	Corr. Coeff.
303	5.289	0.9981	3.343	0.9851
308	5.818	0.9969	4.222	0.9827
313	7.254	0.9969	6.544	0.9841

4.5.1 Mechanism of the oxdn of PhCHO using Quaternary ammonium permanganate

The mechanism of oxidation of PhCHO with $Q^+MnO_4^-$ is found to be the same as that for the oxidation of PhCHO in aqueous acetic acid medium. The reaction is believed to involve the formation and subsequent decomposition of the permanganate ester to give the products.



Scheme 4

The rate law is therefore

$$\frac{d[MnO_4^-]}{dt} = k_2 \left[C_6H_5 — \overset{O}{\overset{\|}{C}} — H \right]^a [Q^+MnO_4^-]^b$$

Where a and b are the order of $C_6H_5COCH_3$ and Quaternary ammonium permangante ion-pair in the organic solvent. The values of a and b are obtained to be unity.

CONCLUSION

In this particular work we have carried out the kinetics of oxidation of two Carbonyl compounds *viz.* Acetophenone and Benzaldehyde and some of its derivatives using $KMnO_4$ and $Q^+MnO_4^-$ as oxidizing agents. There has been certain reports regarding the kinetics of oxidation of some organic substrates using phase transfer catalyst in heterogeneous systems, but the oxidation using $Q^+MnO_4^-$ in organic solvents under homogeneous conditions has not received much attention. Hence in this particular work an attempt has been made in this direction

From the above project (section 4.1- 4.6) it is found that the novel phase transfer technique is superior to the traditional method in many aspects.

- Improved reaction rates
- Lower reaction temperature
- Synthetically easier work-up
- Increased yields

The difficulties with the traditional method are easily overcome by using phase transfer catalytic method. Thus PTC is a welcome cost-effective process in general and is a solution to problems related to yield and purity usually encountered in industrial and developmental laboratories. The simplicity of operation, the rapid reaction rates and the generally high yields of products, ensure that the technique will grow in importance.

The results also provide a consistent picture with the phase transfer scheme and a useful guide to the choice of catalyst, solvent, and other reaction conditions for synthetic applications.

SUMMARY

Sheeba P.S. “Kinetic studies on the oxidation of carbonyl compounds in the presence of phase transfer catalysts” Thesis. Department of Chemistry, University of Calicut

SUMMARY

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The present project has been undertaken with the objective to determine the kinetic results for the oxidation of two important carbonyl compounds *i.e.* Benzaldehyde and Acetophenone and some of its substituents using potassium permanganate. Both the traditional method, which uses a co-solvent and the modern technique of phase transfer catalysis have been employed to study the kinetics.

The traditional method of oxidation of the substrates was carried out using aqueous acetic acid and in this solvent, the effect of the concentration of oxidant, substrate and hydronium ion were examined. In addition the effect of solvent polarity, ionic strength of the medium, temperature and substituents on the rate have also been determined. The thermodynamic and kinetic parameters such as enthalpy of activation, free energy of activation and entropy of activation have also been evaluated to throw some light on the energetic and mechanistic details of the reaction.

The rate of oxidation of benzaldehyde and some of its derivatives have been determined in 50% aqueous acetic acid. The rate of the reaction was found to be proportional to the first powers of permanganate and the aldehyde concentrations. There was also a linear increase of rate with almost first order with respect to the hydrogen ion concentration. The order of reactivities observed shows that the electron withdrawing groups accelerate the rate. The product of oxidation was found to be benzoic acid.

Similarly the rate of oxidation of acetophenone and some of its derivatives have been determined under the same conditions. It was found that one mole of permanganate consumed one mole of acetophenone. A qualitative analysis of the reaction product showed that the product of the oxidation is carboxylic acid, which was identified as benzoic acid. The order with respect to acetophenone and MnO_4^- was found to be unity. There was fractional order dependence with respect to acid concentration. The order of reactivities of the various substituted acetophenones are found to be *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > -H > *p*-CH_3 > *p*-OCH_3-acetophenones.

The phase transfer (PT) technique was carried out using benzene, toluene, dichloromethane, chloroform and carbon tetrachloride as organic solvents. Tetrabutylammonium bromide (TBAB) and tricaprylmethylammonium chloride (TCMAC) were employed as phase transfer catalysts. In order to carry out the kinetic investigation in the organic solvent, the permanganate ions were extracted first from the aqueous to the organic phase. The efficiency of extraction was determined with respect to the Concentration of MnO_4^- in aqueous phase, Structure and Concentration of the quaternary ammonium salt and Nature of the solvent.

The extraction of the permanganate ion in various solvents have been found to be qualitative at low concentrations of quaternary ammonium ions and with an excess of it, permanganate ion is almost completely transported into the organic layer. It is also seen that TCMAC, $(C_{10}H_{21})_3N^+CH_3\ Cl^-$ that has a greater organic structure is found to transport permanganate ion more effectively than the TBAB, $(C_4H_9)_4N^+\ Br^-$.

It is found that the efficiency of extraction of permanganate ion is affected by even slight changes in the organic phase. The chlorocarbons (chloroform and dichloromethane) are somewhat better solvents than the hydrocarbons (benzene and toluene).

Increasing the concentration of permanganate ion in the aqueous phase provides easier transfer of the permanganate ion into the organic phase.

The stability of permanganate ion in various organic solvents was determined by measuring the concentrations of the permanganate ion in the organic solvents for a specified time. The loss of Permanganate ion extracted in various organic solvents with both the catalysts were found to be negligible indicating that these solutions are almost stable and could be used for studying the kinetics of oxidation of the organic substrates.

The kinetics of oxidation of both Benzaldehyde and Acetophenone and some of its derivatives were carried out using the above mentioned phase transferred permanganate ion in organic solvents. The order with respect to substrate and the permanganate ion is found to be one in either case. Moreover the plot for the variation of the catalyst concentration is linear, with fractional order dependence.

The effect of organic solvent on the rate was also determined. It is found that the rate of oxidation tended to increase with the increase in the dielectric constant of the organic solvent. The rate of oxidation of various substituted acetophenones were found to be in the order *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > -H > *p*-CH_3 > *p*-OCH_3. It is thus seen that electron-withdrawing groups accelerate the process. For benzaldehydes also it is found that electron-withdrawing substituents increase and electron-releasing substituents decrease the rate of oxidation.

The oxidation using potassium permanganate in the presence of phase transfer catalyst can be shown to proceed as per the following scheme:

The oxidation using potassium permanganate in the presence of phase transfer catalyst can be shown to proceed as per the following scheme:

$$Q^+X^-_{(aq)} + KMnO_{4\,(aq)} \rightarrow Q^+MnO_4^-{}_{(aq)} + K^+X^-_{(aq)} \qquad (1)$$

$$Q^+MnO_4^-{}_{(aq)} = Q^+MnO_4^-{}_{(org)} \qquad (2)$$

On treating this phase transferred permanganate ion with the organic solvent containing the substrate, the oxidation takes place in the organic phase.

$$Q^+MnO_4^-{}_{(org)} + C_6H_5CHO \rightarrow C_6H_5COOH \qquad (3)$$

$$Q^+MnO_4^-{}_{(org)} + C_6H_5COCH_3 \rightarrow C_6H_5COOH$$

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APPENDIX

KINETIC DATA

4.1 Oxidation of Acetophenone using Potassium Permanganate in Aqueous Acetic Acid Medium

Table 4.1.1 Effect of $[MnO_4^-]$ on the rate of oxdn. of AcPh in 50% aq. HOAc.

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3} Temp. = 308 K

$[MnO_4^-] \times 10^3$ mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.4840	0.9690	1.4601	1.9698
10	0.4769	0.9569	1.4400	1.9505
20	0.4620	0.9280	1.4101	1.9103
30	0.4530	0.9071	1.3800	1.8492
40	0.4452	0.8780	1.3300	1.7801
50	0.4290	0.8630	1.2899	1.7399
60	0.4120	0.8469	1.2600	1.7206
80	0.4030	0.8090	1.2100	1.6485
100	0.3736	0.7580	1.1500	1.5350
120	0.3580	0.7130	1.0950	1.4560
$k_{obs} \times 10^5$ s^{-1}	4.22	4.29	4.26	4.33
Corr. Coef.	0.9957	0.9977	0.9985	0.9970

Table 4.1.2 Effect of [AcPh] on the rate of oxdn. of AcPh in 50% aq. HOAc.

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[AcPh] \times 10^2$ mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9690	0.9519	0.9249	0.8661
10	0.9569	0.9211	0.8801	0.8260
20	0.9280	0.8841	0.8410	0.7751
30	0.9071	0.8521	0.7919	0.7260
40	0.8780	0.8170	0.7571	0.6890
50	0.8630	0.7990	0.7160	0.6200
60	0.8469	0.7620	0.6820	0.5959
80	0.8090	0.6980	0.6030	0.5150
100	0.7580	0.6670	0.5511	0.4610
120	0.7130	0.6110	0.4900	0.4120
$k_{obs} \times 10^5$ s^{-1}	4.29	6.25	8.98	10.82
Corr. Coef.	0.9977	0.9979	0.9993	0.9984

Table 4.1.3 Effect of $[H_2SO_4]$ on the rate of oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

$[H_2SO_4]$ x 10^3 mol dm^{-3}	0.0	2.5	5.0	7.5	12.5	20.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}					
5	0.9690	0.9524	0.9535	0.9495	0.9505	0.9486
10	0.9569	0.9396	0.9405	0.9355	0.9334	0.9315
20	0.9280	0.9175	0.9105	0.9024	0.9014	0.8965
30	0.9071	0.8934	0.8865	0.8785	0.8675	0.8585
40	0.8780	0.8595	0.8545	0.8455	0.8395	0.8334
50	0.8630	0.8474	0.8384	0.8315	0.8204	0.7995
60	0.8469	0.8225	0.8075	0.7995	0.7874	0.7654
80	0.8090	0.7874	0.7755	0.7424	0.7296	0.7135
100	0.7580	0.7386	0.7175	0.6985	0.6805	0.6575
120	0.7130	0.7014	0.6705	0.6514	0.6395	0.6094
k_{obs} x 10^5 s^{-1}	4.29	4.41	4.98	5.45	5.79	6.41
Corr. Coef.	0.9977	0.9990	0.9982	0.9992	0.9995	0.9998

Table 4.1.4 Effect of [NaCl] on the rate of oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

[NaCl] x 10^2 mol dm^{-3}	0.0	0.5	1.0	1.5	5.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}				
5	0.9690	0.9640	0.9621	0.9609	0.9500
10	0.9569	0.9531	0.9510	0.9450	0.9261
20	0.9280	0.9261	0.9230	0.9161	0.8990
30	0.9071	0.9060	0.9031	0.8850	0.8670
40	0.8780	0.8830	0.8699	0.8630	0.8490
50	0.8630	0.8571	0.8540	0.8460	0.8370
60	0.8469	0.8391	0.8350	0.8280	0.8111
80	0.8090	0.8040	0.7931	0.7850	0.7770
100	0.7580	0.7480	0.7440	0.7341	0.7230
120	0.7130	0.7140	0.7099	0.6940	0.6850
k_{obs} x 10^5 s^{-1}	4.29	4.33	4.41	4.60	4.52
Corr. Coef.	0.9977	0.9987	0.9982	0.9985	0.9970

Table 4.1.5 Effect of [$MnSO_4$] on the rate of oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

[$MnSO_4$] x 10^2 mol dm^{-3}	0.0	1.0	1.5	2.0
Time (min)	[MnO_4^-] x 10^3 mol dm^{-3}			
5	0.9690	0.9790	0.9765	0.9806
10	0.9569	0.9695	0.9685	0.9735
20	0.9280	0.9486	0.9524	0.9595
30	0.9071	0.9315	0.9344	0.9455
40	0.8780	0.9105	0.9154	0.9275
50	0.8630	0.8934	0.9005	0.9114
60	0.8469	0.8715	0.8875	0.9024
80	0.8090	0.8505	0.8666	0.8825
100	0.7580	0.8334	0.8424	0.8576
120	0.7130	0.8026	0.8204	0.8384
k_{obs} x 10^5 s^{-1}	4.29	2.84	2.53	2.30
Corr. Coef.	0.9977	0.9934	0.9962	0.9971

Table 4.1.6 Effect of Solvent on the rate of oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} [MnO_4^-] = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

HOAc. %	20	40	50	60	80
Dielectric Constant	61	47	39.8	32	17.5
Time (min)	[MnO_4^-] x 10^3 mol dm^{-3}				
5	0.9600	0.9581	0.9690	0.9595	0.9609
10	0.9474	0.9415	0.9569	0.9472	0.9515
20	0.9026	0.8914	0.9280	0.9206	0.9324
30	0.8795	0.8794	0.9071	0.8917	0.9106
40	0.8504	0.8580	0.8780	0.8741	0.8905
50	0.8345	0.8325	0.8630	0.8575	0.8706
60	**0.8159**	**0.8140**	**0.8469**	**0.8409**	**0.8542**
80	0.7965	0.7609	0.8090	0.7855	0.8304
100	0.7265	0.7424	0.7580	0.7515	0.7851
120	0.6925	0.7086	0.7130	0.7260	0.7279
k_{obs} x 10^5 s^{-1}	5.02	4.52	4.29	4.10	3.68
Corr. Coef.	0.9995	0.9984	0.9977	0.9980	0.9993

Table 4.1.7 Effect of Substituents on the Benzene ring on the rate of oxidation of AcPh in 50% aq. HOAc.

[substrate] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

[Substrate] x 10^2 mol dm^{-3}	PNA	MNA	PBA	PCA	AcPh	PMA	PMyA
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}						
5	0.9415	0.9465	0.9590	0.9581	0.9690	0.9688	0.9743
10	0.9035	0.9154	0.9738	0.9425	0.9569	0.9600	0.9680
15	0.8685	0.8844	-	-	-	-	-
20	0.8365	0.8505	0.9583	0.9105	0.9280	0.9425	0.9555
25	0.8035	0.8265	-	-	-	-	-
30	0.7644	0.7924	0.9437	0.8875	0.9071	-	-
35	0.7374	0.7635	-	-	-	-	-
40	0.7035	0.7305	0.9302	0.8585	0.8780	0.9064	0.9294
50	-	-	0.9125	0.8294	0.8630	-	-
60	-	-	0.8952	0.8026	0.8469	0.8884	0.9105
80	-	-	-	-	0.8090	0.8495	0.8834
100	-	-	-	-	0.7580	0.8175	0.8625
120	-	-	-	-	0.7130	0.7945	0.8315
140	-	-	-	-	-	0.7685	0.8055
160	-	-	-	-	-	0.7525	0.7884
k_{obs} x 10^5 s^{-1}	13.81	12.20	5.94	5.33	4.29	2.80	2.30
Corr. Coef.	0.9995	0.9990	0.9993	0.9995	0.9977	0.9978	0.9986

Table 4.1.8 (a) Effect of Temp. on the rate of oxdn. of AcPh in 50% aq. HOAc.

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9690	0.9548	0.9495	0.9425
10	0.9569	0.9384	0.9294	0.9175
15	-	-	0.9114	0.8915
20	0.9280	0.9145	0.8974	0.8685
25	-	-	0.8756	0.8505
30	0.9071	0.8875	0.8604	0.8346
40	0.8780	0.8645	0.8185	0.7915
50	0.8630	0.8424	0.7924	0.7535
60	0.8469	0.8064	0.7685	0.7095
80	0.8090	0.7405	-	-
100	0.7580	0.7275	-	-
120	0.7130	0.6935	-	-
k_{obs} x 10^5 s^{-1}	4.29	4.80	6.56	8.36
Corr. Coef.	0.9977	0.9929	0.9982	0.9991

Table 4.1.8 (b) Effect of Temp. on the rate of oxdn. of PNA in 50% aq. HOAc.

[PNA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
3	-	-	0.9265	0.9579
5	0.9415	0.9225	-	-
6	-	-	0.8779	0.9188
9	-	-	0.8305	0.8817
10	0.9035	0.8654	-	-
12	-	-	0.7845	0.8492
15	0.8685	0.8134	0.7324	0.8119
18	-	-	0.7035	0.7800
20	0.8365	0.7765	-	-
21	-	-	0.6615	0.7494
24	-	-	0.6155	0.7139
25	0.8035	0.7284	-	-
30	0.7644	0.6814	-	-
35	0.7374	0.6475	-	-
40	0.7035	0.6124	-	-
k_{obs} x 10^5 s^{-1}	13.81	19.49	32.05	44.14
Corr. Coef.	0.9995	0.9995	0.9990	0.9994

Table 4.1.8 (c) Effect of Temp. on the rate of oxdn. of MNA in 50% aq. HOAc.

[MNA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
3	-	-	0.9315	0.9175
5	0.9465	0.9284	-	-
6	-	-	0.8905	0.8564
9	-	-	0.8454	0.7985
10	0.9154	0.8805	-	-
12	-	-	0.8075	0.7494
15	0.8844	0.8374	0.7784	0.7075
18	-	-	0.7334	0.6644
20	0.8505	0.7954	-	-
21	-	-	0.6994	0.6304
24	-	-	0.6784	0.5885
25	0.8265	0.7435	-	-
30	0.7924	0.7025	-	-
35	0.7635	0.6655	-	-
40	0.7305	0.6345	-	-
k_{obs} x 10^5 s^{-1}	12.20	18.50	25.71	34.73
Corr. Coef.	0.9990	0.9994	0.9987	0.9993

Table 4.1.8 (d) Effect of Temp. on the rate of oxdn. of PBA in 50% aq. HOAc.

[PBA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9590	0.9524	0.9414	0.9374
10	0.9415	0.9284	0.9094	0.9004
15	-	0.9054	0.8834	0.8125
20	0.9085	0.8834	0.8538	0.8265
25	-	0.8604	0.8215	0.7985
30	0.8785	0.8414	0.8004	0.7594
35	-	0.8154	0.7744	0.7345
40	0.8514	0.7954	0.7485	0.7004
50	0.8175	-	-	-
60	0.7855	-	-	-
k_{obs} x 10^5 s^{-1}	5.94	8.55	10.90	13.80
Corr. Coef.	0.9993	0.9996	0.9996	0.9992

Table 4.1.8 (e) Effect of Temp. on the rate of oxdn. of PCA in 50% aq. HOAc.

[PCA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9581	0.9554	0.9485	0.9355
10	0.9425	0.9334	0.9225	0.8974
15	-	0.9144	0.8974	0.8665
20	0.9105	0.8954	0.8725	0.8314
25	-	0.8734	0.8504	0.7974
30	0.8875	0.8585	0.8284	0.7684
35	-	0.8364	0.8075	0.7395
40	0.8585	0.8184	0.7845	0.7075
50	0.8294	-	-	-
60	0.8026	-	-	-
k_{obs} x 10^5 s^{-1}	5.33	7.33	8.98	13.20
Corr. Coef.	0.9995	0.9996	0.9999	0.9998

Table 4.1.8 (f) Effect of Temp. on the rate of oxdn. of PMA in 50% aq. HOAc.

[PMA] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9688	0.9691	0.9615	0.9583
10	0.9500	0.9590	0.9485	0.9374
20	0.9425	0.9384	0.9194	0.9024
30	-	-	0.8914	0.8684
40	0.9064	0.8974	0.8725	0.8334
50	-	-	0.8435	0.8064
60	0.8884	0.8634	0.8175	0.7674
80	0.8495	0.8215	-	-
100	0.8175	0.7855	-	-
120	0.7945	0.7525	-	-
140	0.7685	0.7234	-	-
160	0.7525	0.6964	-	-
k_{obs} x 10^5 s^{-1}	2.80	3.60	4.87	6.60
Corr. Coef.	0.9978	0.9997	0.9991	0.9993

Table 4.1.8 (g) Effect of Temp. on the rate of oxdn. of PMyA in 50% aq. HOAc.

$[PMyA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9743	0.9752	0.9699	0.9665
10	0.9680	0.9607	0.9654	0.9564
20	0.9555	0.9535	0.9464	0.9334
30	-	-	0.9274	0.9104
40	0.9294	0.9244	0.9125	0.8874
50	-	-	0.8914	0.8715
60	0.9105	0.8924	0.8734	0.8485
80	0.8834	0.8704	-	-
100	0.8625	0.8374	-	-
120	0.8315	0.8125	-	-
140	0.8055	0.7814	-	-
160	0.7884	0.7634	-	-
$k_{obs} \times 10^5$ s^{-1}	2.30	2.64	3.22	3.95
Corr. Coef.	0.9986	0.9990	0.9984	0.9994

Table 4.1.10 Effect of [Benzoic acid] on the oxdn. of AcPh in 50% aq. HOAc.

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[C_6H_5COOH] \times 10^2$ mol dm^{-3}	0.0	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9690	0.9650	0.9641	0.9619
10	0.9569	0.9542	0.9531	0.9460
20	0.9280	0.9250	0.9250	0.9181
30	0.9071	0.9051	0.9048	0.8872
40	0.8780	0.8819	0.8709	0.8648
50	0.8630	0.8560	0.8562	0.8483
60	0.8469	0.8382	0.8360	0.8300
80	0.8090	0.8028	0.7947	0.7874
100	0.7580	0.7470	0.7463	0.7361
120	0.7130	0.7129	0.7109	0.6970
$k_{obs} \times 10^5$ s^{-1}	4.29	4.37	4.41	4.40
Corr. Coef.	0.9977	0.9987	0.9992	0.9984

4.2 Oxidation of Benzaldehyde using Potassium Permanganate in Aqueous Acetic Acid Medium

Table 4.2.1 Effect of $[MnO_4^-]$ on the rate of oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} Temp. = 308 K

$[MnO_4^-] \times 10^3$ mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.4352	0.9070	1.3628	1.7481
10	0.4030	0.8005	1.2055	1.6381
15	0.3580	0.7432	1.1458	1.4660
20	0.3354	0.6770	1.0640	1.3700
25	0.2979	0.6250	0.9475	1.2001
30	0.2722	0.5622	0.8180	1.065
35	0.2433	0.5050	0.7906	0.9899
40	0.2258	0.4724	0.7280	0.9381
50	0.1859	0.3986	0.6044	0.7590
60	0.1695	0.3342	0.4890	0.6300
$k_{obs} \times 10^4$ s^{-1}	3.001	2.993	3.051	3.135
Corr. Coef.	0.9963	0.9991	0.9973	0.9982

Table 4.2.2 Effect of $[C_6H_5CHO]$ on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[C_6H_5CHO] \times 10^2$ mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.8680	0.8569	0.8190
10	0.8005	0.7420	0.7080	0.6785
15	0.7432	0.6674	0.5759	0.5156
20	0.6770	0.6120	0.4800	0.4194
25	0.6250	0.5513	0.4190	0.3410
30	0.5622	0.4995	0.3485	0.2802
35	0.5050	0.4252	0.2958	0.2285
40	0.4724	0.3637	0.2652	0.2002
$k_{obs} \times 10^4$ s^{-1}	2.993	3.907	5.642	6.882
Corr. Coef.	0.9991	0.9952	0.9975	0.9976

Table 4.2.3 Effect of $[H_2SO_4]$ on the rate of oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[H_2SO_4] \times 10^3$ mol dm^{-3}	0.0	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.8688	0.8665	0.8369
10	0.8005	0.8193	0.7661	0.6930
15	0.7432	0.7584	0.6690	0.5910
20	0.6770	0.6676	0.6032	0.5150
25	0.6250	0.6210	0.5512	0.4359
30	0.5622	0.5711	0.4515	0.3536
35	0.5050	0.4998	0.4120	0.3184
40	0.4724	0.4616	0.3536	0.2702
$k_{obs} \times 10^4$ s^{-1}	2.993	3.105	4.226	5.362
Corr. Coef.	0.9991	0.9967	0.9974	0.9987

Table 4.2.4 Effect of [NaCl] on the rate of oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

[NaCl] $\times 10^2$ mol dm^{-3}	0.0	0.5	1.0	1.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.9112	0.9176	0.9201
10	0.8005	0.8245	0.8324	0.8456
15	0.7432	0.7699	0.7765	0.7915
20	0.6770	0.6986	0.7155	0.7344
25	0.6250	0.6530	0.6772	0.6986
30	0.5622	0.5932	0.6246	0.6532
35	0.5050	0.5445	0.5789	0.6071
40	0.4724	0.5187	0.5525	0.5911
50	0.3986	0.4445	0.4865	0.5263
60	0.3342	0.3885	0.4301	0.4749
$k_{obs} \times 10^4$ s^{-1}	2.993	2.583	2.264	1.976
Corr. Coef.	0.9991	0.9983	0.9978	0.9963

Table 4.2.5 Effect of [$MnSO_4$] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[MnSO_4] \times 10^2$ mol dm^{-3}	0.0	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.9190	0.9215	0.9226
10	0.8005	0.8321	0.8497	0.8512
15	0.7432	0.7695	0.7754	0.7778
20	0.6770	0.7205	0.7350	0.7460
25	0.6250	0.6815	0.6999	0.7015
30	0.5622	0.6046	0.6153	0.6204
35	0.5050	0.5820	0.5917	0.6130
40	0.4724	0.5585	0.5620	0.5851
50	0.3986	0.4950	0.5122	0.5315
60	0.3342	0.4443	0.4713	0.4805
$k_{obs} \times 10^4$ s^{-1}	2.993	2.176	2.061	1.953
Corr. Coef.	0.9991	0.9936	0.9893	0.9900

Table 4.2.6 Effect of Solvent on the rate of oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

HOAc. %	20	40	50	60	80
Dielectric Constant	61	47	39.8	32	17.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}				
5	0.9290	0.9275	0.9070	0.8708	0.8702
10	0.8455	0.8352	0.8005	0.8184	0.7512
15	0.7700	0.7645	0.7432	0.7502	0.6723
20	0.7015	0.6950	0.6770	0.6703	0.6205
25	0.6556	0.6449	0.6250	0.6272	0.5602
30	0.6018	0.5910	0.5622	0.5615	0.5005
35	0.5566	0.5312	0.5050	0.4812	0.4309
40	0.5221	0.5060	0.4724	0.4705	0.3742
$k_{obs} \times 10^4$ s^{-1}	2.752	2.917	2.993	3.135	3.838
Corr. Coef.	0.9983	0.9983	0.9991	0.9938	0.9965

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Table 4.2.7 Effect of Substituents on the Benzene ring on the rate of oxidation of C_6H_5CHO in 50% aq. HOAc.

[substrate] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

[Substrate] x 10^2 mol dm^{-3}	PNB	MNB	PCB	-H-	PMB	PMyB	MMyB
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}						
5	0.9290	0.9215	0.9115	0.9070	0.9062	0.8952	0.9292
10	0.8526	0.8501	0.8256	0.8005	0.7783	0.7654	0.8475
15	0.7972	0.7816	0.7712	0.7432	0.6926	0.6805	0.7692
20	0.7561	0.7209	0.6950	0.6770	0.6598	0.6415	0.7011
25	0.7119	0.6999	0.6515	0.6250	0.5980	0.5792	0.6535
30	0.6655	0.6486	0.5899	0.5622	0.5472	0.5260	0.5996
35	0.6493	0.6218	0.5460	0.5050	0.4812	0.4505	0.5380
40	0.6054	0.5986	0.5208	0.4724	0.4160	0.3958	0.5092
50	0.5726	0.5513	0.4572	0.3986	-	-	-
60	0.5434	0.5092	0.3904	0.3342	-	-	-
					-		
k_{obs} x 10^4 s^{-1}	1.623	1.730	2.537	2.993	3.435	3.665	2.897
Corr. Coef.	0.9832	0.9865	0.9973	0.9991	0.9936	0.9948	0.9987

Table 4.2.8 (a) Effect of Temp. on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.8985	0.8779	0.8540
10	0.8005	0.7516	0.7350	0.7120
15	0.7432	0.6804	0.6219	0.5558
20	0.6770	0.6352	0.5542	0.4490
25	0.6250	0.5825	0.4898	0.3650
30	0.5622	0.5210	0.4255	0.3058
35	0.5050	0.4598	0.3222	0.2682
40	0.4724	0.3940	0.2921	0.2308
$k_{obs} \times 10^4$ s^{-1}	2.993	3.619	5.197	6.337
Corr. Coef.	0.9991	0.9934	0.9948	0.9957

Table 4.2.8 (b) Effect of Temp. on the rate of oxdn. of PNB in 50% aq. HOAc.

[PNB] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9290	0.9192	0.9095	0.8708
10	0.8526	0.8358	0.8152	0.7700
15	0.7972	0.7700	0.7550	0.6710
20	0.7561	0.7222	0.6810	0.6012
25	0.7119	0.6854	0.6333	0.5305
30	0.6655	0.6208	0.5702	0.4710
35	0.6493	0.5850	0.5115	0.4155
40	0.6054	0.5592	0.4816	0.3820
50	0.5726	0.4972	0.3990	0.3022
60	0.5434	0.4466	0.3154	0.2611
$k_{obs} \times 10^4$ s^{-1}	1.623	2.164	3.124	3.753
Corr. Coef.	0.9832	0.9935	0.9923	0.9981

Table 4.2.8 (c) Effect of Temp. on the rate of oxdn. of MNB in 50% aq. HOAc.

[MNB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9215	0.9194	0.9102	0.9005
10	0.8501	0.8330	0.8190	0.7915
15	0.7816	0.7642	0.7542	0.6940
20	0.7209	0.7198	0.6795	0.6095
25	0.6999	0.6802	0.6310	0.5354
30	0.6486	0.6005	0.5685	0.4790
35	0.6218	0.5811	0.5093	0.4112
40	0.5986	0.5500	0.4786	0.3600
50	0.5513	0.4960	0.4120	0.3119
60	0.5092	0.4443	0.3617	0.2605
k_{obs} x 10^4 s^{-1}	1.730	2.180	2.840	3.849
Corr. Coef.	0.9865	0.9923	0.9968	0.9948

Table 4.2.8 (d) Effect of Temp. on the rate of oxdn. of PCB in 50% aq. HOAc.

[PCB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9115	0.9012	0.8940	0.8865
10	0.8256	0.8183	0.7752	0.7560
15	0.7712	0.7493	0.6675	0.6254
20	0.6950	0.6658	0.6010	0.5466
25	0.6515	0.6205	0.5503	0.4518
30	0.5899	0.5584	0.4572	0.3782
35	0.5460	0.4766	0.4198	0.3214
40	0.5208	0.4618	0.3584	0.2794
k_{obs} x 10^4 s^{-1}	2.537	3.308	4.241	5.577
Corr. Coef.	0.9973	0.9960	0.9977	0.9996

Table 4.2.8 (e) Effect of Temp. on the rate of oxdn. of PMB in 50% aq. HOAc.

[PMB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.9062	0.8915	0.8845	0.8452
10	0.7783	0.7710	0.7610	0.6910
15	0.6926	0.6604	0.6432	0.5218
20	0.6598	0.5999	0.5570	0.4202
25	0.5980	0.5472	0.4615	0.3545
30	0.5472	0.4574	0.3960	0.2896
35	0.4812	0.4202	0.3318	0.2344
40	0.4160	0.3614	0.2809	0.2158
k_{obs} x 10^4 s^{-1}	3.435	4.187	5.484	6.705
Corr. Coef.	0.9936	0.9976	0.9997	0.9950

Table 4.2.8 (f) Effect of Temp. on the rate of oxdn. of PMyB in 50% aq. HOAc.

[PMyB] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.8952	0.8880	0.8572	0.8315
10	0.7654	0.7516	0.7015	0.6542
15	0.6805	0.6702	0.5602	0.4916
20	0.6415	0.5716	0.4750	0.3812
25	0.5792	0.5105	0.4020	0.3115
30	0.5260	0.4265	0.3350	0.2510
35	0.4505	0.3990	0.2732	0.1915
40	0.3958	0.3418	0.2416	0.1732
k_{obs} x 10^4 s^{-1}	3.665	4.490	6.068	7.676
Corr. Coef.	0.9948	0.9978	0.9985	0.9966

Table 4.2.8 (g) Effect of Temp. on the rate of oxdn. of MMyB in 50% aq. HOAc.

$[MMyB] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

Temp. (K)	308	313	318	323
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9292	0.9095	0.8902	0.8862
10	0.8475	0.7762	0.7710	0.7554
15	0.7692	0.6856	0.6616	0.6244
20	0.7011	0.6512	0.5955	0.5416
25	0.6535	0.5810	0.5460	0.4592
30	0.5996	0.5415	0.4492	0.3810
35	0.5380	0.4792	0.4015	0.3293
40	0.5092	0.4075	0.3417	0.2754
$k_{obs} \times 10^4$ s^{-1}	2.897	3.512	4.448	5.550
Corr. Coef.	0.9987	0.9931	0.9975	0.9970

Table 4.2.10 Effect of [Benzoic acid] on the oxdn. of C_6H_5CHO in 50% aq. HOAc.

$[C_6H_5CHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3} Temp. = 308 K

$[C_6H_5COOH] \times 10^2$ mol dm^{-3}	0.0	1.0	1.5	2.0
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.9070	0.9065	0.9067	0.9061
10	0.8005	0.8007	0.7995	0.8002
15	0.7432	0.7449	0.7540	0.7474
20	0.6770	0.6860	0.6844	0.6792
25	0.6250	0.6342	0.6459	0.6404
30	0.5622	0.5734	0.5655	0.5713
35	0.5050	0.5188	0.5274	0.5170
40	0.4724	0.4834	0.4950	0.4815
50	0.3986	0.4096	0.4157	0.4116
60	0.3342	0.3487	0.3402	0.3396
$k_{obs} \times 10^4$ s^{-1}	2.993	2.867	2.886	2.913
Corr. Coef.	0.9991	0.9992	0.9984	0.9989

4.5 Oxidation of Acetophenone using Quaternary Ammonium Permanganate

Table 4.5.1 Effect of $[Q^+MnO_4^-]$ on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0 x 10^{-2} mol dm^{-3}, Solvent - Benzene , PTC -TCMAC , Temp. = 303 K

$[Q^+MnO_4^-]$ x 10^3 mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.4010	0.8870	1.3652	1.9608
10	0.3589	0.8011	1.2088	1.7815
20	0.3096	0.6675	0.9989	1.5311
30	0.2654	0.5626	0.8774	1.3100
40	0.2287	0.4802	0.7512	1.0859
50	0.1866	0.4110	0.6470	0.9260
60	0.1642	0.3570	0.5515	0.7950
k_{obs} x 10^4 s^{-1}	2.694	2.755	2.663	2.740
Corr. Coef.	0.9989	0.9988	0.9978	0.9997

Table 4.5.1 Effect of $[Q^+MnO_4^-]$ on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0 x 10^{-2} mol dm^{-3}, Solvent - Benzene , PTC -TBAB , Temp. = 303 K

$[Q^+MnO_4^-]$ x 10^3 mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.4035	0.8912	1.3688	1.9614
10	0.3788	0.7955	1.2612	1.9092
20	0.3410	0.6773	1.1486	1.7105
30	0.3054	0.6454	1.0110	1.5010
40	0.2762	0.6109	0.9151	1.3756
50	0.2445	0.5225	0.8213	1.2114
60	0.2180	0.4546	0.7185	1.0962
k_{obs} x 10^4 s^{-1}	1.846	1.850	1.896	1.811
Corr. Coef.	0.9997	0.9848	0.9990	0.9987

Table 4.5.2 Effect of [AcPh] on the rate of oxdn. of AcPh in Organic solvent

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Solvent – Benzene, PTC – TCMAC, Temp. = 303 K

[AcPh] x 10^2 mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.8870	0.8825	0.8792	0.8705
10	0.8011	0.7890	0.7571	0.7440
20	0.6675	0.5958	0.5150	0.4950
30	0.5726	0.4720	0.3732	0.3542
40	0.4802	0.3680	0.2810	0.2511
50	0.4110	0.2970	0.2015	0.1770
60	0.3570	0.2224	0.1542	0.1233
$k_{obs} \times 10^4$ s^{-1}	2.759	4.133	5.323	5.964
Corr. Coef.	0.9991	0.9995	0.9989	0.9997

Table 4.5.2 Effect of [AcPh] on the rate of oxdn. of AcPh in Organic solvent

$[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Solvent – Benzene, PTC – TBAB, Temp. = 303 K

[AcPh] x 10^2 mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.8912	0.8904	0.8792	0.8701
10	0.7955	0.7900	0.7572	0.7421
20	0.6773	0.6674	0.6212	0.6010
30	0.6454	0.5852	0.5160	0.4840
40	0.6109	0.4800	0.4220	0.3955
50	0.5225	0.4020	0.3158	0.2616
60	0.4546	0.3542	0.2689	0.2260
$k_{obs} \times 10^4$ s^{-1}	1.850	2.790	3.573	4.118
Corr. Coef.	0.9848	0.9984	0.9981	0.9948

Table 4.5.3 Effect of [TCMAC] on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}
Solvent - Benzene Temp. = 303 K

[TCMAC] x 10^3 mol dm^{-3}	2.0	2.5	3.0	3.5
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.8870	0.8862	0.8850	0.8814
10	0.8011	0.8004	0.7915	0.7852
20	0.6675	0.6520	0.6460	0.6314
30	0.5626	0.5515	0.5387	0.5271
40	0.4802	0.4793	0.4561	0.4418
50	0.4110	0.4016	0.3812	0.3645
60	0.3570	0.3317	0.3118	0.3001
k_{obs} x 10^4 s^{-1}	2.755	2.909	3.101	3.216
Corr. Coef.	0.9988	0.9988	0.9994	0.9994

Table 4.5.3 Effect of [TBAB] on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0 x 10^{-2} mol dm^{-3} $[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}
Solvent - Benzene Temp. = 303 K

[TBAB] x 10^3 mol dm^{-3}	2.0	2.5	3.0	3.5
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.8912	0.8903	0.8852	0.8816
10	0.7955	0.7892	0.7754	0.7582
20	0.6773	0.6641	0.6431	0.6255
30	0.6454	0.6283	0.6060	0.5841
40	0.6109	0.5899	0.5642	0.5410
50	0.5225	0.5010	0.4817	0.4602
60	0.4546	0.4305	0.4100	0.3815
k_{obs} x 10^4 s^{-1}	1.850	2.003	2.118	2.279
Corr. Coef.	0.9848	0.9861	0.9859	0.9854

Table 4.5.4 Effect of Solvent on the rate of oxdn. of AcPh in Organic solvents

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC - TCMAC Temp. = 303 K

Organic solvent	Benzene	Toluene	Carbontetra-chloride	Chloroform	Dichloromethane
Intrinsic Dielectric Constant	2.27	2.40	2.22	4.70	8.90
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}				
5	0.8870	0.8890	0.8814	0.8922	0.8910
10	0.8011	0.8342	0.8215	0.8688	0.8570
20	0.6675	0.6984	0.6870	0.7367	0.7154
30	0.5626	0.5960	0.5812	0.6666	0.6346
40	0.4802	0.5266	0.5004	0.5892	0.5587
50	0.4110	0.4570	0.4360	0.5100	0.4890
60	0.3570	0.4070	0.3815	0.4772	0.4377
$K_{obs} \times 10^4$ s^{-1}	2.755	2.406	2.575	1.992	2.203
Corr. Coef.	0.9988	0.9980	0.9987	0.9965	0.9982

Table 4.5.4 Effect of Solvent on the rate of oxdn. of AcPh in Organic solvents

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC - TBAB Temp. = 303 K

Organic solvent	Benzene	Toluene	Carbontetra-chloride	Chloroform	Dichloromethane
Intrinsic Dielectric Constant	2.27	2.40	2.22	4.70	8.90
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}				
5	0.8912	0.8950	0.8962	0.8960	0.8950
10	0.7955	0.8046	0.7994	0.8254	0.8156
20	0.6773	0.6941	0.6895	0.7146	0.7002
30	0.6454	0.6623	0.6552	0.6792	0.6692
40	0.6109	0.6342	0.6269	0.6555	0.6460
50	0.5225	0.5440	0.5360	0.5872	0.5616
60	0.4546	0.4758	0.4660	0.5090	0.4913
$K_{obs} \times 10^4$ s^{-1}	1.850	1.731	1.784	1.539	1.638
Corr. Coef.	0.9848	0.9835	0.9834	0.9831	0.9823

Table 4.5.5 Effect of Substituents on the Benzene ring on the rate of oxidation of AcPh in Organic solvents

[substrate] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC, Solvent – Benzene, Temp. = 303 K

[Substrate] x 10^2 mol dm^{-3}	PNA	MNA	PBA	PCA	AcPh	PMA	PMyA
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}						
3	0.8622	0.8654	-	-	-	-	-
5	-	-	0.8716	0.8732	0.8870	0.8915	0.8992
6	0.7452	0.7613	-	-	-	-	-
9	0.5612	0.6000	-	-	-	-	-
10	-	-	0.7615	0.7752	0.8011	0.8150	0.8398
12	0.4355	0.4699	-	-	-	-	-
15	0.3373	0.3718	-	-	-	-	-
20	0.2519	0.2822	0.5820	0.6013	0.6675	0.6899	0.7510
25	0.2152	0.2374	-	-	-	-	-
30	-	-	0.4532	0.4756	0.5626	-	-
40	-	-	0.3544	0.3872	0.4802	0.5900	0.6443
50	-	-	0.2731	0.3018	0.4110	-	-
60	-	-	0.2248	0.2651	0.3570	0.5092	0.5618
80	-	-	-	-	-	0.4434	0.5010
100	-	-	-	-	-	0.3899	0.4552
k_{obs} x 10^4 s^{-1}	11.215	10.432	4.153	3.703	2.755	1.400	1.182
Corr. Coef.	0.9884	0.9915	0.9993	0.9974	0.9988	0.9878	0.9909

Table 4.5.5 Effect of Substituents on the Benzene ring on the rate of oxidation of AcPh in Organic solvents

[substrate] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

[Substrate] x 10^2 mol dm^{-3}	PNA	MNA	PBA	PCA	AcPh	PMA	PMyA
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}						
3	0.8715	0.8793	-	-	-	-	-
5	-	-	0.8855	0.8902	0.8912	0.9001	0.9025
6	0.7032	0.7209	-	-	-	-	-
9	0.5430	0.5755	-	-	-	-	-
10	-	-	0.7610	0.7795	0.7955	0.8540	0.8682
12	0.4816	0.5223	-	-	-	-	-
15	0.4122	0.4516	-	-	-	-	-
20	0.3090	0.3472	0.6331	0.6546	0.6773	0.7656	0.7854
25	0.1842	0.2481	-	-	-	-	-
30	-	-	0.5904	0.6123	0.6454	-	-
40	-	-	0.5313	0.5600	0.6109	0.7302	0.7690
50	-	-	0.4206	0.4418	0.5225	-	-
60	-	-	0.3266	0.3566	0.4546	0.7106	0.7410
80	-	-	-	-	-	0.6412	0.6712
100	-	-	-	-	-	0.5793	0.6143
k_{obs} x 10^4 s^{-1}	11.062	9.181	2.729	2.533	1.850	0.6870	0.6060
Corr. Coef.	0.9922	0.9966	0.9851	0.9855	0.9848	0.9751	0.9763

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Table 4.5.6 (a) Effect of Temp. on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8870	0.8814	0.8782
10	0.8011	0.7945	0.7718
20	0.6675	0.6462	0.6054
30	0.5626	0.5400	0.4892
40	0.4802	0.4418	0.3806
50	0.4110	0.3830	0.3054
60	0.3570	0.3215	0.2754
$k_{obs} \times 10^4$ s^{-1}	2.755	3.205	3.638
Corr. Coef.	0.9988	0.9987	0.9959

Table 4.5.6 (b) Effect of Temp. on the rate of oxdn. of AcPh in Organic solvent

[AcPh] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8912	0.8901	0.8810
10	0.7955	0.7842	0.7796
20	0.6773	0.6650	0.6562
30	0.6454	0.6314	0.6143
40	0.6109	0.5855	0.5605
50	0.5225	0.4860	0.4432
60	0.4546	0.3918	0.3506
$k_{obs} \times 10^4$ s^{-1}	1.850	2.222	2.544
Corr. Coef.	0.9848	0.9827	0.9841

Table 4.5.7 (a) Effect of Temp. on the rate of oxdn. of PNA in Organic solvent

$[PNA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
3	0.8622	0.8613	0.8544
6	0.7452	0.7056	0.6900
9	0.5612	0.5138	0.4842
12	0.4355	0.3810	0.3362
15	0.3373	0.2742	0.2130
18	-	0.2005	0.1856
20	0.2519	-	-
21	-	0.1754	0.1432
25	0.2152	-	-
$k_{obs} \times 10^4$ s^{-1}	11.215	15.720	17.480
Corr. Coef.	0.9884	0.9962	0.9931

Table 4.5.7 (b) Effect of Temp. on the rate of oxdn. of PNA in Organic solvent

$[PNA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
3	0.8715	0.8624	0.8608
6	0.7132	0.7088	0.6915
9	0.5430	0.5204	0.4866
12	0.4816	0.3850	0.3402
15	0.4122	0.2811	0.2214
18	-	-	-
20	0.3090	0.2118	0.1915
21	-	0.1842	0.1516
25	0.1842	-	-
$k_{obs} \times 10^4$ s^{-1}	11.062	15.210	16.620
Corr. Coef.	0.9922	0.9963	0.9904

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Table 4.5.8 (a) Effect of Temp. on the rate of oxdn. of MNA in Organic solvent

$[MNA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
3	0.8654	0.8612	0.8561
6	0.7613	0.7404	0.7322
9	0.6000	0.5815	0.5606
12	0.4699	0.4432	0.4088
15	0.3718	0.3524	0.3017
18	-	0.2710	-
20	0.2822	-	0.2236
21	-	0.2216	-
25	0.2374	-	
$k_{obs} \times 10^4$ s^{-1}	10.432	13.070	15.160
Corr. Coef.	0.9915	0.9983	0.9969

Table 4.5.8 (b) Effect of Temp. on the rate of oxdn. of MNA in Organic solvent

$[MNA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
3	0.8793	0.8704	0.8656
6	0.7209	0.7150	0.6960
9	0.5755	0.5562	0.5244
12	0.5223	0.5015	0.4532
15	0.4516	0.4333	0.3845
18	-	0.3180	0.2632
20	0.3472	-	-
21	0.2481	0.2398	0.1946
25	-	-	-
$k_{obs} \times 10^4$ s^{-1}	9.181	11.380	13.360
Corr. Coef.	0.9966	0.9906	0.9919

Table 4.5.9 (a) Effect of Temp. on the rate of oxdn. of PCA in Organic solvent

$[PCA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8716	0.8701	0.8666
10	0.7615	0.7542	0.7431
20	0.5820	0.5709	0.5423
30	0.4532	0.4418	0.4014
40	0.3544	0.3402	0.3025
50	0.2731	0.2632	0.2240
60	0.2249	0.2053	0.1602
$k_{obs} \times 10^4$ s^{-1}	4.153	5.392	6.252
Corr. Coef.	0.9993	0.9888	0.9909

Table 4.5.9 (b) Effect of Temp. on the rate of oxdn. of PCA in Organic solvent

$[PCA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8855	0.8814	0.8793
10	0.7610	0.7502	0.7316
20	0.6331	0.6205	0.6083
30	0.5904	0.5795	0.5515
40	0.5313	0.5144	0.4941
50	0.4206	0.4057	0.3852
60	0.3266	0.2958	0.2810
$k_{obs} \times 10^4$ s^{-1}	2.729	3.700	3.861
Corr. Coef.	0.9851	0.9884	0.9884

Table 4.5.10 (a) Effect of Temp. on the rate of oxdn. of PBA in Organic solvent

$[PBA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8732	0.8710	0.8662
10	0.7752	0.7622	0.7510
20	0.6013	0.5840	0.5711
30	0.4756	0.4612	0.4502
40	0.3872	0.3554	0.3486
50	0.3018	0.2842	0.2655
60	0.2651	0.2358	0.2145
$k_{obs} \times 10^4$ s^{-1}	3.703	4.932	5.239
Corr. Coef.	0.9974	0.9846	0.9888

Table 4.5.10 (b) Effect of Temp. on the rate of oxdn. of PBA in Organic solvent

$[PBA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8902	0.8890	0.8845
10	0.7795	0.8115	0.7601
20	0.6546	0.6680	0.6342
30	0.6123	0.5643	0.5426
40	0.5600	0.4844	0.4611
50	0.4418	0.4152	0.3720
60	0.3566	0.3615	0.3356
$k_{obs} \times 10^4$ s^{-1}	2.533	3.058	3.588
Corr. Coef.	0.9855	0.9825	0.9838

Table 4.5.11(a) Effect of Temp. on the rate of oxdn. of PMA in Organic solvent

$[PMA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8915	0.8902	0.8862
10	0.8150	0.7966	0.7815
20	0.6899	0.6793	0.6642
40	0.5900	0.6484	0.6295
60	0.5092	0.6158	0.5993
80	0.4434	0.5286	0.5097
100	0.3899	0.4626	0.4402
$k_{obs} \times 10^4$ s^{-1}	1.400	1.800	1.907
Corr. Coef.	0.9878	0.9843	0.9832

Table 4.511 (b) Effect of Temp. on the rate of oxdn. of PMA in Organic solvent

$[PMA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.9001	0.8955	0.8916
10	0.8540	0.8510	0.8402
20	0.7656	0.7542	0.7466
40	0.7302	0.7414	0.7308
60	0.7106	0.7392	0.7235
80	0.6412	0.6758	0.6566
100	0.5793	0.6106	0.5933
$k_{obs} \times 10^4$ s^{-1}	0.6870	1.017	1.090
Corr. Coef.	0.9751	0.9655	0.9716

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Table 4.5.12(a) Effect of Temp. on the rate of oxdn. of PMyA in Organic solvent

$[PMyA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8992	0.8915	0.8896
10	0.8398	0.8376	0.8253
20	0.7510	0.7480	0.7372
40	0.6443	0.6958	0.6793
60	0.5618	0.6302	0.6011
80	0.5010	0.5911	0.5652
100	0.4552	0.5463	0.5074
$k_{obs} \times 10^4$ s^{-1}	1.182	1.462	1.658
Corr. Coef.	0.9909	009959	0.9969

Table 4.512 (b) Effect of Temp. on the rate of oxdn. of PMyA in Organic solvent

$[PMyA] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.9025	0.8992	0.8925
10	0.8682	0.8615	0.8532
20	0.7854	0.7748	0.7611
40	0.7690	0.7610	0.7436
60	0.7410	0.7499	0.7245
80	0.6712	0.7022	0.6802
100	0.6143	0.6505	0.6206
$k_{obs} \times 10^4$ s^{-1}	0.6060	0.8820	0.9940
Corr. Coef.	0.9763	0.9737	0.9786

4.6 Oxidation of Benzaldehyde using Quaternary Ammonium Permanganate

Table 4.6.1 Effect of $[Q^+MnO_4^-]$ on the rate of oxdn. of PhCHO in Org. solvent

[PhCHO] = 1.0 x 10^{-2} mol dm^{-3} , Solvent - Benzene, PTC -TCMAC , Temp.= 303 K

$[Q^+MnO_4^-]$ x 10^3 mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.4005	0.8750	1.3553	1.9509
10	0.3569	0.8061	1.2078	1.7715
15	0.3010	0.6595	0.9889	1.5204
20	0.2558	0.5686	0.8776	1.2990
25	0.2307	0.4902	0.7612	1.0699
30	0.1912	0.4010	0.6440	0.9380
35	0.1599	0.3621	0.5415	0.7750
k_{obs} x 10^4 s^{-1}	5.078	5.289	5.039	5.135
Corr. Coef.	0.9964	0.9981	0.9989	0.9961

Table 4.6.1 Effect of $[Q^+MnO_4^-]$ on the rate of oxdn. of PhCHO in Org. solvent

[PhCHO] = 1.0 x 10^{-2} mol dm^{-3} , Solvent - Benzene , PTC -TBAB, Temp.= 303 K

$[Q^+MnO_4^-]$ x 10^3 mol dm^{-3}	0.5	1.0	1.5	2.0
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.4005	0.8899	1.3589	1.9514
10	0.3678	0.7845	1.2512	1.9082
15	0.3310	0.6675	1.1460	1.7505
20	0.3034	0.6394	1.0514	1.5020
25	0.2661	0.6009	0.9089	1.3656
30	0.2345	0.5125	0.8313	1.2135
35	0.2069	0.4446	0.7098	1.0882
k_{obs} x 10^4 s^{-1}	3.393	3.343	3.469	3.354
Corr. Coef.	0.9967	0.9850	0.9983	0.9895

Table 4.6.2 Effect of [PhCHO] on the rate of oxdn. of PhCHO in Org. solvent

$[MnO_4^-]$=1.0 x 10^{-3} mol dm^{-3}, Solvent – Benzene, PTC – TCMAC, Temp.= 303 K

[PhCHO] x 10^2 mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.8750	0.8725	0.8752	0.8695
10	0.8061	0.7850	0.7501	0.7460
15	0.6595	0.5758	0.5120	0.4920
20	0.5686	0.4690	0.3692	0.3552
25	0.4902	0.3580	0.2840	0.2501
30	0.4010	0.2950	0.2115	0.1700
35	0.3621	0.2219	0.1332	0.1213
k_{obs} x 10^4 s^{-1}	5.289	7.588	10.15	11.17
Corr. Coef.	0.9981	0.9961	0.9961	0.9954

Table 4.6.2 Effect of [PhCHO] on the rate of oxdn. of PhCHO in Org. solvent
$[MnO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3}, Solvent – Benzene, PTC – TBAB, Temp. = 303 K

[PhCHO] x 10^2 mol dm^{-3}	1.0	1.5	2.0	2.5
Time (min)	$[MnO_4^-]$ x 10^3 mol dm^{-3}			
5	0.8899	0.8884	0.8592	0.8611
10	0.7845	0.7760	0.7422	0.7411
15	0.6675	0.6544	0.6112	0.6110
20	0.6394	0.5742	0.5140	0.4790
25	0.6009	0.4600	0.4200	0.3895
30	0.5125	0.4000	0.3338	0.2556
35	0.4446	0.3342	0.2609	0.2220
k_{obs} x 10^4 s^{-1}	3.343	5.335	6.724	7.730
Corr. Coef.	0.9850	0.9972	0.9949	0.9875

Table 4.6.3 Effect of [TCMAC] on the rate of oxdn. of PhCHO in Org. solvent

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
Solvent - Benzene Temp. = 303 K

$[TCMAC] \times 10^3$ mol dm^{-3}	2.0	2.5	3.0	3.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.8750	0.8852	0.8810	0.8804
10	0.8061	0.8014	0.7825	0.7742
15	0.6595	0.6500	0.6450	0.6214
20	0.5686	0.5535	0.5657	0.5221
25	0.4902	0.4773	0.4541	0.4388
30	0.4010	0.4066	0.3792	0.3605
35	0.3621	0.3326	0.3108	0.3011
$k_{obs} \times 10^4$ s^{-1}	5.289	5.392	5.761	6.022
Corr. Coef.	0.9981	0.9976	0.9980	0.9981

Table 4.6.3 Effect of [TBAB] on the rate of oxdn. of PhCHO in Org. solvent

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
Solvent - Benzene Temp. = 303 K

$[TBAB] \times 10^3$ mol dm^{-3}	2.0	2.5	3.0	3.5
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}			
5	0.8899	0.8900	0.8752	0.8716
10	0.7845	0.7849	0.7554	0.7482
15	0.6675	0.6635	0.6231	0.6235
20	0.6394	0.6278	0.5960	0.5521
25	0.6009	0.5885	0.5442	0.5320
30	0.5125	0.5009	0.4617	0.4502
35	0.4446	0.4301	0.4000	0.3785
$k_{obs} \times 10^4$ s^{-1}	3.343	3.623	3.865	4.126
Corr. Coef.	0.9850	0.9868	0.9872	0.9878

Table 4.6.4 Effect of Solvent on the rate of oxdn. of PhCHO in Org. solvents

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC - TCMAC Temp. = 303 K

Organic solvent	Benzene	Toluene	Carbontetra-chloride	Chloroform	Dichloromethane
Intrinsic Dielectric Constant	2.27	2.40	2.22	4.70	8.90
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}				
5	0.8750	0.8851	0.8784	0.8890	0.8912
10	0.8061	0.8289	0.8255	0.8555	0.8654
15	0.6595	0.6869	0.6630	0.7145	0.7342
20	0.5686	0.5860	0.5752	0.6255	0.6645
25	0.4902	0.5254	0.5024	0.5564	0.5852
30	0.4010	0.4554	0.4240	0.4780	0.5240
35	0.3621	0.4064	0.3725	0.4298	0.4522
$k_{obs} \times 10^4$ s^{-1}	5.289	4.636	4.928	3.869	2.203
Corr. Coef.	0.9981	0.9954	0.9957	0.9901	0.9982

Table 4.6.4 Effect of Solvent on the rate of oxdn. of PhCHO in Org. solvents

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC - TBAB Temp. = 303 K

Organic solvent	Benzene	Toluene	Carbontetra-chloride	Chloroform	Dichloromethane
Intrinsic Dielectric Constant	2.27	2.40	2.22	4.70	8.90
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}				
5	0.8899	0.8890	0.8925	0.8860	0.8850
10	0.7845	0.8023	0.7940	0.8244	0.8106
15	0.6675	0.6922	0.6795	0.7126	0.7032
20	0.6394	0.6635	0.6553	0.6592	0.6651
25	0.6009	0.6211	0.6259	0.6455	0.6440
30	0.5125	0.5355	0.5264	0.5272	0.5636
35	0.4446	0.4658	0.4620	0.5090	0.4963
$k_{obs} \times 10^4$ s^{-1}	3.343	3.097	3.189	2.928	2.721
Corr. Coef.	0.9850	0.9833	0.9838	0.9812	0.9838

Table 4.6.5 Effect of Substituents on the Benzene ring on the rate of oxidation of PhCHO in Organic solvents

[substrate] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC , Solvent – Benzene, Temp. = 303 K

[Substrate] x 10^2 mol dm^{-3}	PCB	MNB	PNB	PMB	PhCHO	PMyB	MMyB
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}						
3	0.8512	0.8562	-	-	-	-	-
5	-	-	0.8654	0.8652	-	0.8845	0.8851
6	0.7325	0.7559	-	-	0.8750	-	-
9	0.5545	0.5985	-	-	-	-	-
10	-	-	0.7541	0.7655	0.8061	0.8020	0.8245
12	0.4263	0.4568	-	-	-	-	-
15	0.3252	0.3685	0.5562	0.6121	0.6595	0.6755	0.6566
18	0.2469	0.2814	-	-	0.5686	-	-
20	0.2056	0.2298	0.4465	0.4656	0.4902 0.4010 0.3621	0.5863	0.6332
21	-	-	0.3444	0.3875	-	-	-
25	-	-	0.2751	0.2968	-	0.5210	0.5526
30	-	-	0.2265	0.2456	-	0.4521	0.4998
35	-	-	-	-	-	0.3677	0.4550
k_{obs} x 10^4 s^{-1}	13.570	12.580	7.872	6.805	5.289	3.703	2.510
Corr. Coef.	0.9973	0.9972	0.9979	0.9964	0.9981	0.9973	0.9951

Table 4.6.5 Effect of Substituents on the Benzene ring on the rate of oxidation of PhCHO in Organic solvents

[substrate] = 1.0×10^{-2} mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

[Substrate] x 10^2 mol dm^{-3}	PCB	MNB	PNB	PMB	PhCHO	PMyB	MMyB
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}						
3	0.8655	0.8662	-	-	-	-	-
5	-	-	0.8754	0.8852	0.8899	0.8895	0.8951
6	0.7002	0.7199	-	-	-	-	-
9	0.5325	0.5765	-	-	-	-	-
10	-	-	0.7641	0.7855	0.7845	0.8450	0.8645
12	0.4753	0.4501	-	-	-	-	-
15	0.3082	0.4685	0.6262	0.6421	0.6675	0.7500	0.7666
20	0.2999	0.3514	-	-	-	-	-
25	0.1765	0.2398	0.5465	0.5656	0.6394	0.6821	0.7332
30	-	-	0.4444	0.4675	0.6009	-	-
35	-	-	0.3751	0.3968	0.5125	0.6656	0.6826
40	-	-	0.3265	0.3456	0.4446	0.6421	0.6698
50	-	-	-	-		0.5877	0.6050
60							
$k_{obs} \times 10^4$ s^{-1}	13.06	10.91	5.181	4.805	3.343	1.235	1.082
Corr. Coef.	0.9765	0.9872	0.9856	0.9857	0.9850	0.9878	0.9856

Table 4.6.6 (a) Effect of Temp. on the rate of oxdn. of PhCHO in Org. solvent

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TCMAC Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8750	0.8865	0.8689
10	0.8061	0.7854	0.7700
15	0.6595	0.6432	0.6021
20	0.5686	0.5399	0.4789
30	0.4902	0.4421	0.3705
35	0.4010	0.3822	0.3026
40	0.3621	0.3196	0.2654
$k_{obs} \times 10^4$ s^{-1}	5.289	5.818	7.254
Corr. Coef.	0.9981	0.9969	0.9969

Table 4.6.6 (b) Effect of Temp. on the rate of oxdn. of PhCHO in Org. solvent

$[PhCHO] = 1.0 \times 10^{-2}$ mol dm^{-3} $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}
PTC – TBAB Solvent – Benzene

Temp. (K)	303	308	313
Time (min)	$[MnO_4^-] \times 10^3$ mol dm^{-3}		
5	0.8899	0.8895	0.8802
10	0.7845	0.7755	0.7754
15	0.6675	0.6625	0.6523
20	0.6394	0.6245	0.6056
25	0.6009	0.5785	0.5565
30	0.5125	0.4752	0.4455
35	0.4446	0.3925	0.3465
40			
$k_{obs} \times 10^4$ s^{-1}	3.343	4.222	6.544
Corr. Coef.	0.9850	0.9829	0.9841