KINETIC STUDIES ON THE MONOCHROMATE OXIDATION OF PRIMARY ALCOHOLS UNDER PHASE TRANSFER CATALYSIS

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Submitted to the Faculty of Science, University of Calicut
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By

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DECLARATION

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

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CERTIFICATE

The thesis presented herewith embodies the observations on **Kinetic studies on the monochromate oxidation of primary alcohols under phase transfer catalysis**. This is an authentic record of the research work carried out by **Bijudas. K.** under my supervision in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry of the University of Calicut. This work or part thereof has not been presented for the award of any other degree.

Dr. T.D. Radhakrishnan Nair

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PREFACE

This thesis reports in four chapters the results of the kinetic investigations carried out by the author on the kinetic studies of the monochromate oxidation of primary alcohols under phase transfer catalysis.

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

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

The last chapter presents the results and discussion of the work done. Mechanism and rate law of the oxidation of primary alcohols in non-polar organic media and in aqueous acetic acid medium have been discussed separately. This is followed by summary, references and appendix of kinetic data.

LIST OF ABBREVIATIONS

PTC	: Phase Transfer Catalysis
PT	: Phase Transfer
TBAB	: Tetrabutylammonium bromide
TBPB	: Tetrabutylphosphonium bromide
Q^+	: Quaternary onium cation
$Q^+HCrO_4^-$	: Quaternary onium monochromate
$PhCH_2OH$ or BA	: Benzyl alcohol
RCH_2OH	: Primary alcohol
p-$OCH_3C_6H_4CH_2OH$ or P-OCH_3 BA	: p-methoxybenzyl alcohol
p-$CH_3C_6H_4CH_2OH$ or p-CH_3 BA	: p-methylbenzyl alcohol
p-$ClC_6H_4CH_2OH$ or p-Cl BA	: p-chlorobenzyl alcohol
p-$NO_2C_6H_4CH_2OH$ or p-NO_2 BA	: p-nitrobenzyl alcohol
Aq. HOAc	: Aqueous acetic acid

CONTENTS

CHAPTER I

INTRODUCTION

1.0. PHASE TRANSFER CATALYSIS

Oxidation of organic compounds using different oxidising agents is of great significance synthetically. The use of catalysts, both homogeneous and heterogeneous can bring about remarkable improvements by way of product purity, yield, ease of preparation, ease of reactivity etc. The introduction of phase transfer catalysts (PT catalysts) about fifty decades ago has revolutionalised organic synthesis in respect of anion dissolution in non-polar solvents coupled with their ability to catalyse the reactions. The choice of phase transfer catalysts helped in the synthesis of many organic materials in a big way, especially related to pharmaceuticals and fine chemicals. This unique ability to catalyse certain reactions selectively has many advantages in synthetic processes. The fact that these materials in the form of quaternary ammonium or phosphonium salts have many advantages compared to the classical phase transfer catalysts,viz the crown ethers which are toxic, costly and relatively difficult to prepare.

Phase transfer catalysis (PTC) is a technique which can be used to carry out a variety of chemical reactions under mild conditions with improved results. PTC technique is now utilized in many applications, from research in chemistry to full-scale synthetic production of chemicals like pharmaceuticals, fine chemicals, polymers, dyes etc. It is also of great importance to develop technological methods to minimize problems related to

environmental pollution. PTC technique is used in pollution prevention, pollution treatment and removal or destruction of impurities in waste and product streams. Cost reduction and pollution prevention are the two most powerful driving forces in the chemical industry today, and these can be achieved to a great extent by the phase transfer catalysis technique, if properly adopted.

The technique of phase transfer catalysis has been in use for the commercial manufacture of chemicals worth $ 10 billion or more per year. The scope of PTC technology is most appropriately understood by considering a range of reactions for which PTC is made applicable. The 1700 patents and the nearly 8000 publications on PTC fall into 30 or so major reaction categories, most of which are used in the production of monomers, polymers, agricultural chemicals, pharmaceuticals, additives, flavours and fragrances, dyes, explosives, surfactants, petrochemicals, rubber and wide range of other products related to fine organic chemicals.

1.1. NATURE OF PHASE TRANSFER CATALYSIS

The phase transfer catalyst is a vehicle and it transfers anionic reactants into non-polar media and the transferred anions make the reaction to take place with ease. This is quite significant when we see that reactions between substrate located in an organic phase and reactant located in the aqueous phase are slow and ineffective.

The simple approach used earlier to accelerate rates of reactions of a two phase process (aqueous phase-organic phase) was to effect rapid stirring, so as to increase interaction between the reactants.[1] A different approach was to employ a dipolar aprotic solvent such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, hexamethylphosphoramide (HMPA) etc. which are effective in liberating reactive anions by solvating cations.[2] These solvents ensure mutual miscibility and solubility of both ionic salts and organic substrates and help to increase the rate of reaction. They solvate cationic part of the salt leaving the anion in a relatively 'bare' or desolvated situation. However, there are considerable practical disadvantages connected with the use of these solvents. The drawbacks of using these solvents are that they are costly, difficult to purify, and toxic in nature. Moreover it is difficult to keep such solvents in anhydrous state and difficult to recover.

Phase transfer catalysis can easily overcome the problems in such situations. This technique has been shown to enhance the reactivity in different types of reactions.[3-13] The method involves transfer of anions from the polar medium into the non-polar organic media in the form of an ion-pair with the cationic moiety of the catalyst with appropriate size and lipophilicity. The anions thus transferred and poorly solvated in the organic media exhibit greater reactivity. This enables the substrate to react faster in the non-polar media in the presence of PT catalyst.

The commonly used phase transfer catalysts are quaternary ammonium or phosphonium salts[4-6,14,15] (generally known as quaternary onium salts). Compounds like n-alkyl phosphoramides (particularly n-dodecyl or n-hexadecyl), methylene bridged phosphorous and sulphur oxides, tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1)[16] are also used as phase transfer catalysts. The classical phase transfer catalysts are the crown ethers,[17-20] cryptates etc. when used in catalytic quantities can act as phase transfer materials. Polyethylene glycols[21-24], otherwise known as poor chemist's crown also has the properties, though to a much lower extent as PT catalysts.

The advantages of PTC over the conventional methods are as follows.

- Use of expensive and toxic anhydrous dipolar aprotic solvents can be avoided.
- High reactivity and selectivity of the species ensured.
- Elimination of dangerous, inconvenient and expensive reactants such as NaH, $NaNH_2$, t-BuOK, R_2NLi etc. can be done and NaOH, KOH, K_2CO_3 etc. can be used.
- Synthetically easier to work up as the reaction requires lower temperature.
- Activation energies are considerably reduced.
- Ensure high yield of the desired product and minimise industrial waste.

The simplicity of the procedure, the increased reaction rates, the high yield of the product and the comparatively low cost of the process make PTC a pervasive and widely accepted technique in the chemical industry. The PTC technique has been found to be applicable to a variety of reactions like nucloeophilic substitution[25-32], elimination[33-38], carbene reactions[39-44], esterification[45-48], etherification[49-53], alkylation[54-61], condensation[62-65], addition[66-68], polymerization[69-74], isomerisation[75-78], hydrolysis[79-82], oxidation-reduction,[83-86] etc.

1.2. BRIEF HISTORY OF PHASE TRANSFER CATALYSIS

The technique of phase transfer catalysis, a convenient synthetic method has originated only in the later part of the last century. The foundations of the technique were laid by M. Makosza, C.M. Starks and A. Brandstrom in the mid 1960's.

Makosza and coworkers in 1965 initiated a systematic exploration of alkylations and subsequently of other reactions in two phase systems containing mainly concentrated aqueous alkali metal hydroxides. The descriptive term they originally used were 'catalytic two-phase reactions', 'catalytic alkylation of anions' and 'catalytic generation of carbenes'.[87]

Simultaneously Charles M. Starks took patents on 'catalysis of heterogeneous reactions'.[88] Starks has introduced the term 'phase transfer catalysis' for the first time. Further more, he gave a mechanistic concept

unifying the different reactions under PTC. This provided an enormous impetus to the development of this technique.

At the same time A. Brandstrom developed a process called 'ion-pair extraction' and this method logically leads to PTC technique.[89] The ion-pair extraction method is used to extract anions from an aqueous layer into non- polar organic solvents like chloroform or methylene chloride. Most of the anions can be extracted as ion-pairs into the organic phase, with quaternary ammonium as cationic part. The ion-pairs have a tendency to associate in the organic phase and hence to overcome the unfavourable extraction barriers.

Another piece of work related to phase transfer catalysis is that of Gibson and Hosking.[90] They showed that triphenylmethylarsonium permanganate can be prepared, isolated and dissolved in chloroform, where it can act as an excellent oxidising agent.

1.3. PRINCIPLE OF PHASE TRANSFER CATALYSIS

The working of phase transfer catalysis involving quaternary onium salts is based on the formation of certain equilibria. Usually PT catalysts are soluble in water as well as in non-polar media. However, most of the organic substrates dissolve only in organic solvents. When a solution of the reactant inorganic anion is mixed with a solution of the organic substrate in organic medium, they form two phases. The aqueous phase is a reservoir of the

nucleophile and the organic phase contains the substrate. Since the anionic aqueous phase is immiscible with the substrate containing organic phase, there will be practically no reaction in the absence of any interfacial phenomena[91]. In such circumstances if a small amount of quaternary ammonium or phosphonium halide or bisulphate, which contains a lipophilic cation is added to the heterogeneous two phase system, rapid reaction takes place. Since the lipophilic cation enjoys solubility both in aqueous and in organic phases, it exchanges its anion with the excess of anion in the aqueous salt solution and bring it for reaction in the organic phase. The quaternary ion is often called as 'quat' and is represented by the symbol 'Q'. The exchange of anion is an equilibrium process as shown in equation 1.1.

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

The anion paired with Q^+ is transferred into the organic phase. A second equilibrium termed phase transfer equilibrium then follows and is shown in equation 1.2

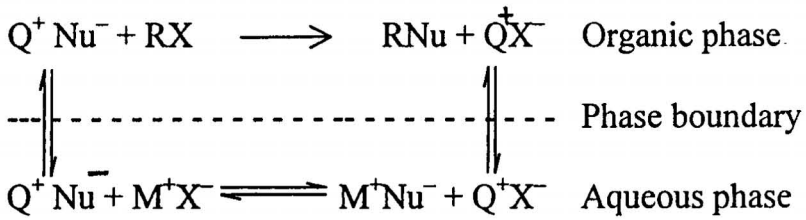
$$Q^+Nu^-_{(aq)} \rightleftharpoons Q^+Nu^-_{(org)} \qquad (1.2)$$

Once the nucleophile or base (represented by Nu) is in non-polar organic media, the reaction (equation 1.3) takes place leading to product formation. In the case of a nucleophilic substitution reaction, Q^+ would ultimately be paired with the nucleophile, thus generating the Q^+X^-, which is subjected to further equilibrium as shown in equation 1.4.

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

$$Q^+X^-_{(org)} \rightleftharpoons Q^+X^-_{(aq)} \quad (1.4)$$

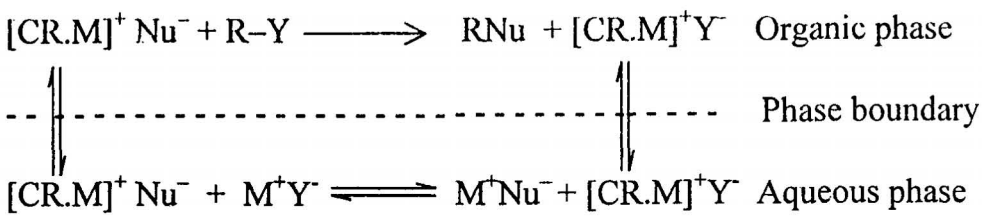
These equilibria and consequent chemical process have been shown by Starks in a classic diagram of phase transfer catalytic cycle shown in scheme 1.1 and is known after him.



Scheme 1.1. Stark's phase transfer catalytic cycle

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

Crown ethers also act in a similar manner to act as phase transfer agents. However the mode of action is different. They envelop the cation and make it larger, softer and more soluble in the organic phase. The phase transfer cycle using a crown ether can be represented in scheme 1.2 in which CR represents the crown.



Scheme 1.2. Phase transfer catalytic cycle with crown ethers

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 stabilising interactions and the anion is therefore more nucleophilic than it would be in water or in alcohol. These anions are known as 'naked' anions or 'bare' anions.

There are two basic requirements for a substance to act as a PT catalyst. The catalyst must be able to transfer one of the reactants from its normal phase into the normal phase of the other reactant and the transferred reagent in the new phase must be available in a highly active form. In order to fulfil these requirements, at first, the PT catalyst must be cationic and must have enough organic structure so that the catalyst can be substantially partitioned into the organic phase with the desired anion. Secondly the effective cation-anion binding must be 'loose' enough to allow high anion reactivity.[92] In addition to the above essential requirements, additional parameters like stability of the catalyst under the reaction conditions,

availability of the catalyst, cost, ease of removal or recovery and selectivity in catalytic activity etc. are to be considered.

1.4. QUATERNARY SALTS AS PT CATALYSTS[93-97]

Numerous quaternary ammonium, phosphonium, antimonium, bismathonium and tertiary sulphonium salts have been claimed to be PT catalysts. However, in practice only a limited number of ammonium and phosophonium salts are widely being used [89,97,98]. This is based on some factors involved in their anion transfer ability, reactivity, stability etc. The simple notation, $R_4N^+X^-$ and $R_4P^+X^-$ are used for ammonium and phosphonium salts respectively.

1.4.1. Factors in the selection of quaternary salts as PT catalyst

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

a) Various combination of R groups

The primary requirement of the groups R is that they collectively should 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. A catalyst, which is soluble in organic phase

will be better in phase transfer catalysed reactions involving anion transfer from aqueous to organic phase. Commonly used quaternary salts have a total of 10-30 carbon atoms.

According to Herriot and Picker,[32] the larger R groups with almost symmetric structure are most effective both in anion transfer and in reactivity. Quaternary salts of the type $R\text{-}N^{+}(R^{1})_{3}X^{-}$ in which $R^{1} >> R$ are frequently used because of their ease of preparation or commercial availability and their efficiency in reactions. The striking effect of even small changes in carbon structure is illustrated from the increase in the distribution ratio (α).

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

The ratio increases by a factor of about 2 for each CH_2 group added in a given homologous series.[99] The organic structure of the catalyst cation not only affects its ability to transport an anion from the aqueous phase to the organic phase, but also it strongly affects the rate of the organic phase reactions. Catalyst with R^{1} is butyl or larger appears to activate anions more strongly because they provide for 'near-maximum' cation-anion inter ionic distances. Ugelstad *et al*[92] found that the high reactivity of the quaternary salts resulted from the greater distance of separation of the anion and cation which reduces the cation-anion interaction energy as compared to the potassium salt.

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

$$E = e^2N/\varepsilon r = \frac{33.18}{\varepsilon r} \text{kcal mol}^{-1}$$

Where r is the effective distance separating the centres of positive and negative charges expressed in A°, ε is the dielectric constant of the medium employed, N is the Avogadro's number and e is the charge of the electron. This expression shows that cation-anion interaction energy is inversely proportional to r and ε. For quaternary salts r is generally greater and hence cation-anion interaction energy is considerably reduced in a particular solvent, which will appear in the reduction of the free energy of activation for displacement reaction by that amount and hence rate is increased.

Quaternary salts with cationic part as tetrabutyl, trioctylmethyl, tricaprylylmethyl etc. are more useful when the organic phase reaction is very slow. Aryl substituted quaternary salts are usually poor PT catalysts for simple displacement reactions for reasons which are not clear. The salts having one long alkyl group and three methyl or ethyl groups or one pyridyl group at the quaternary centre are rather good emulsifying agents but often are poor PT catalysts. This is due to their tendency to form micelles and

remain in the aqueous phase or if salted out of the aqueous phase, they may even form a third phase if the organic phase is relatively non polar.

b) Different central onium atom

Quaternary ammonium and phosphonium salts have been successfully used as PT catalysts. Commercially, ammonium salts are more widely available in a large variety of organic structures and are less expensive. Phosphonium salts are thermally stable up to 150-170°C, where as ammonium salts lose their activity at temperature greater than 110°C. This difference has much significance in industry, since reaction rates can be increased by conducting reactions under pressure, which invariably causes an increase in temperature. Phosphonium salts are more sensitive to hydroxide ions and are irreversibly converted into R_3PO under alkali conditions.[100,101] So R_4N^+ catalysts are preferred over R_4P^+ in strong alkaline medium.

c) Different anions in the original catalyst

The activity of a quaternary salt as a PT catalyst depends 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 concept[102], so that this cation tends to pair with the softest anions available in the solution and transfer it into the organic phase. Therefore catalysts in the iodide form show less activity than

those of in the chloride or bromide form in displacement reactions. The more commonly used catalysts have chloride, bromide or hydrogen sulphate as the anion moiety.

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

$$R_4N^+ I^-_{(org)} + OH^-_{(aq)} \rightleftharpoons R_4N^+OH^-_{(org)} + I^-_{(aq)} \qquad (1.5)$$

The $[OH^-]/[I^-]$ exchange coefficient is low, only 0.002% of the catalyst will be in the active $R_4N^+OH^-$ form. But if $R_4N^+Cl^-$ is used as PT catalyst, about 50% of the catalyst will be in the active $R_4N^+OH^-$ form. The approximate exchange coefficient (α) of the various active anions associated with the catalyst cation (Q^+ = TBA) is given below.[32]

System	α
MnO_4^- / Cl^-	200
ClO^- / Cl^-	2.5
OH^- / I^-	0.002
OH^- / Cl^-	5

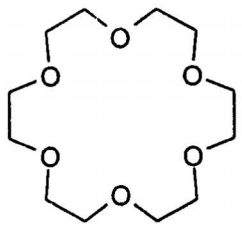
d) Polarity of the organic phase

The solubility and partitioning behaviour of the quaternary salts are markedly affected by slight changes in the nature of organic phase. Solubility and partitioning of quaternary salts are increased by increasing the polarity of the aprotic organic phase. Commonly used solvents for PTC reactions are aromatic solvents (benzene, toluene, o-dicholrobenzene) and chlorocarbons (dichloromethane, 1,2-dichloroethane, chloroform etc.). Chlorocarbons show higher extraction power and can be easily removed. Brandstrom[103] has determined a large number of apparent extraction constants between water and various solvents using tetrabutylammonium bromide as PT catalyst.

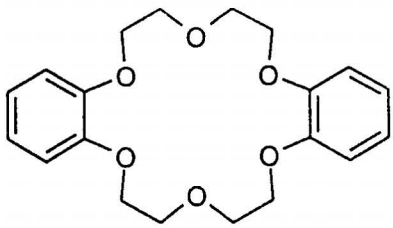
1.5. CROWN ETHERS AS PT CATALYSTS

Crown ethers[17-20] (macrocyclic ethers) are large heterocyclic ring compounds having several oxygen atoms usually in a regular pattern. They have the property of forming complexes with a variety of cationic substrates, like alkali metal cations, alkaline earth cations or ammonium ions and can dissolve homogenously 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 ion.

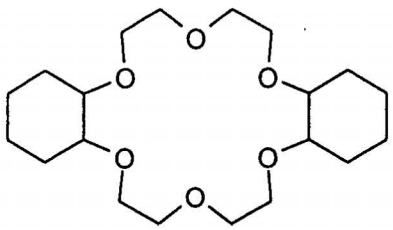
The common commercially available crown ethers are 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6 and 15-crown-5.



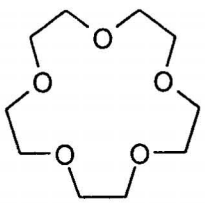
18-crown-6



Dibenzo-18-crown-6



Dicyclohexano-18-crown-6



15-crown-5

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

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

The crown ethers and the quaternary ammonium salts have many similarities in activity as phase transfer catalysts. However, the high cost, high toxicity and difficulty in preparation are some of the factors against crown ethers for their choice as PT catalysts.

1.6. PHASE TRANSFER CATALYSIS APPLIED TO OXIDATION REACTIONS

It has been reported that many inorganic oxidants such as hypochlorite, chromic acid, chromate, dichromate, hydrogen peroxide, permanganate, bromate, iodate etc. can be transferred into organic phase using PT catalysts and oxidation reactions can be carried out smoothly in organic phase. This method is applicable to the oxidation of many type of compounds like olefins, oxoacids, unsaturated esters, aliphatic and aromatic alcohols and carbonyl compounds.

1.7. PHASE TRANSFER ASSISTED CHROMATE OXIDATION

Chromate is one of the most useful selective oxidizing agent in organic synthesis. The major use of chromium compounds in synthetic chemistry is in the oxidation of primary and secondary alcohols to aldehydes and ketones. The use of chromate ions as a selective oxidant for a variety of organic reactions have been reviewed by Stewart,[104] D.G. Lee,[105] Waters[106] and K.B.Wiberg.[107]

Numerous studies have been made on the extraction of $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ into organic solutions by quaternary ammonium cations[108-110] like triphenylsulphonium,[111] triphynelselenonium,[112] triphenyltin,[113] di-π-cyclopentadienyltitanium cations[114] and various amines.[115] These studies indicate that $HCrO_4^-$ and $HCr_2O_7^-$ are readily phase transferred as long as the aqueous phase is acidic, but almost no transfer of chromate anions occurs from alkaline aqueous solutions in the absence of acid.

Very little work on the use of phase transferred chromate ions as oxidant for organic materials has been reported. However, work using anion exchange resins[116-120] indicates quaternary ammonium dichromate salts in organic media are of low oxidising power but high selectivity. Thus, a commercial resin, Amberlyst A-26, was converted to the $HCrO_4^-$ form by stirring 35 g of the chloride form of the resin in a solution of 15 g of CrO_3 in 100 mL of water. The resin so obtained did not noticeably lose activity on storing in air at room temperature for several weeks or on refluxing for five hours in benzene. Stirring the resin with a solution of alcohol[119] or benzylic or allylic halides[120] in various refluxing solvents (hexane, benzene, chloroform or tetrahydrofuran) gave the corresponding aldehydes or ketones in high yields. No traces of carboxylic acids or other by-products were detected in all these experiments. After the reaction was complete, the

product solution was simply filtered off, leaving all the chromium firmly bound to the resin.

The dichromate anion $Cr_2O_7^{2-}$, in contrast to $HCrO_4^-$, is difficult to be transferred into organic solution, as is typical of divalent anions. However it has been shown that commercially available quaternary salt Adogen 464 (a mixture of trialkyl (C_6-C_{10}) methylammonium chlorides from Ashland chemical Co.) is effective for the transfer of dichromate into methylene chloride, chloroform, carbon tetrachloride and benzene using solid crushed $K_2Cr_2O_7$.[121] These solutions are stable for several days before darkening. In the absence of acids these solutions are mild oxidants.

CHAPTER II

REVIEW AND SCOPE OF THE PRESENT WORK

2.1. REVIEW OF THE PRESENT WORK

2.1.1. Kinetics of the oxidation of primary alcohols

The kinetics and mechanism of the oxidation of primary alcohols, both aliphatic and aromatic by different oxidants have been reported.

The kinetics and mechanism of the oxidation of benzyl alcohols to benzaldehyde by bromine were studied in aqueous acetic acid medium at various added buffer concentrations.[122] Benzyl alcohol is oxidised by bromine at 25°C at a fairly faster rate and the mechanism involves hydride ion transfer which has been confirmed by studies using α-α-dideuteriobenzyl alcohol.

The kinetics of oxidation of benzyl alcohols to benzaldehyde by acid permanganate in the presence of fluoride ion has been studied by K.K. Banerji.[123] The activation enthalpies and entropies for the ten compounds are linearly related. The reaction constant, ρ has been found to be -1.76 which indicates electron deficient carbon centre in the transition state. A mechanism involving hydride ion transfer from the carbon of alcohol to the oxidant is suggested.

Mathur *et al*[124] studied the kinetics and mechanism of the oxidation of ten ortho-substituted benzyl alcohols by acid permanganate in acetic acid medium. The reaction showed first order kinetic behaviour with respect to [alcohol], [permanganate] and $[H^+]$. The correlation of the rate of oxidation

with Charton's extended Hammet equation, involving inductive, resonance and steric parameters gave excellent results. The polar reaction constants have negative value. The reaction is subject to steric acceleration by ortho- substituents.

Kinetics of the oxidation of substituted benzyl alcohols by quinolinium dichromate in dimethylformamide (DMF) in the presence of added acid were reported.[125] The reaction is first order with respect to the concentration of alcohol, QDC and the acid. Electron donating substituents accelerate the reaction where as electron withdrawing substituents retard the reaction rate. The rate data is in accordance with Hammett's relationship. The kinetic isotopic effect $k_H/k_D = 5.89$ at 313 K was obtained. A mechanism involving a hydride ion transfer from the alcohol to the oxidant has been reported.

The oxidation of benzyl alcohol and its methoxy, chloro and nitro substituted derivatives by permanganate was studied in aqueous acetic acid medium in the presence of perchloric acid.[126] The reaction is first order with respect to $[MnO_4^-]$ and $[XC_6H_4CH_2OH]$, but the order is complex with respect to $[H^+]$. The reaction involves protonation of the alcohol in a fast pre-equilibrium step, followed by a rate determining oxidation step. A two electron transfer step has been suggested for benzyl alcohol, chloro and nitro

substituted alcohols while the oxidation of methoxy compound involves a one electron transfer via free radical mechanism.

The oxidation of substituted benzyl alcohols to benzyaldehyde by bis(2,2'-bipyridyl)copper(II) permanganate (BBCP) has been reported.[127] The reaction is first order with respect to [BBCP]. Michaelis-Menten type kinetics were observed with respect to the alcohols. The rates of oxidation of meta and para-substituted benzyl alcohols were correlated in terms of Charton's triparametric LDR equation where as ortho substituted benzyl alcohols were correlated with a four parametric LDR equation. The results of correlation analysis point to an electron deficient reaction centre in the transition state.

Oxidation of benzyl alcohol and some ortho, meta and para-monosubstituted benzyl alcohols by benzyltrimethylammonium chlorobromate (BTMACB) in aqueous acetic acid was studied.[128] The corresponding benzaldehydes were formed. The reaction is first order with respect to the concentration of BTMACB and that of alcohol. The rate of the reaction increases with increase in polarity of the medium. Suitable mechanism has been proposed.

Oxidation of benzyl alcohol and some ortho, meta and para-manosubstituted benzyl alcohols using quinolinium flurochromate as the oxidant in dimethyl sulphoxide has been reported.[129] Benzaldehyde was

reported as the product. The reaction is first order each in both [QFC] and the [alcohol]. The reaction is promoted by hydrogen ions. Oxidation of α,α-dideuteriobenzyl alcohol has exhibited a substantial primary kinetic isotopic effect. The rate of oxidation of para and meta substituted benzyl alcohols have been correlated in terms of Charton's triparametric LDR equation, where as the oxidation of ortho substituted benzyl alcohols with tetraparametric LDR equation. A suitable mechanism has been proposed.

The oxidation of benzyl alchol and substituted benzyl alcohols by bromate in the presence of mercury(II) ion have been reported.[130] Increase in acidity of the medium enhances the rate and the rate constant correlates well with the acidity function H_0. From the effect of ionic strength and dielectric constant, the reaction has been found to be between a positive ion and a dipole. The rate-limiting step involves both the C-H bond breaking and C-O bond formation in a concerted manner.

Kinetics of the oxidation of benzyl alcohol by diperiodatonickelate (IV) has been studied in aqueous alkaline medium.[131] The order with respect to [oxidant] and [benzyl alcohol] have been found to be unity. The rate of oxidation increases with increase in [OH^-], however added [periodate] retards the rate. Monoperiodatonickelate(IV) has been found to be the reactive species of oxidant from salt effect studies. Suitable mechanism has been proposed.

Kinetics of the oxidation of primary aliphatic alcohols by acid permanganate was reported.[132] The C-H bond rupture in the rate determining step is evident from studies with labelled carbinols.

Kinetics and mechanism of the oxidation of primary aliphatic alcohols by bis(2,2'-bipyridyl)copper(II) permanganate have been reported.[133] The oxidation leads to the formation of corresponding aldehydes. The reaction is first order with respect to [BBCP]. Michaelis-Menten type kinetics was observed with respect to the alcohols. The reaction rate increases with increase in hydrogen ion concentration. The oxidation of 1,1'-dideuterioethanol exhibited a substantial kinetic isotopic effect showing hydride ion transfer mechanism.

Kinetics and mechanism of the oxidation of primary aliphatic alcohols by tetrabutylammonium tribromide in aqueous acetic acid have been investigated.[134] The corresponding aldehydes were formed. The reaction is first order with respect to TBATB. Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is susceptible to both polar and steric effects. A mechanism involving transfer of hydride ion in the rate-determining step has been proposed.

Kinetics of the oxidation of primary aliphatic alcohols by sodium N-bromobenzenesulphonamide in hydrochloric acid medium has been reported.[135] The reaction is first order with respect to [BAB] and fractional

order with respect to [alcohol], [H^+] and [Cl^-]. The conjugate acid, $C_6H_5SO_2NHBr$ is assumed to be the reactive species.

The oxidation of primary aliphatic alcohols using N-bromo-3,5-dinitrobenzamide (NBDNB) in acid solution was reported forming corresponding aldehydes.[136] The reaction is first order each in [oxidant] and [alcohol] and is catalysed by hydrogen ions. The observed hydrogen ion dependence of the reaction indicates that both NBDNB and its protonated from are reactive oxidising agents. The activation parameters of the oxidation have been evaluated. A mechanism involving transfer of a hydride ion to the oxidant in the rate-determining step has been proposed.

Kinetics of the oxidation of some aliphatic primary alcohols by t-butyl hypochlorite has been reported.[137] The order of the reaction is one each with respect to alcohol and t-butyl hypochlorite. The effect of ionic strength, [H^+] and various metallic chlorides on reaction rate have been studied. The various activation parameters have been evaluated. A mechanism involving ester formation is proposed.

Kinetics and mechanism of the oxidation of primary alcohols by N-chloronicotinamide in aqueous acetic acid medium was reported.[138] The reaction showed first order dependence on [NCN], [H^+] and [Cl^-]. A small increase in rate is observed in [alcohol]. A suitable mechanism has been proposed.

2.1.2. PHASE TRANSFER CATALYSIS IN OXIDATION

It has been reported that many inorganic oxidants can be transferred into the organic phase by using PT catalysts[4,6,15] Oxidants like hypochlorite, dichromate, chromate, hydrogen peroxide, permanganate etc. can be transferred into organic phase using quaternary onium salts as PT catalysts. The phase transferred oxidant can be used for effecting the oxidation of various organic substrates in organic media.

Oxidation with hypochlorite

The use of hypochlorite as an oxidising agent in PTC reactions received considerable attention after Lee and Freedman[139] have demonstrated that hypochlorite ion can be transferred into an organic phase using quaternary ammonium salts. The substrates used were alcohols and amines. An interesting and unexpected type of solvent effect in accelerating the rate has also been discovered with use of ethyl acetate.

A synergetic action of the electron transfer catalyst in the presence of a common PT catalyst, trioctylmethylammonium chloride to promote the oxidation of alcohols has been reported.[140] The results revealed that the direct oxidation of benzyl alcohol with sodium hypochlorite is very slow. But the reaction rate is accelerated by the use of PT catalysts. Benzyl alcohol does not react with aqueous hypochlorite where the carbinol is dissolved in an organic solvent like benzene. However,benzyl alcohol gets oxidised by

sodium hypochlorite in the presence of benzyltriethylammonium chloride as the PT catalyst in a two phase system[141] consisting of water and a non-polar organic solvent. The results obtained provide evidence for the initial chlorination at the alpha carbon. Since no reaction takes place in the absence of PT catalysts, it is evident that the OCl^- ion migrates into the organic phase for effecting the oxidation.

Heterogenous oxidation of benzyl alcohol using hypochlorite ion with PT catalyst has been carried out in an agitated vessel with a flat interface.[142] The observed reaction rates are proportional to the interfacial concentration of cetyltrimethylammonium hypochlorite in the organic phase, which is formed by the ion exchange between bromide and hypochlorite ions. Cetyltrimethylammonium bromide and toluene were chosen as the best catalyst and the solvent respectively.

A triphasic solid-solid-liquid catalytic system for the inexpensive and selective oxidation of secondary alcohols by calcium hypochlorite was reported.[143] In contrast with the result under homogenous phase, steric and geometric factors were found to affect rate constants. The catalyst is recovered without any regeneration process and it could be used several times with no loss of activity and the phenomenon is quite interesting.

In a study on the oxidation of benzyl alcohol by aqueous sodium hypochlorite in the presence of quaternary ammonium salts, benzaldehyde

and benzyl benzoate were obtained as products.[144] The concentration of organic phase and the pH of the aqueous phase affect the product distribution. A dilute organic phase and a low pH favoured benzaldehyde while a concentrated organic phase and a high pH favoured benzyl benzoate as the product.

Aromatic aldehydes were oxidised to carboxylic acids in high yields using sodium hypochlorite as oxidant.[145] The reaction was strongly influenced by pH of the aqueous phase and showed maximum rate at a pH 9-11. Similarly, the extraction of hypochlorite ion was maximum at these pH. The maxima are attributed to co-extraction of hypochlorous acid along with the hypochlorite anion into the organic phase, the former significantly increases the rate.

The kinetics of anodic oxidation of benzyl alcohol in the two phase system involving both the redox indicator, OCl^-/Cl^- and a PT catalyst were investigated.[146] The reaction mechanism and the factors which affect the current efficiency for benzaldehyde production were explored. The result showed that benzyl alcohol was mainly oxidised in the organic phase by the shuttling of the ClO^-/Cl^- mediator.

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 by Do and Chou.[147] The results showed that the oxidation of benzyl alcohol in two immiscible aqueous/methylene chloride system occurred in the organic phase when the speed of stirring was greater than 500 rpm. The experimental results also revealed that the order of the reaction with respect to benzyl alcohol and the catalyst are one each.

A spectroscopic analysis of reaction rates has been carried out by Trifonov and Kuzmanova.[148] They examined the rate of oxidation of benzyl alcohol using hypochlorite and the plot of E Vs $t_{½}$ (where E is optical density and t is time) was found to be linear. The PT catalysts used were aliquat 336, tetrabutylammonium hydrogen sulphate and tetrabutylammonium bromide.

Amsterdamsky[149] has proposed a procedure for the oxidation of benzhydrol to benzophenone using bleach as oxidising agent in ethyl acetate using tetrabutylammonium hydrogen sulphate as PT catalyst. The oxidation was essentially complete in 30 minutes and the yield ranges from 70-85%.

The oxidation of alkyl and aryl substituted hydroquinones with aqueous sodium hypochlorite in various organic solvents in the presence of tetrbutylammonium hydrogen sulphate has been reported.[150] Hydroquinones are oxidised to quinones. Methylene chloride and chloroform are found to be the suitable solvents for the oxidation of monosubstituted hydroquinones compared to ethyl acetate and benzene.

Phase transfer catalysed oxidation of alcohols with sodium hypochlorite in ethyl acetate media has been reported.[151] Products are obtained in good yield. These reactions are mild, efficient and safe. The experimental procedure and work-ups are very convenient.

B. Oxidation with hydrogen peroxide

Quarternary 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 to benzaldehyde[152] with H_2O_2 in water-methylene chloride system containing $RuCl_3$ and a PT catalyst.

Ballistreri *et al*[153] have reported a phase transfer procedure for the oxidation of terminal alkynes. The catalytic system involves dilute H_2O_2 solution, Na_2MO_4 (M = Mo, W) and mercuric acetate. Oxidation did not take place without mercuric acetate. By the appropriate choice of pH of the aqueous phase, PT catalyst and metal, carboxylic acid or keto aldehydes can be selectively obtained in fairly good yield.

The selective oxidation of primary aliphatic alcohols to carboxylic acids (60-70% selectivity), secondary alcohols to ketones (100% selectivity), primary benzylic alcohols to aldehydes (95-100% selectivity) and allylic alcohols to ketones (80% selectivity) was performed in H_2O_2-$RuCl_3.3H_2O$ PT catalyst system at a high substrate : $RuCl_3$ ratio.[154] It has been found that PT

catalyst has a dual role of extracting $RuCl_3$ and H_2O_2 into the organic phase and to protect the metallic catalyst against reduction.

The activity of single and mixed ammonium and phosphonium salts grafted on a 'gel type' styrene-7% divinylbenzene copolymer in the oxidation of benzyl alcohol with hydrogen peroxide by phase transfer catalysis has been reported.[155] A wide variety of catalysts with different quaternary chain length substituents were examined. The activity of polymer supported ammonium and phosphonium salts increased with the number of carbon atoms contained in the alkyl radicals of the onium and of the functionalisation degree with phosphonium groups.

C. Oxidation with Permanganate

Starks has reported that terminal olefins can be oxidised with $KMnO_4$ to carboxylic acid using PT catalyst.[156] when 1-octene was added to a mixture of aqueous potassium permanganate and 5% solution of quaternary salt in benzene, hexanoic acid was obtained in quantitative yield.

Sankarshana *et al*[157] have reported the kinetics of phase transfer catalysed oxidation of 2-ethyl-1-hexanol, n-heptanol and n-hexanol by quaternary ammonium permanganate. The oxidation of each alcohol by permanganate ion is found to be first order with respect to each of the reactants resulting in an overall second order rate expression.

Weber and Shepherd[158] have reported the controlled oxidation of olefins to the corresponding cis-glycols in moderate yields by $KMnO_4$ in dichloromethane using benzyltriethylammonium chloride as PT catalyst.

Herriot and Picker[159] have carried out the oxidation of several organic substrates (phenyl acetonitrile, benzyl alcohol, trans-stilbene, 1-octanol and 1-octene) by $KMnO_4$ using tetrabutylammonium bromide and tricaprylylmethylammonium chloride as PT catalyst.

Kinetics and mechanism of the oxidation of unsaturated carboxylic acids by methyltributylammonium permanganate in methylene chloride have been reported.[160] The involvement of free radical is indicated during the oxidation of acrylic acid and methacrylic acid. The reaction is believed to be initiated by the formation of an organometallic complex and its rearrangement leads to the formation of a reactive manganese(V) cyclic ester, which undergoes a rapid reduction to Mn(III).

Kinetics of the oxidation of methyl (E) cinnamates with quaternary ammonium permanganate in methylene chloride has been reported.[161] An attempt has been made to visualize a mechanism in which the reaction can proceed through similar intermediate but via either an electron rich or an electron deficient transition state depending on the demands of the substituents.

Freeman and Kappos[162] have reported the oxidation of cycloalkenes in methylene chloride using cetyltrimethylammonium permanganate (CTAP). The order of the reaction with respect to [permanganate ions] and [cycloalkene] is unity. The kinetic data were consistent with the initial interaction between cycloalkene and permanganate ion (charge transfer complex) with [2+2] cycloaddition leading to an intermediate. A very fast reaction of the intermediate affords 1,2-diol and manganese dioxide.

Rathore *et al*[163] have reported a convenient method for the selective oxidative cleavage of aryl substituted olefins to carbonyl compounds in good yields with cetyltrimethylammonium permanganate at room temperature.

Kinetics of the oxidation of benzyl alcohol, substituted benzyl alcohols and benzyl cyanide by potassium permanganate using different PT catalysts has been reported in various solvents.[164] A correlation of structure and activity of the catalyst was made. Tetrabutylammonium bromide and tricaprylylmethylammonium chloride were found to be the better catalysts and benzene was the better solvent in this study.

Kinetics of the oxidation of aliphatic aldehydes by quaternary ammonium permanganate in methylene chloride was reported with special regard to colloidal manganese (IV) intermediate.[165]

The oxidation of endo-dicyclopentadiene by permanganate ion in dichloromethane using quaternary salt as PT catalyst has been reported.[166]

The reaction is first order with respect to [permanganate ion] and [alkene]. The formation of a cyclic manganate(V) diester intermediate was proposed.

The kinetics of the oxidation of higher aliphatic alcohols with tertrabutylammonium permanganate has been reported.[167] The oxidation proceeds partly auto catalytically. The rate constants of both catalytic and non catalytic reactions have been evaluated.

A spectrophotometric method to study the kinetics of the oxidation of cyclohexene with $KMnO_4$ in biphase system has been reported.[168] Kinetic parameters in the presence of PT catalyst were reported.

Kinetics of the oxidation of benzyl alcohols and benzyl ethers using permanganate solubilized in methylene chloride using TDA-1 as PT catalyst has been reported.[169]

Kinetics of the oxidation of aliphatic alcohols by cetyltrimethylammonium permanganate has been investigated.[170] The reactions are auto catalytic, colloidal manganese dioxide as one of the reaction products has been identified as the auto catalyst.

The kinetics and mechanism of Mn(VII) oxidation of substituted alkyl (E) cinnamates by cetyltrimethylammonium permanganate have been studied in chloroform medium.[171] A mechanism was proposed from the formation of aldehydes and Mn(III). The formation of cyclic manganate(V)

diester intermediate is supported by a large negative entropy of activation. A negatively charged transition sate is also supported by the Hammet plot.

Nair *et al*[172] made detailed kinetic studies on the permanganate oxidation of acetophenones using tetrabutylammonium bromide and tricaprylylmethylammonium chloride as PT catalysts. The reaction showed first order dependence each on [ketones] and the [permanganate ions]. The rate coefficients fit well with the Hammet equation.

Nair *et al*[173] studied the kinetics of the oxidation of some 1-aryl ethanols in various organic solvents using permanganate in the presence of tetrabutylammonium bromide and tricaprylylmethylammonium chloride as PT catalysts. The reaction showed first order dependence each on [alcohol] and [permanganate] ions. A unique substituent effect has been observed where in both the electron donating and electron withdrawing groups enhanced the reaction rate compared to the parent compound.

Oxidation with chromate

Hutchins *et al*[121] showed that solubilization of potassium dichromate can be effected in several organic solvents using 2:1 ratio of adogen 464 to dichromate. The resulting orange solution is fairly stable at ambient temperature and used for the oxidation of alcohols under neutral condition.

Pletcher and Tait[174,175] have studied the oxidation of alcohols with stoichiometric quantity of dichromate in 3M aqueous sulphuric acid using tetrabutylammonium bisulphate as PT catalyst. They suggested that the reaction proceeded by disproportionation of chromate ester in which the proton catalysed 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 the oxidation of benzyl alcohol by chromic acid was studied in two phase system in an aqueous solution.[176] The order of the reaction with respect to both [substrate] and [reactant] is one and a partial order with respect to acid concentration. The use of two phase system allowed to obtain clean kinetic results by preventing further oxidation of benzaldehyde to carboxylic acid.

Gelbard *et al*[177] reported the use of onium salts as PT catalysts to obtain a complex chromate salt which is soluble in aprotic organic solvents. This complex chromate was used for the oxidation of several alcohols.

The oxidation of alcohols to corresponding carbonyl compounds in good yield under mild conditions has been reported.[178] Tricaprylylmethylammonium chloride was used as PT catalyst in dichloromethane.

A thorough and systematic analysis of the kinetics and mechanism of the oxidation of benzyl chloride by chromate in liquid-liquid phase transfer catalysis has been reported.[179] This system presents a complex case of consecutive and parallel reactions in which benzyl alcohol was formed as an intermediate which is further oxidised to benzaldehyde. The reactive species may be dichromate, chromate or perchromate which depends on the pH of the aqueous phase. It was observed that $Q^+HCrO_4^-$ is the active species in this study.

2.2. SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

The encouraging results of permanganate oxidation under PTC conditions prompted to take up such studies with the chromate system. The observation during investigations regarding transfer of monochromate ions from acidified aqueous potassium dichromate solutions to non-polar media and the selective oxidation it ensured were challenging. This is quite significant and hence the present work.

The present investigation has been under taken mainly to determine the kinetic aspects of the oxidation of primary aliphatic and aromatic alcohols and some of its derivatives using phase transferred monochromate ion. Studies on kinetic and mechanistic aspects of the oxidation of primary alcohols by phase transferred monochromate ions are scanty and the present work is initiated into this area.

Detailed kinetic studies have been carried out on the oxidation of benzyl alcohol, para-substituted benzyl alcohols and aliphatic alcohols, namely 1-butanol, 1-pentanol 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol using phase transferred monochromate ion as the oxidant. Tetrabutylammounium bromide and tetrabutylphosphonium bromide were used as PT catalysts. The reactions were carried out in different non-polar solvents such as benzene, toluene and chloroform. The following are the chief objectives of the present work.

1. To study the nature of product and the stoichiometry of the phase transfer assisted oxidation of primary alcohols with monochromate in non-polar media.

2. To study the rate of oxidation of benzyl alcohol, para-substituted benzyl alcohols and aliphatic alcohols in benzene medium using phase transferred monochromate in non-polar media to evaluate the kinetic parameters such as order of the reaction, rate coefficients and activation parameters.

3. To study the temperature coefficient of the reaction rates in order to evaluate activation energies and related thermodynamic parameters.

4. To study the effect of dielectric constant of the organic medium on the rate of reaction.

5. To study the effect of substituents on the rate of oxidation of benzyl alcohol in benzene.

6. To propose a mechanism in consistent with the observed rate data.

7. To make a comparative study on the kinetics of dichromate oxidation of benzyl alcohol and para-substituted benzyl alcohols in homogenous aqueous acetic acid medium for comparing the results with that of phase transfer catalysed process.

CHAPTER III
EXPERIMENTAL

This chapter deals with the materials and methods employed for the kinetic investigation of the oxidation of primary alcohols using monochromate in non-polar organic solvents and the kinetic investigation in aqueous acetic acid medium.

3.1. Oxidation using monochromate in non-polar solvents

3.1.1. Materials

Analar grade potassium dichromate is used and its solution was prepared in doubly distilled water. Benzyl alcohol (AR) was further purified by distillation under reduced pressure. The substituents, 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol and 4-methylbenzyl alcohol (Lancaster, England) were used as such. Aliphatic alcohols,viz 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol were purified according to the standard procedure.[180] The phase transfer catalysts, tetrabutylammonium bromide (SRL, Mumbai), and tetrabutylphosphonium bromide (Merck KGaA, Germany) were used as such. The organic solvents such as benzene, toluene and chloroform were purified according to the standard procedure.[180] All the purified solvents were refluxed for 1-2 hours with a mixture of PT catalyst and potassium dichromate and then distilled.

3.1.2. Kinetic investigations

The kinetic studies were carried out at various temperatures in a constant temperature bath fitted with thermoregulators to maintain the accuracy of temperature within a variation of $\pm$ 0.1°C. A known volume of 0.05 mol dm^{-3} aqueous potassium dichromate which contains 2 mol dm^{-3} H_2SO_4 is mixed with equal volume of benzene containing 0.1 mol dm^{-3} PT catalyst and the resulting two phase solution is stirred for half an hour using a magnetic stirrer. The $Q^+HCrO_4^-$ formed in benzene was separated and made anhydrous by adding a little anhydrous sodium sulphate. The concentration of extracted $HCrO_4^-$ is spectrophotometrically determined using a Shimadzu 1601 UV-VIS spectrophotometer. The oxidant solution remained stable for about five hours enabling convenient kinetic study. A known volume of $Q^+HCrO_4^-$ was mixed with known volume of benzene and the mixture was thermostated for 20 minutes at the desired temperature. To this reaction mixture required volume of previously thermostated alcohol in benzene was added using a calibrated pipette. The reaction was carried out under pseudo-first order conditions by keeping [alcohol] >> [$Q^+HCrO_4^-$]. Aliquots of reaction mixture was withdrawn at regular time intervals and the progress of the reaction was monitored spectrophotometrically by measuring the absorption of $HCrO_4^-$ ion at λ_{max} 365 nm.

The experiments were carried out at various concentrations of oxidant and substrate and at various temperatures and in various organic solvents.

3.1.3. Stoichiometry

The stoichiometry of the reaction between the oxidant and substrate was determined by taking excess of [chromate ions] over [alcohol] and allowing the reaction for completion. Under this condition all the alcohol taken would be completely reacted leaving the unreacted chromate. The concentration of remaining chromate is estimated spectrophotometrically and from this the stoichiometry of the reaction is determined.

3.1.4. Product analysis

Product analysis was carried out in a heterogenous system. Primary alcohol (0.1 mol) dissolved in 50 mL benzene which contains 0.01 mol PT catalyst was mixed with 50 mL $K_2Cr_2O_7$ (0.5 mol) containing 2 mol dm^{-3} H_2SO_4. The mixture was stirred vigorously using a magnetic stirrer. The benzene layer was extracted with ether three times. This organic layer was again extracted with 10% sodium bicarbonate and both organic and aqueous layers were separated. A saturated solution of 2,4-dinitrophenylhydrazine in HCl was added to the organic layer and kept overnight in refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, recrystallised from ethanol, dried and weighed. The product was analysed with its melting point and other qualitative analytical

methods. The aqueous layer after extraction with sodium bicarbonate was acidified with concentrated HCl.

3.2. Oxidation in acetic acid medium

The kinetics of the oxidation of primary aromatic alcohols were studied in aqueous acetic acid (20% v/v). Acetic acid (E. Merck) was purified according to the reported method.[180] The effect of oxidant concentration, effect of substrate concentration, effect of polarity of the medium, effect of added salt, effect of mineral acid and the effect of temperature etc. on the reaction rate were investigated. Various activation parameters were computed. Kinetic studies were carried out under the condition [alcohol] >> [dichromate] and the concentration of unreacted dichromate ion was determined iodometrically at regular intervals of time. The stoichiometry of the reaction was determined under the condition [dichromate] >> [alcohol] and the product analysis was also carried out.

3.3. EVALUATION OF RATE CONSTANTS[181-184]

The pseudo-first order rate constants were determined from the linear plots of log of concentration of $HCrO_4^-$ versus time. The slope of these plots were calculated by liner regression analysis (by the method of least squares). From the slopes rate constants were calculated.

3.4. THERMODYNAMIC PARAMTERS[184-186]

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

The energy of activation was calculated by using Arrhenius equation.

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

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

A plot of log k vs 1/T gave a linear relationship with a slope equal to Ea/2.303 R and the value of Ea is calculated.

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

$$k = \frac{k_b T}{h} \exp \frac{T\Delta S^{*} - \Delta H^{\#}}{RT}$$

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

where k_b is Boltzmann constant and h is Planck's constant.

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

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

The free energy of activation $\Delta G^{\neq}$ can be calculated from the equation,

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

CHAPTER IV
RESULTS AND DISCUSSION

The experimental results on the kinetic investigations on the oxidation of benzyl alcohol and some of its para-substituted derivatives in benzene using phase transferred monochromate are presented in the first section of this chapter. The results on similar investigations on the oxidation of primary aliphatic alcohols,viz 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1- octanol, 1-nonanol and 1-decanol are presented in the second section. In the third and the final section kinetic studies on the oxidation of benzyl alcohol and its para-substituted derivatives with potassium dichromate in aqueous acetic medium are presented for the purpose of comparison.

4.1. OXIDATION OF PRIMARY AROMATIC ALCOHOLS USING PHASE TRANSFERRED MONOCHROMATE

The kinetic studies on the oxidation of benzyl alcohol and its p-methoxy, p-methyl and p-chloro derivatives were carried out using phase transferred monochromate in benzene. Tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB) were used as PT catalysts. The oxidation of benzyl alcohol was also carried out in toluene and chloroform. Apart from deriving the kinetic and thermodynamic parameters on these oxidations, investigations related to dielectric properties of the solvents to throw light on mechanistic details were subjects of investigation in the present study.

4.1.1. Stoichiometry and product analysis

The stoichometry of the reaction was established by equilibrating known excess concentration of the phase transferred oxidant with known amount of the alcohol. One mole of the monochromate was found to be equivalent to three moles of the alcohol,viz benzyl alcohol.

$$3PhCH_2OH + Cr(VI) \rightarrow 3PhCHO+Cr(IV) + 6H^+$$

The product, benzaldehyde obtained in yield >90% was identified as its 2,4-dinitrophenylhydrazone (DNP).

4.1.2. Effect of addition of acrylonitrile

The oxidation of benzyl alcohol by phase transferred monochromate in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and this rules out the involvement of any radical intermediate in the reaction.

4.1.3. Kinetic studies

The kinetic measurements were carried out under conditions where $[PhCH_2OH] >> [Q^+HCrO_4^-]$, where Q^+ is quaternary ammonium cation or quaternary phosphonium cation. The progress of the reaction was followed spectrophotometrically using a Shimadzu 1601 UV-VIS spectrophotometer. The absorbance of $HCrO_4^-$ ions were measured as a function of time at

365 nm. The pseudo-first order rate constants, k_{obs} were computed from the linear least square plots of log [$HCrO_4^-$] versus time.

4.1.3.1. Effect of the concentration of oxidant ($Q^+HCrO_4^-$) on the rate of oxidation

The oxidation of benzyl alcohol was carried out with different initial concentrations of the oxidant using TBPB and TBAB as PT catalyst and specific rates were determined from the linear plots of log [oxidant] versus time and the values (Table 4.1.1) agree with first order reaction with respect to the oxidant ($HCrO_4^-$) concentration {Fig. 4.1.1(a) and (b)}.

Table 4.1.1 Effect of [oxidant] on the rate of oxidation of benzyl alcohol

[$PhCH_2OH$] x 10^1 = 2.0 mol dm^{-3} Temperature - 308 K

Medium - Benzene

$[Q^+HCrO_4^-]$ x10^3 (mol dm^{-3})	TBPB		TBAB	
	k_{obs}x10^5 (s^-)	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)
4.0	8.6363	4.3181	7.6767	3.8383
5.0	8.5979	4.2989	7.7919	3.8959
6.0	8.6363	4.3181	7.7151	3.8575
8.0	8.5979	4.2989	7.6767	3.8383

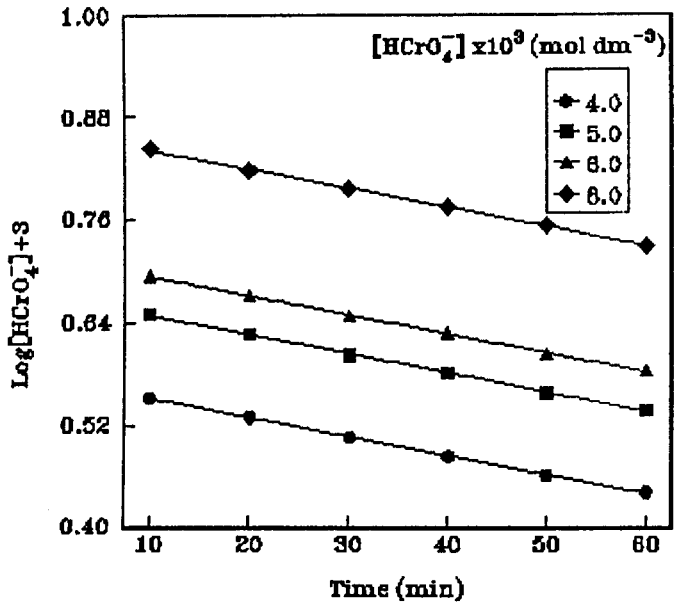


Fig.4.1.1(a). Effect of [oxidant] on the rate of oxidation of benzyl alcohol

PT catalyst -TBPB

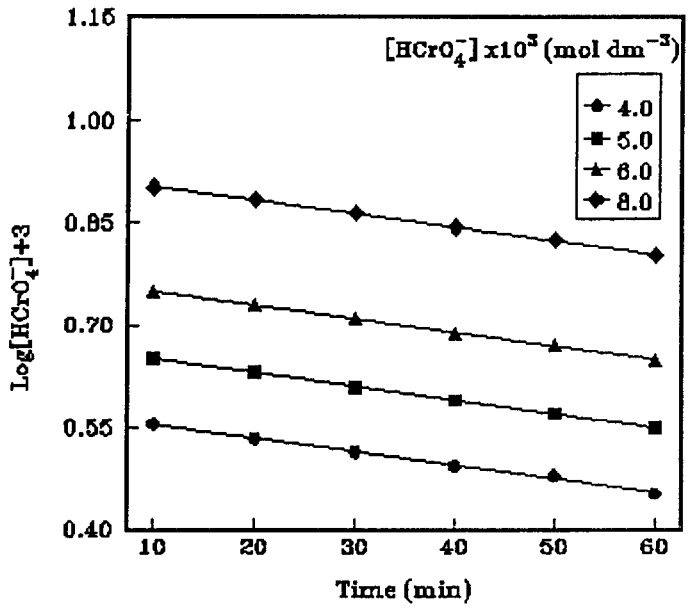


Fig.4.1.1(b). Effect of [oxidant] on the rate of oxidation of benzyl alcohol

PT catalyst -TBAB

4.1.3.2. Effect of the concentration of substrate on the rate of oxidation

The effect of [substrate] on the rate of oxidation was studied with different initial concentrations of the substrate. The observed rate constant increased linearly with increase in the concentration of benzyl alcohol. Further the second order rate constants k_2, obtained by dividing the k_{obs} values by the respective concentration of benzyl alcohol were found to be constant indicating first order dependence of the reaction with respect to [substrate]. These results are presented in Table 4.1.2. and in Fig. 4.1.2.1(a) and (b).

Table 4.1.2 Effect of [substrate] on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K.

Medium - Benzene

$[PhCH_2OH] \times 10^1$ (mol dm^{-3})	TBPB		TBAB	
	$k_{obs} \times 10^5$ (s^-)	$k_2 \times 10^4$ ($dm^3 mol^{-1}s^{-1}$)	$k_{obs} \times 10^5$ (s^{-1})	$k_2 \times 10^4$ (dm^3 $mol^{-1}s^{-1}$)
1.2	4.9131	4.0943	4.2989	3.5824
1.6	6.6403	4.1502	5.9494	3.7184
2.0	8.5979	4.2989	7.7919	3.8952
3.0	13.0887	4.3629	11.7069	3.9023

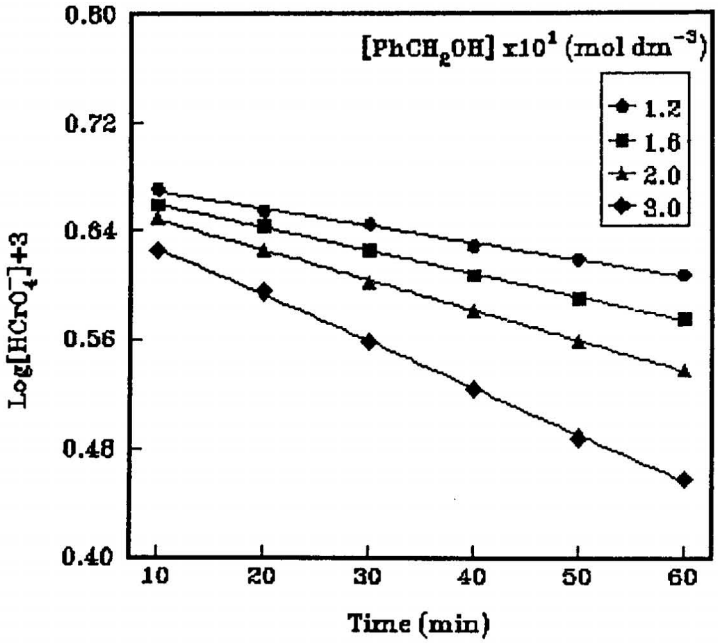


Fig.4.1.2.1(a). Effect of [substrate] on the rate of oxidation of benzyl alcohol.

PT catalyst - TBPB

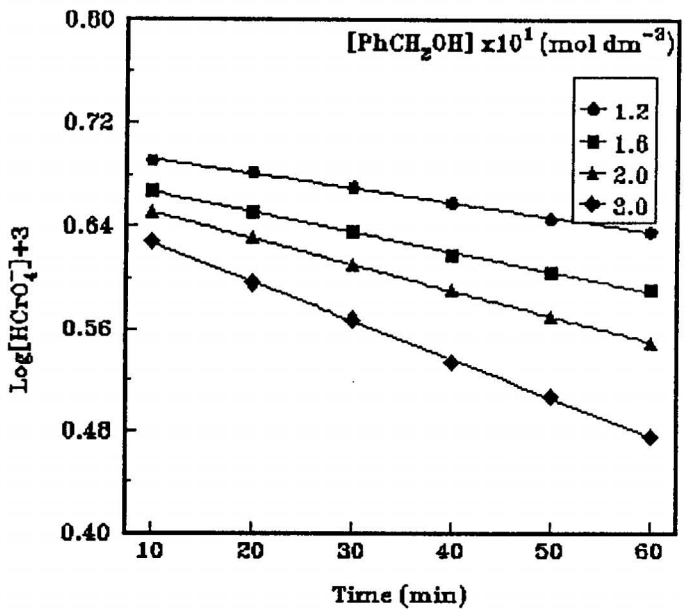


Fig.4.1.2.1(b). Effect of [substrate] on the rate of oxidation of benzyl alcohol

PT catalyst -TBAB

The first order dependence on [substrate] is further confirmed by the log-log plot of k_{obs} Vs substrate concentration (Fig. 4.1.2.2) with unit slope.

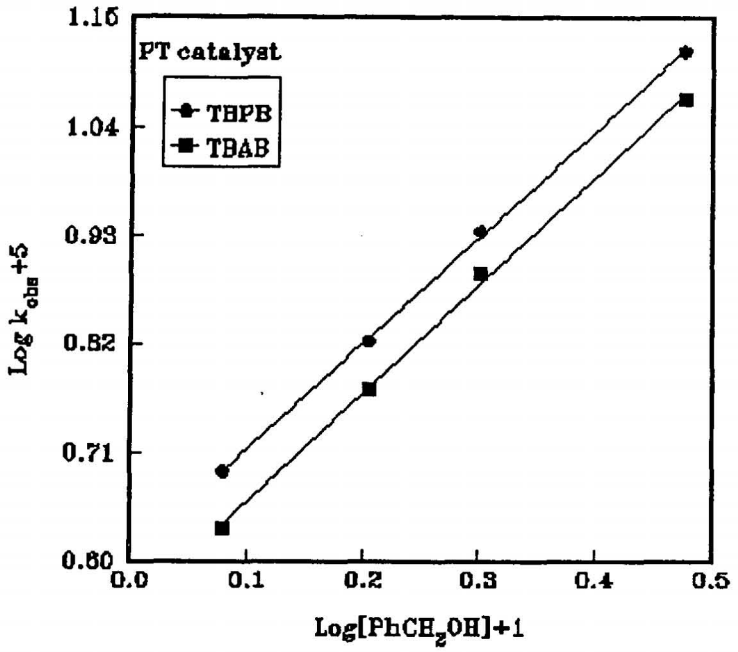


Fig.4.1.2.2. Plot of log k_{obs} Vs log [substrate]

The plot of $1/k_{obs}$ versus $1/[PhCH_2OH]$ is linear ($r = 0.9997$ and 0.9989 for TBPB and TBAB respectively) with an intercept on the rate co-ordinate (Fig. 4.1.2.3). This proves the existence of a long lived intermediate and implies Michaelis-Menten type kinetics with respect to benzyl alcohol.

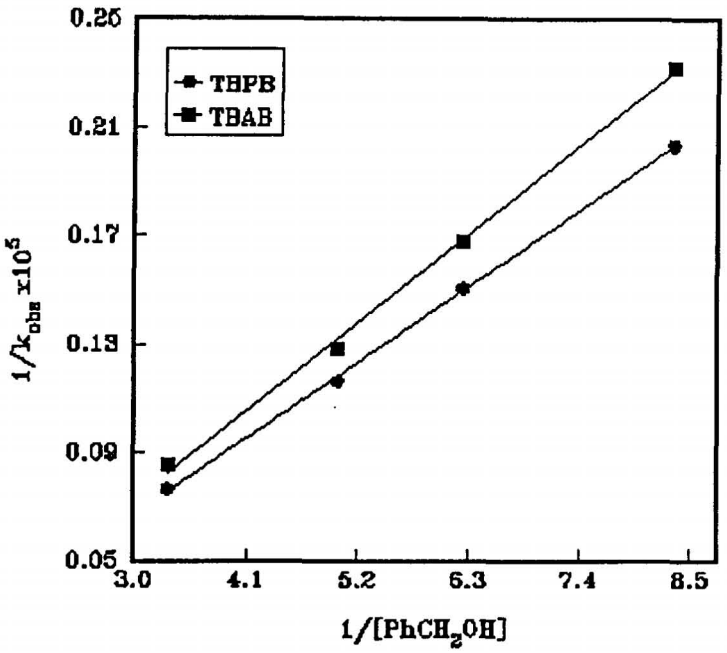


Fig.4.1.2.3. Lineweaver-Burke plot of $1/k_{obs}$ Vs $1/[PhCH_2OH]$

4.1.3.3. Effect of dielectric constant of the medium

The influence of intrinsic dielectric constant of the medium on the rate of oxidation of benzyl alcohol was carried out by conducting the reaction in various solvents like benzene, toluene and chloroform. It has been observed that the rate of oxidation increased with increase in polarity of the medium. The order of reactivity in various organic solvents is given as chloroform>toluene> benzene. These results are presented in Table 4.1.3 and in Fig. 4.1.3.1. (a) and (b).

Table 4.1.3. Effect of dielectric constant of the medium on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1 = 2.0 mol dm^{-3}

Temperature - 308 K

Solvent	Intrinsic dielectric constant	TBPB		TBAB	
		k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)	k_{obs}x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)
Benzene	2.27	8.5979	4.2989	7.7919	3.8959
Toluene	2.40	9.5191	4.7595	8.7514	4.3757
Chloroform	4.70	11.6302	5.8151	10.7857	5.3929

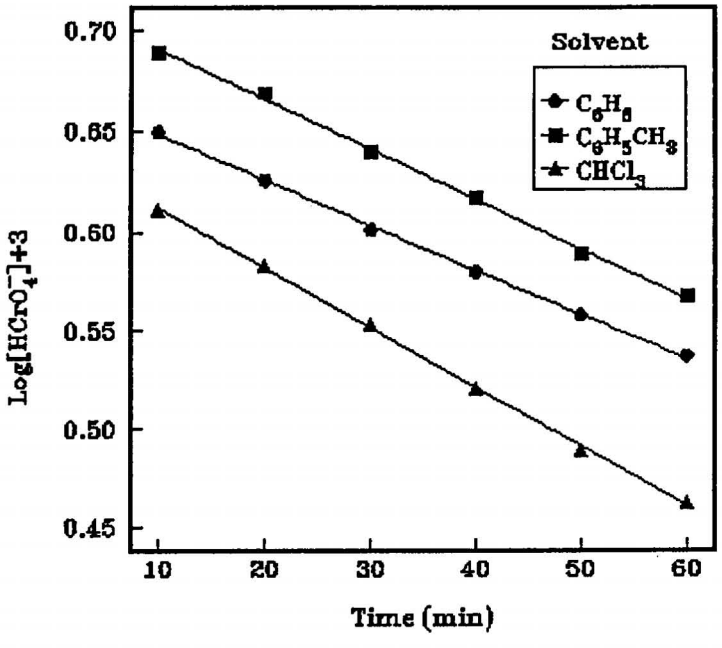


Fig.4.1.3.1(a). Effect of dielectric constant of the medium on the rate of oxidation of benzyl alcohol.

PT catalyst -TBPB

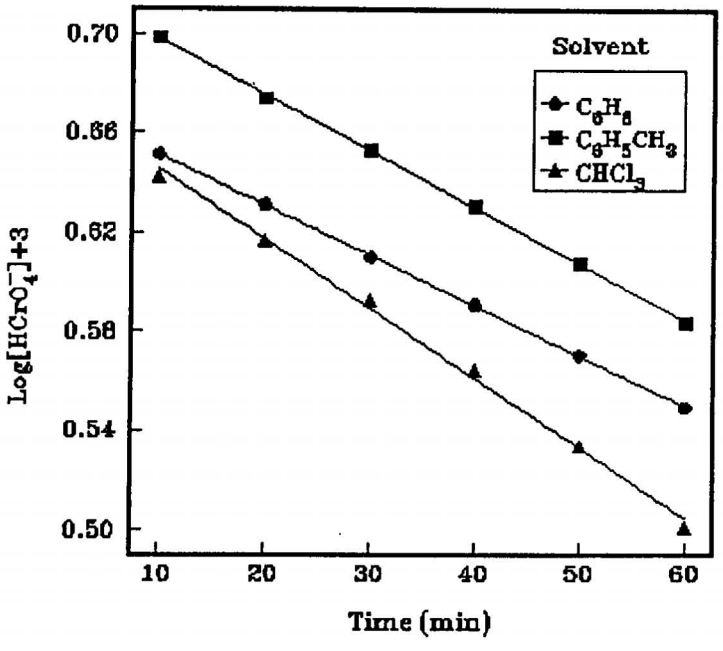


Fig.4.1.3.1(b). Effect of dielectric constant of the medium on the rate of oxidation of benzyl alcohol.

PT catalyst -TBAB

The plot of log k_2 versus 1/D, where D is the dielectric constant of the medium is almost linear with negative slope with correlation coefficient (r=0.9708 and 0.9650 for TBPB and TBAB respectively) (Fig. 4.1.3.2).

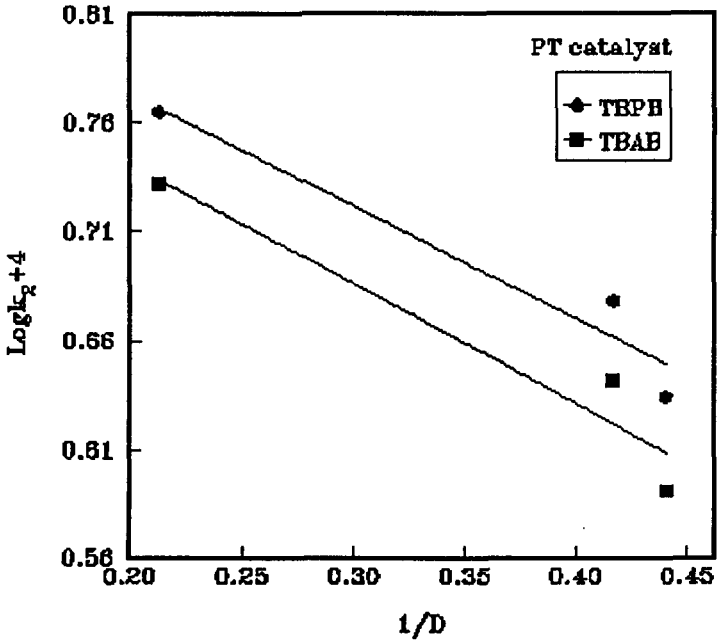


Fig.4.1.3.2. Plot of log k_2 Vs 1/D

4.1.3.4. Effect of substituents on the rate of oxidation of benzyl alcohol

The effect of substituents such as p-methoxy, p-methyl and p-chloro on the phase transferred monochromate oxidation of benzyl alcohol in the non-polar medium has been investigated. These results are presented in Table 4.1.4 and in Fig. 4.1.4.1(a) and (b). The rate constants obtained for the oxidation of various substituted benzyl alcohols are found to be in the order of p-OCH_3 > p-CH_3 > $PhCH_2OH$ > p-Cl. The electron-releasing substituents accelerate the oxidation process and electron-withdrawing susbtituents retard the process. Electron deficiency at the reaction centre thus appears to enhance the rate of these reactions.

Table 4.1.4 Effect of substituents on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [Substrate] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene Temperature - 303 K

Substrate	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)
$PhCH_2OH$	7.0242	3.5121	6.1413	3.0707
p-OCH_3 BA	11.3310	5.6654	9.4072	4.7036
p-CH_3 BA	8.5299	4.2649	7.5889	3.7945
p-Cl BA	6.5241	3.2620	5.5656	2.7828

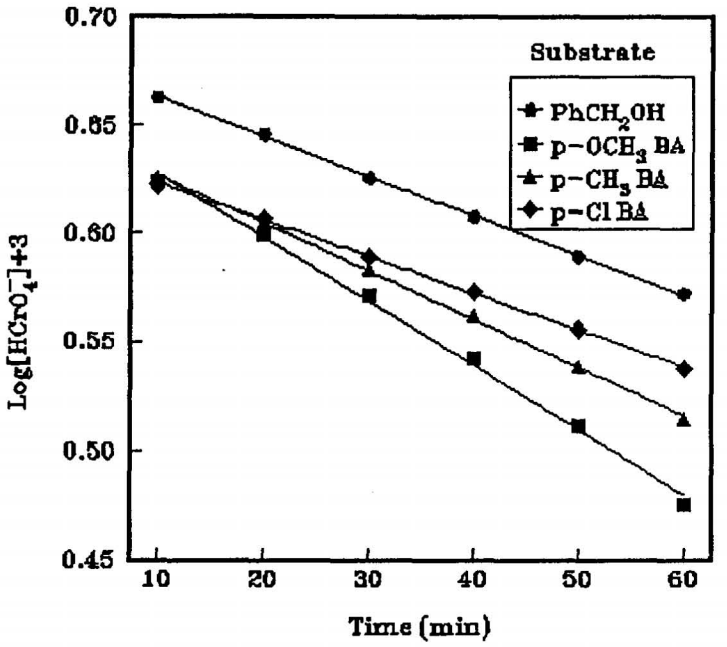


Fig.4.1.4.1(a). Effect of substituents on the rate of oxidation of benzyl alcohol.

PT catalyst -TBPB

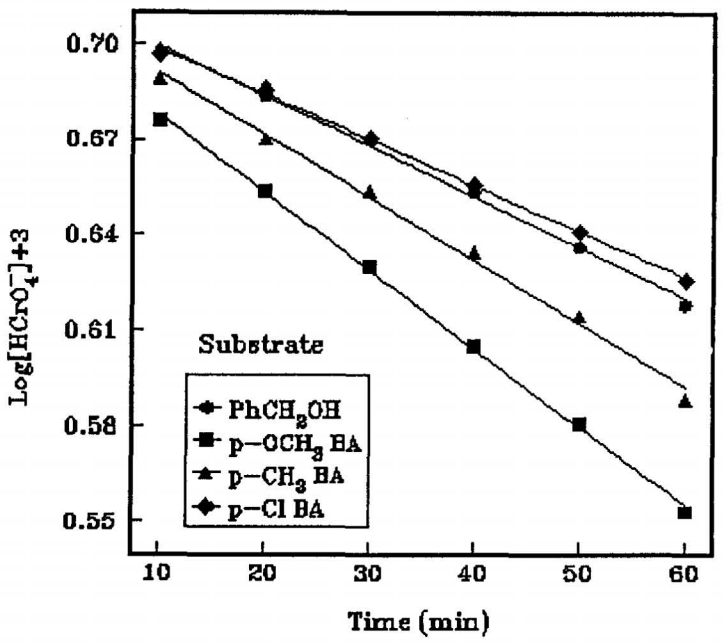


Fig.4.1.4.1(b). Effect of substituents on the rate of oxidation of benzyl alcohol.

PT catalyst -TBAB

The kinetic data on the effect of substituents were used for obtaining the Hammet plot and the rate data fitted well into the Hammet equation. The plot of log k_2 versus σ, where σ is the substituent constant were found to be linear showing that there is excellent correlation between the substituent effect and the reactivity.[187]

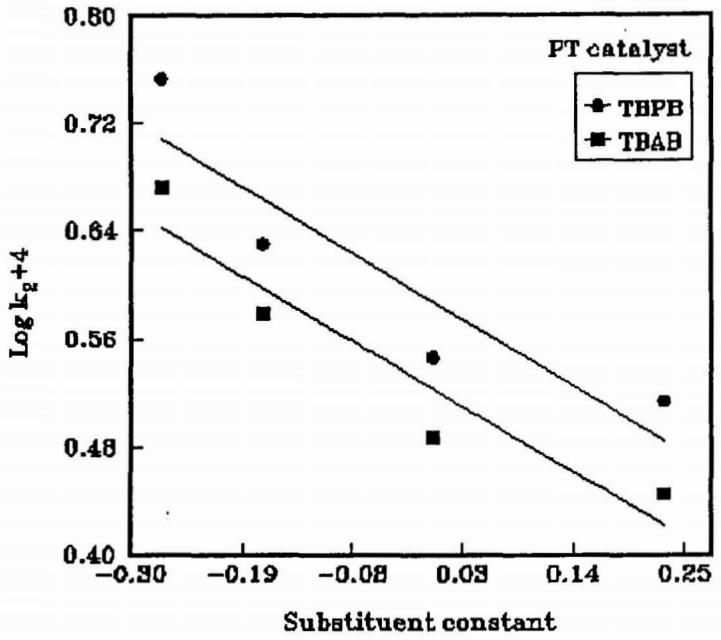


Fig.4.1.4.2. Hammet plot for the oxidation of benzyl alcohols

4.1.3.5. Effect of temperature on the rate of oxidation of benzyl alcohols

In order to study the energetics involved in these oxidation reactions under PTC, the influence of temperature on the rate of oxidation of benzyl alcohol and its para-substituted derivatives with the phase transferred monochromate were studied. The temperature range chosen was 303 K to 318 K. There was linear increase of rates with increase in temperature. The activation parameters for the oxidation of alcohols were determined by the least square fitting of the Arrhenius equation $K=A.e^{-Ea/RT}$. The plots of log k_2 Vs 1/T and log k_2/T Vs 1/T were used for this purpose[188], where k_2 is the second order rate constant.

4.1.3.5.1. Effect of temperature on the rate of oxidation of benzyl alcohol

The effect of temperature on the rate of oxidation of benzyl alcohol using phase transferred monochromate is presented in Table 4.1.5.1 and in Fig. 4.1.5.1(a) and (b)

Table 4.1.5.1 Effect of temperature on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)	k_{obs} 10^5 (s^{-1})	k_2 x10^4 (dm^3 $mol^{-1}s^{-1}$)
303	7.0242	3.5121	6.1413	3.0707
308	8.5979	4.2989	7.7918	3.8959
313	9.9413	4.9707	9.2888	4.6444
318	12.2827	6.1414	10.8625	5.4312

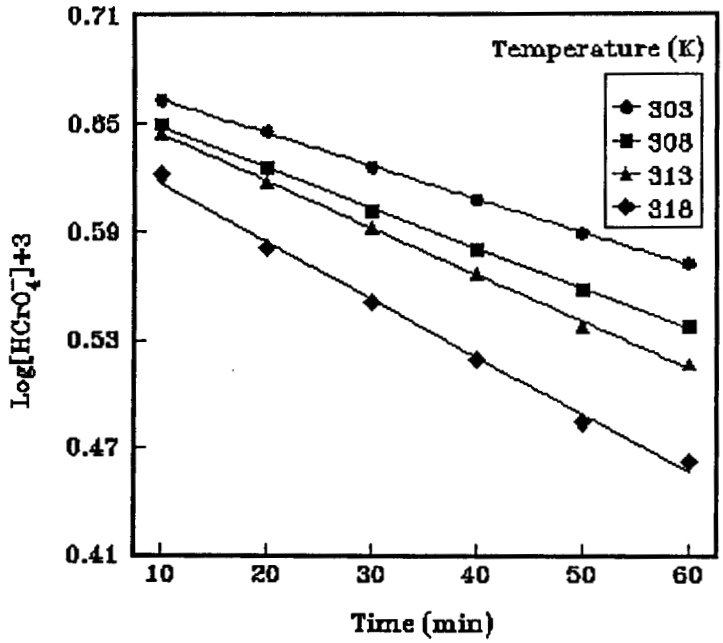


Fig.4.1.5.1(a). Effect of temperature on the rate of oxidation of benzyl alcohol.

PT catalyst -TBPB

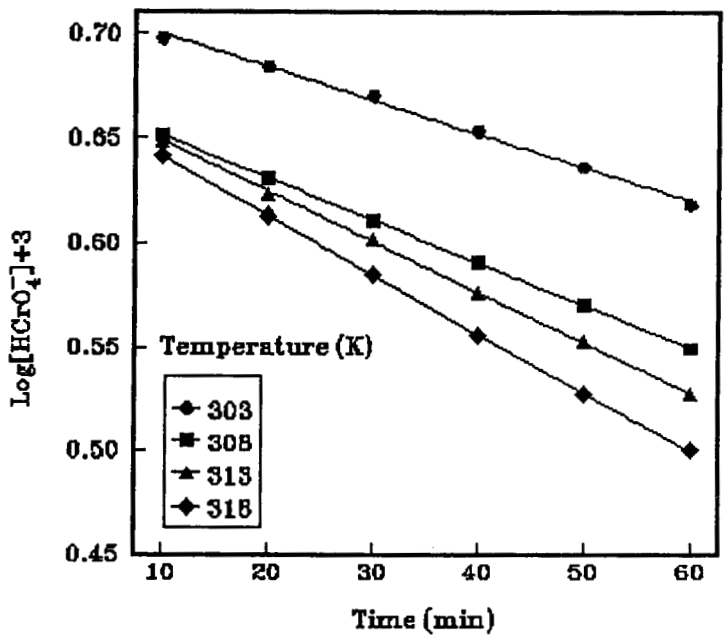


Fig.4.1.5.1(b). Effect of temperature on the rate of oxidation of benzyl alcohol.

PT catalyst-TBAB

4.1.3.5.2 Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol

The effect of temperature on the rate oxidation of p-methoxybenzyl alcohol using phase transferred monochromate is presented in Table 4.1.5.2 and in Fig. 4.1.5.2(a) and (b).

Table 4.1.5.2 Effect of temperature on the rate of oxidation of p- methoxybenzyl alcohol

$[Q^+HCrO_4^-]$ $x10^3$ = 5.0 mol dm^{-3} Medium - Benzene

$[p\text{-}OCH_3C_6H_4CH_2OH]$ $x10^1$ = 2.0 mol dm^{-3}

Temperature (K)	TBPB		TBAB	
	k_{obs} $x10^4$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)	k_{obs} $x10^5$ (s^{-1})	k_2x10^4 (dm^3 $mol^{-1}s^{-1}$)
303	1.1331	5.6654	9.4072	4.7036
308	1.2793	6.3963	11.1490	5.5744
313	1.5392	7.6959	12.9030	6.4517
318	1.7809	8.9044	15.4640	7.7321

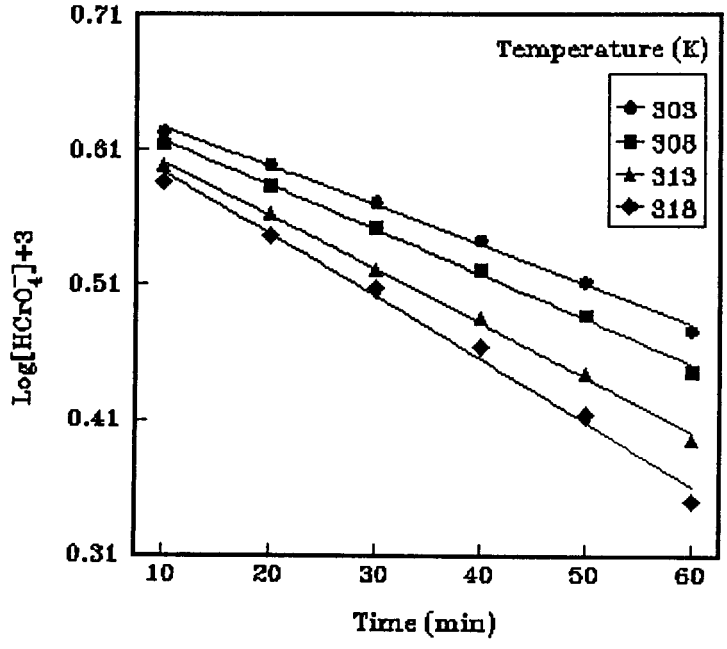


Fig.4.1.5.2(a). Effect of temperature on the rate oxidation of p-methoxybenzyl alcohol.

PT catalyst -TBPB

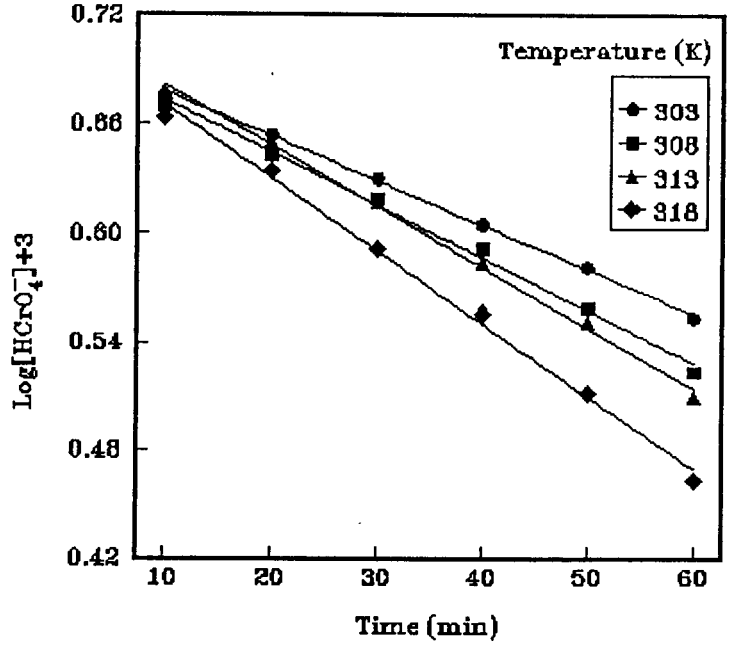


Fig.4.1.5.2(b). Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol.

PT catalyst -TBAB

4.1.3.5.3. Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol

The effect of temperature on the rate of oxidation of p-methylbenzyl alcohol using phase transferred monochromate is presented in Table 4.1.5.3 and in Fig. 4.1.5.3(a) and (b).

Table 4.1.5.3 Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol

$[Q^+HCrO_4^-]$ $x10^3$ = 5.0 mol dm^{-3} Medium - Benzene

$[p\text{-}CH_3C_6H_4CH_2OH]$ $x10^1$ = 2.0 mol dm^{-3}

Temperature (K)	TBPB		TBAB	
	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)
303	8.5299	4.2649	7.5889	3.7945
308	10.5270	5.2635	9.2997	4.6499
313	11.6760	5.8381	11.3760	5.6879
318	14.6640	7.3318	12.7630	6.3815

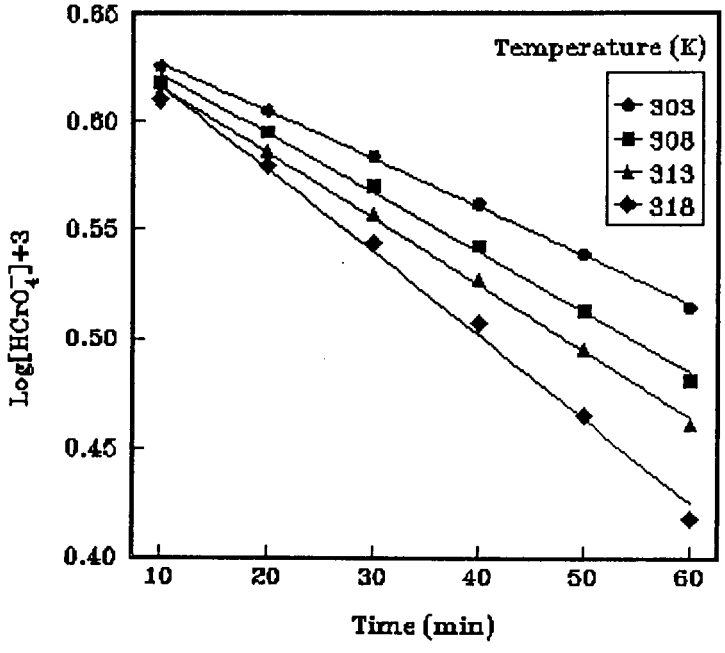


Fig.4.1.5.3(a). Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol.

PT catalyst –TBPB

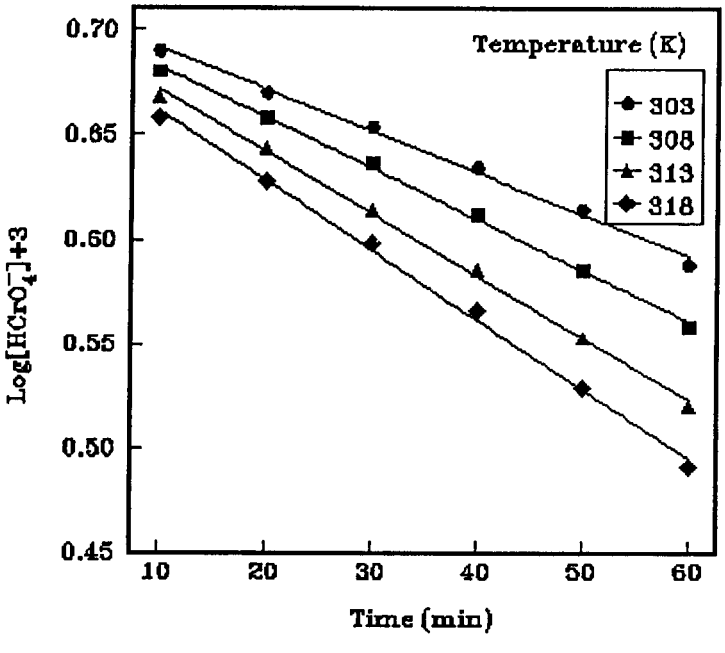


Fig.4.1.5.3(b). Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol.

PT catalyst -TBAB

4.1.3.5.4. Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol

The effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol using phase transferred monochromate is presented in Table 4.1.5.4 and in Fig. 4.1.5.4(a) and (b).

Table 4.1.5.4 Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol

$[Q^+HCrO_4^-]$ $x10^3$ = 5.0 mol dm^{-3} Medium - Benzene

$[p\text{-}ClC_6H_4CH_2OH]$ $x10^1$ = 2.0 mol dm^{-3}

Temperature (K)	TBPB		TBAB	
	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)
303	6.5241	3.2620	5.5656	2.7828
308	7.9256	3.9628	7.0143	3.5071
313	9.7417	4.8708	8.6231	4.3115
318	11.7530	5.8765	10.2100	5.1050

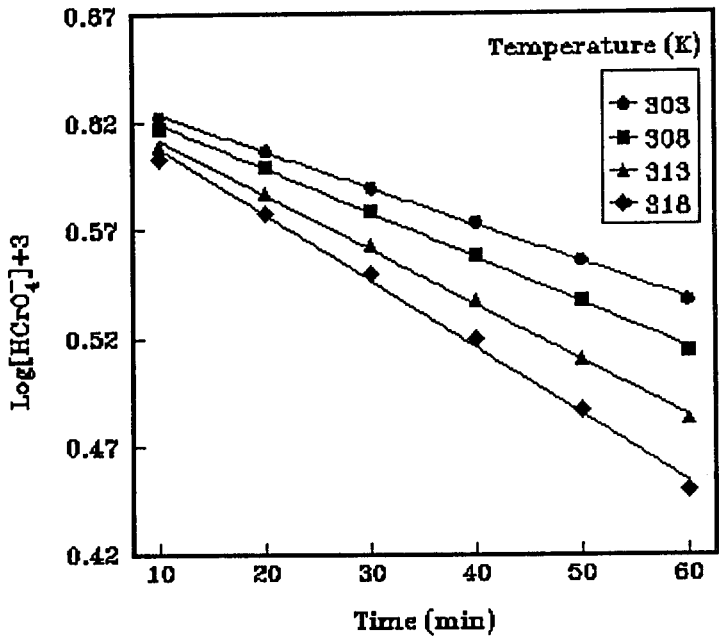


Fig.4.1.5.4(a). Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol.

PT catalyst -TBPB

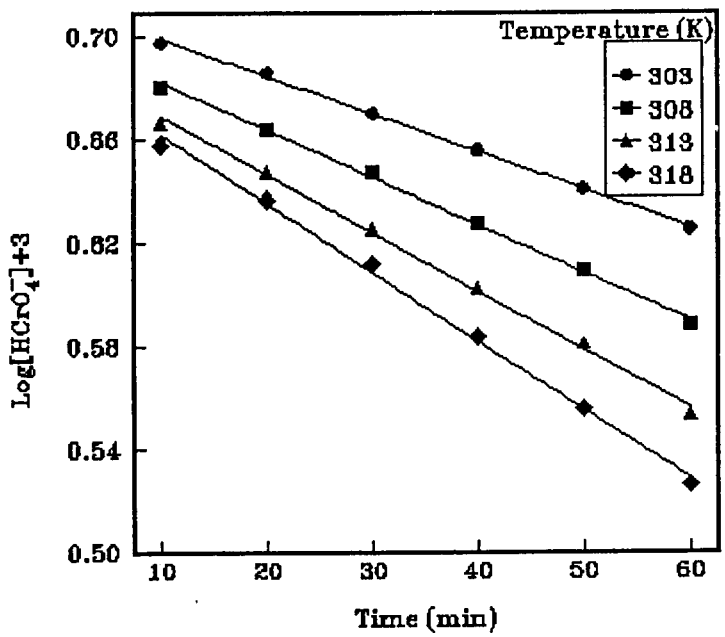


Fig.4.1.5.4(b). Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol.

PT catalyst -TBAB

The values of various thermodynamic parameters were calculated from the plot of log k_2 Vs 1/T {Fig. 4.1.5.5(a) and (b)} and from the plot of log k_2/T Vs 1/T {(Fig. 4.1.5.6(a) and (b)}. The values of various thermodynamic parameters are presented in Table 4.1.5.5(a) and (b).

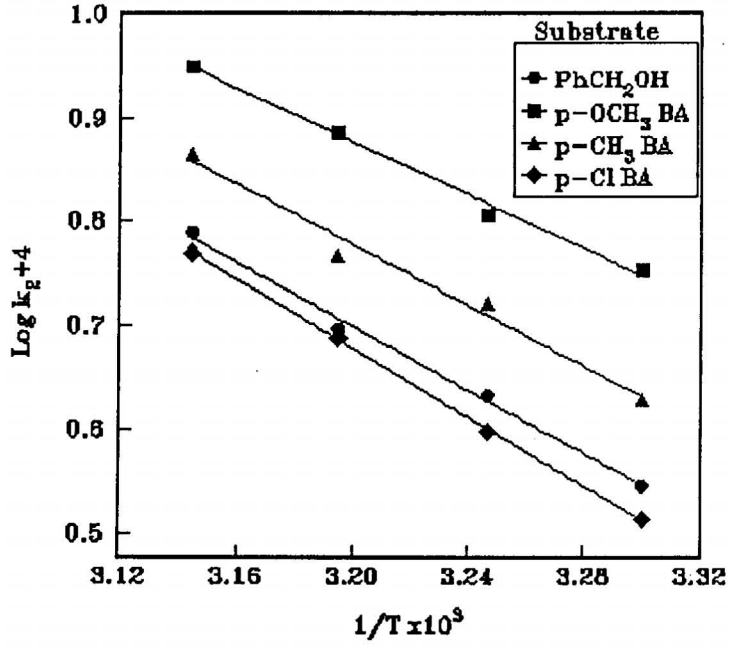


Fig.4.1.5.5(a). Plot of log k_2 Vs 1/T for the oxidation of benzyl alcohols.

PT catalyst -TBPB

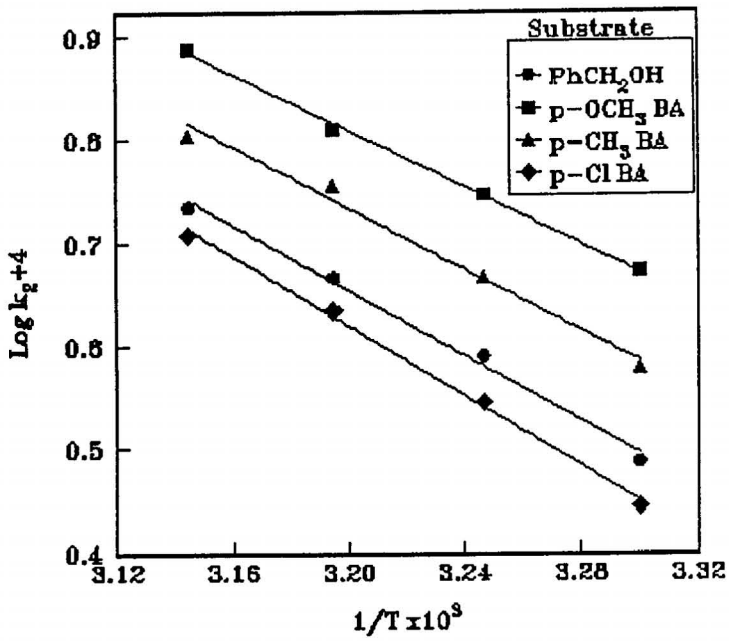


Fig.4.1.5.5(b). Plot of log k_2 Vs 1/T for the oxidation of benzyl alcohols.

PT catalyst -TBAB

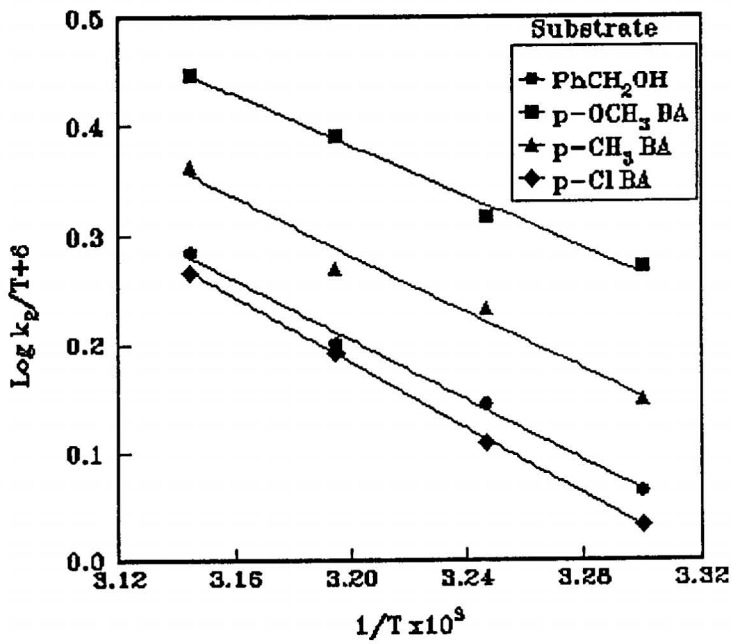


Fig.4.1.5.6(a). Plot log k_2/T Vs 1/T for the oxidation of benzyl alcohols.

PT catalyst -TBPB

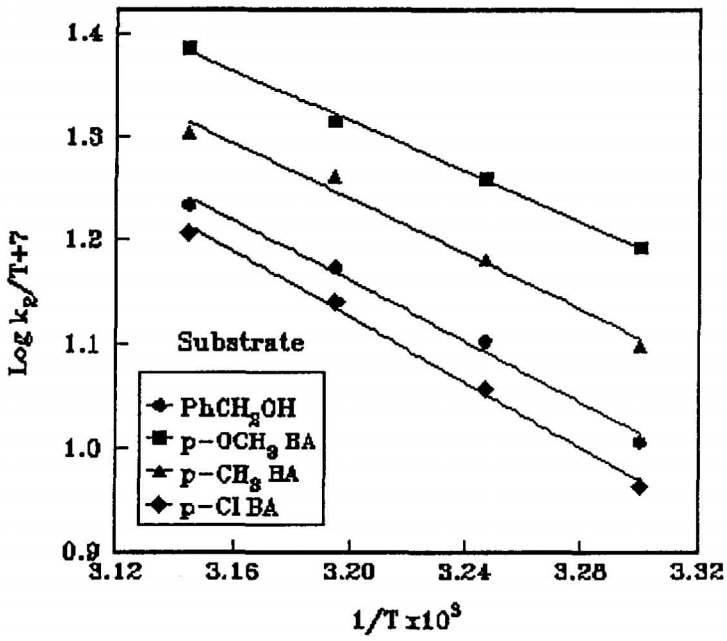


Fig.4.1.5.6(b). Plot log k_2/T Vs 1/T for the oxidation of benzyl alcohols.

PT catalyst -TBAB

Table 4.1.5.5(a) Activation parameters for the oxidation of the benzyl alcohols

Medium - Benzene PT catalyst - TBPB

Temperature - 303 K

Substrate	$k_2 x10^4$ ($dm^3mol^{-1}s^{-1}$)	Ea (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\neq}$ (kJ mol^{-1})
$PhCH_2OH$	3.5121	29.19	26.61	223.40	94.30
p-OCH_3 BA	5.6654	24.70	22.11	234.28	93.10
p-CH_3 BA	4.2649	27.70	25.12	226.71	93.81
p-Cl BA	3.2620	31.61	29.07	215.90	94.49

Table 4.1.5.5(b) Activation parameters for the oxidation of the benzyl alcohols

Medium - Benzene PT catalyst - TBAB

Temperature - 303 K

Substrate	$k_2 x10^4$ ($dm^3 mol^{-1} s^{-1}$)	Ea (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ ($JK^{-1} mol^{-1}$)	$\Delta G^{\neq}$ (kJ mol^{-1})
$PhCH_2OH$	3.0707	30.28	27.70	220.92	94.64
p-OCH_3 BA	4.7036	26.24	23.65	230.74	93.57
p-CH_3 BA	3.7945	28.27	25.69	225.80	94.11
p-Cl BA	2.7828	32.51	29.94	214.35	94.89

4.2. OXIDATION OF PRIMARY ALIPHATIC ALCOHOLS USING PHASE TRANSFERRED MONOCHROMATE

The kinetic studies on the oxidation of primary aliphatic alcohols using phase transferred monochromate were also carried out in benzene. Product analysis, stoichiometry, induced polymerization and the effect of concentration of the oxidant and the substrate were carried out by taking 1-octanol as typical compound. The activation parameters were determined for 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol. Tetrabutylphosphonium bromide and tetrabutylammonium bromide were used as PT catalyst.

4.2.1. Stoichiometry and product analysis

The stoichiometry of the oxidation of aliphatic alcohols by phase transferred monochromate was determined as in the case of benzyl alcohol (Section 4.1.1). It was found that one mole of monochromate is equivalent to three moles of benzyl alcohol.

$$3\ RCH_2OH + Cr(VI) \rightarrow 3\ RCHO + Cr(IV) + 6H^+$$

The product, 1-octanal was identified as its 2,4-dinitrophenylhydrazone (DNP). The yield of the product was about 90%.

4.2.2 Effect of addition of acrylonitrile

The oxidation of aliphatic alcohols by phase transferred monochromate in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and this rules out the involvement of any radical intermediate.

4.2.3. Kinetic studies

The kinetic measurements were carried out under conditions were [alcohol] >> $[Q^+HCrO_4^-]$ where Q^+ is quaternary ammonium cation or quaternary phosphonium cation.

4.2.3.1 Effect of the concentration of oxidant ($Q^+HCrO_4^-$) on the rate of oxidation

The oxidation of 1-octanol was carried out with different initial concentrations of the oxidant using TBPB and TBAB as PT catalyst and rates were measured. The plot of log [oxidant] versus time were found to be linear at various concentrations of the oxidant. This proves that the reaction is first order with respect to the concentration of the oxidant. This was further confirmed from the constancy in the values of specific rates (k_{obs}) for the different concentrations of the oxidant for a given concentration of the substrate. The results of these investigations are presented in Table 4.2.1 and in Fig. 4.2.1(a) and (b).

Table 4.2.1 Effect [oxidant] on the rate of oxidation of 1-octanol

[1-ocatnol] $x10^1 = 2.0$ mol dm^3 Medium - benzene

Temperature - 308 K

$[Q^+HCrO_4^-]$ $x10^3$ (mol dm^{-3})	TBPB		TBAB	
	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)	k_{obs} $x10^5$ (s^{-1})	k_2 $x10^4$ (dm^3 $mol^{-1}s^{-1}$)
4.0	4.1191	2.0595	3.0586	1.5293
5.0	4.2825	2.1412	3.1573	1.5787
6.0	4.0752	2.0376	3.0794	1.5397
8.0	4.2364	2.1182	3.0652	1.5326

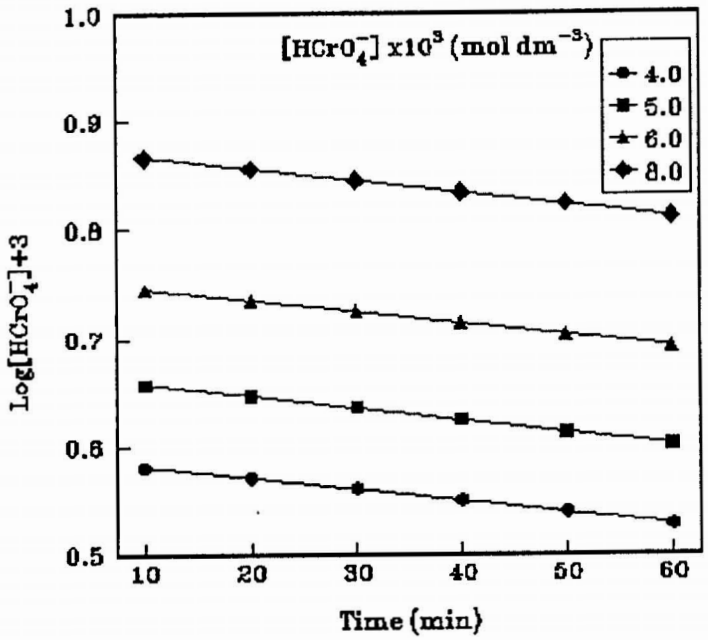


Fig.4.2.1(a). Effect of [oxidant] on the rate of oxidation of 1-octanol.

PT catalyst -TBPB

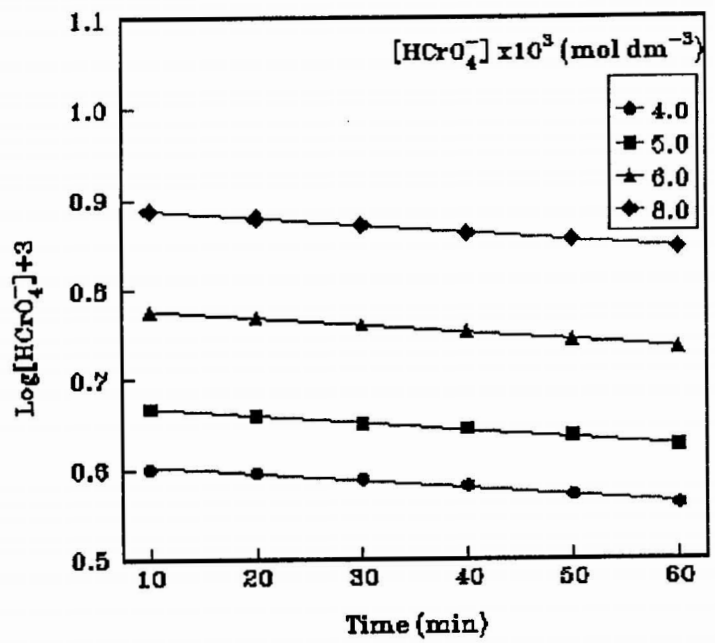


Fig.4.2.1(b). Effect of [oxidant] on the rate of oxidation of 1-octanol.

PT catalyst -TBAB

4.2.3.2. Effect of the concentration of substrate on the rate of oxidation

The effect of [substrate] on the rate of oxidation was studied with different initial concentrations of the substrate. The observed rate constant increased linearly with the increase in the concentration of 1-octanol. Further the second order rate constants (k_2) were found to be constant indicating first order dependence of the reaction with respect to [substrate]. These results are presented in Table 4.2.2 and in Fig. 4.2.2.1(a) and (b).

Table 4.2.2 Effect of [substrate] on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} Medium - Benzene

Temperature - 308 K.

[1-octanol] x10^1 (mol dm^{-3})	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3mol^{-1}s^{-1}$)
1.2	1.9652	1.6377	1.6154	1.3462
1.6	3.0498	1.9061	2.5618	1.6011
2.0	4.2825	2.1412	3.1573	1.5787
3.0	5.7333	1.9111	4.4064	1.4688

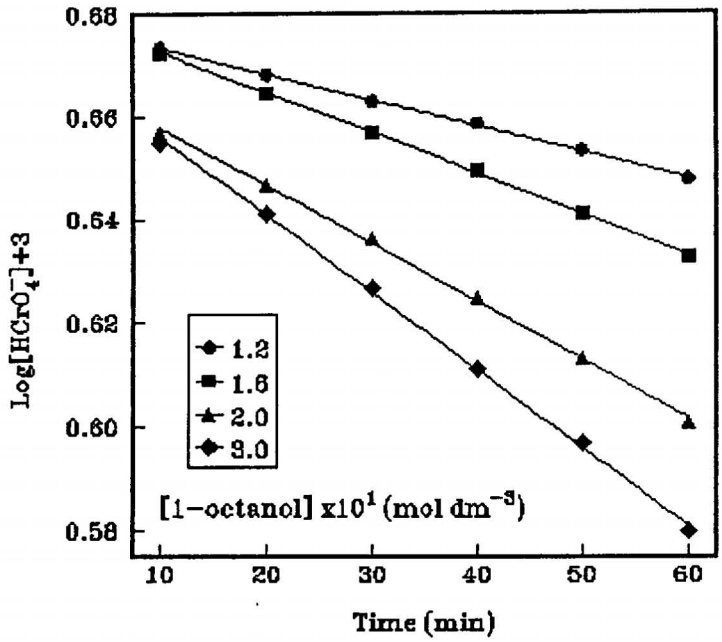


Fig.4.2.2.1(a). Effect of [substrate] on the rate of oxidation of 1-octanol.

PT catalyst -TBPB

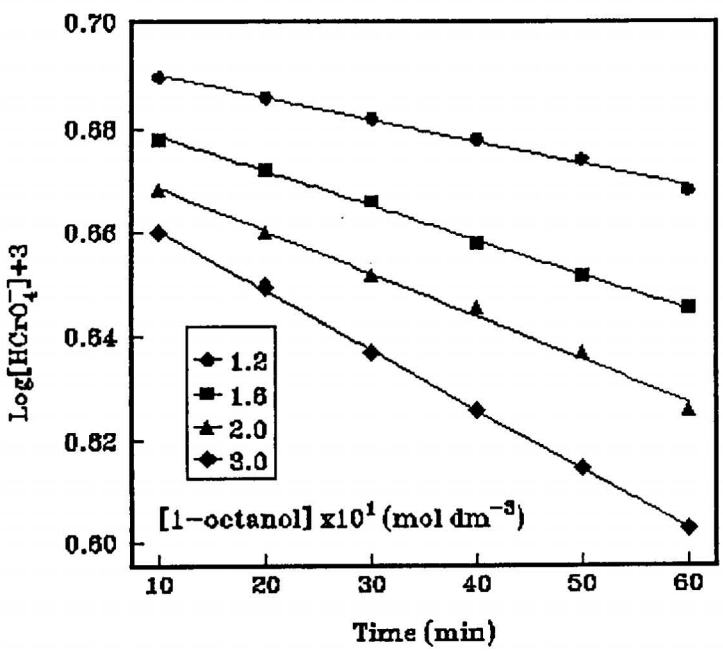


Fig.4.2.2.1(b). Effect of [substrate] on the rate of oxidation of 1-octanol.

PT catalyst -TBAB

The first order dependence on [substrate] is further confirmed by the plot of log k_{obs} versus log [substrate] which is linear with a slope of unity (Fig. 4.2.2.2).

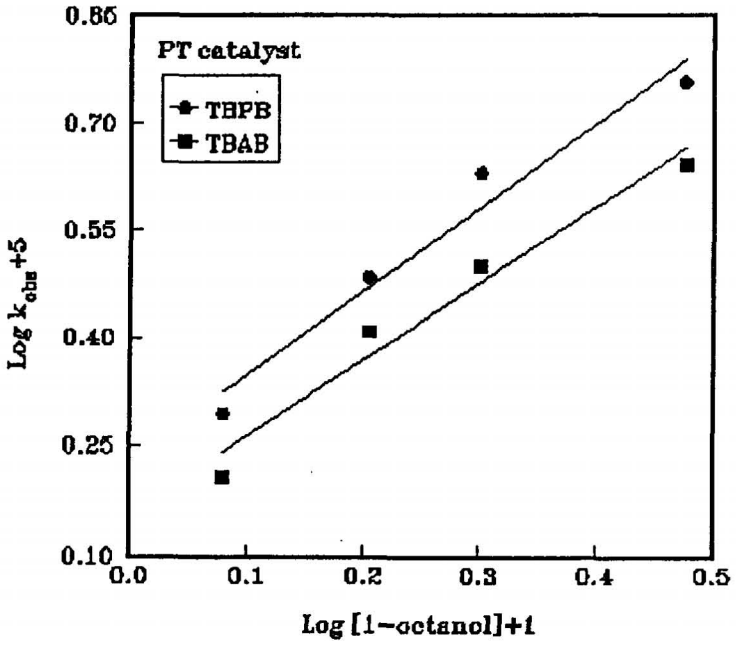


Fig.4.2.2.2. Plot of log k_{obs} Vs log [substrate]

The plot of $1/k_{obs}$ versus 1/[1-octanol] is linear (r = 0.9823 and 0.9813 for TBPB and TBAB respectively) with an intercept on the rate coordinate (Fig. 4.2.2.3). This proved the existence of a long lived intermediate and implies Michaelis-Menten type kinetics with respect to alcohol.

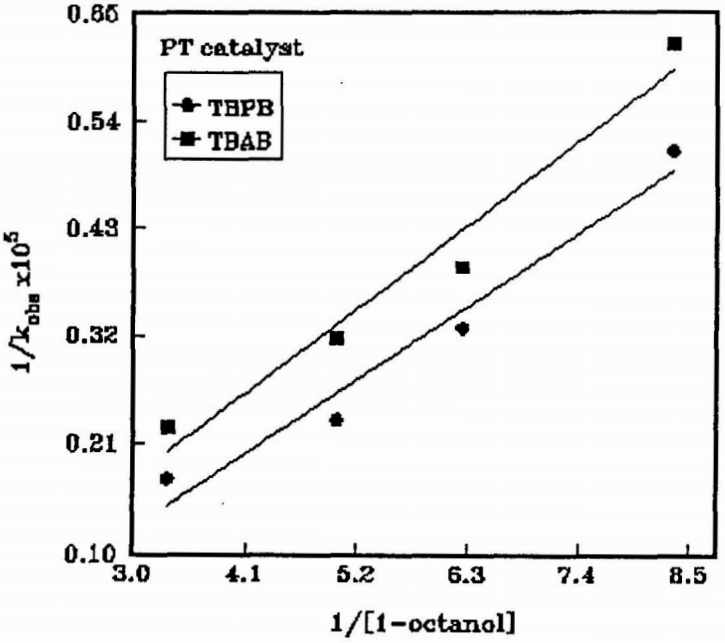


Fig.4.2.2.3. Lineweaver-Burke plot of $1/k_{obs}$ Vs 1/[1-octanol]

4.2.3.3 Effect of temperature on the rate of oxidation of aliphatic alcohols

The influence of temperature on the rate of oxidation of aliphatic alcohols namely 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol using phase transferred monochromate were studied in the temperature range 303 K to 318 K. The activation parameters for the oxidation of respective alcohols were determined.

4.2.3.3.1. Effect of temperature on the rate of oxidation of 1-butanol

The effect of temperature on the rate of oxidation of 1-butanol using phase transferred monochromate is presented in Table 4.2.3.1 and in Fig. 4.2.3.1(a) and (b).

Table 4.2.3.1 Effect of temperature on the rate of oxidation of 1-butanol

$[Q^+HCrO_4^-]$ x10^3 =5.0 mol dm^{-3} [1-butanol] x10^1= 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^5 ($dm^3mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^5 ($dm^3mol^{-1}s^{-1}$)
303	1.9268	9.6342	1.3873	6.9364
308	2.3162	11.5810	2.0102	10.0510
313	2.8612	14.3060	2.3535	11.7670
318	3.4512	17.2560	2.7417	13.7080

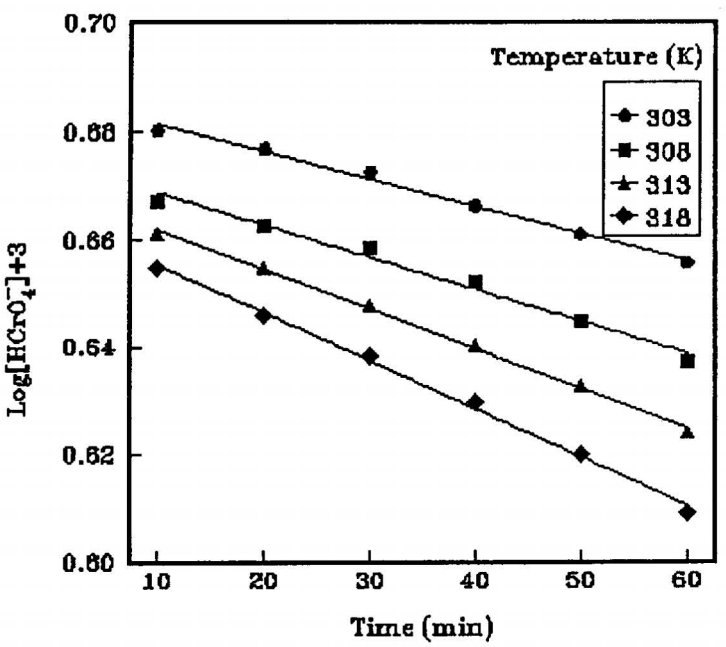


Fig.4.2.3.1(a). Effect of temperature on the rate of oxidation of 1-butanol.

PT catalyst -TBPB

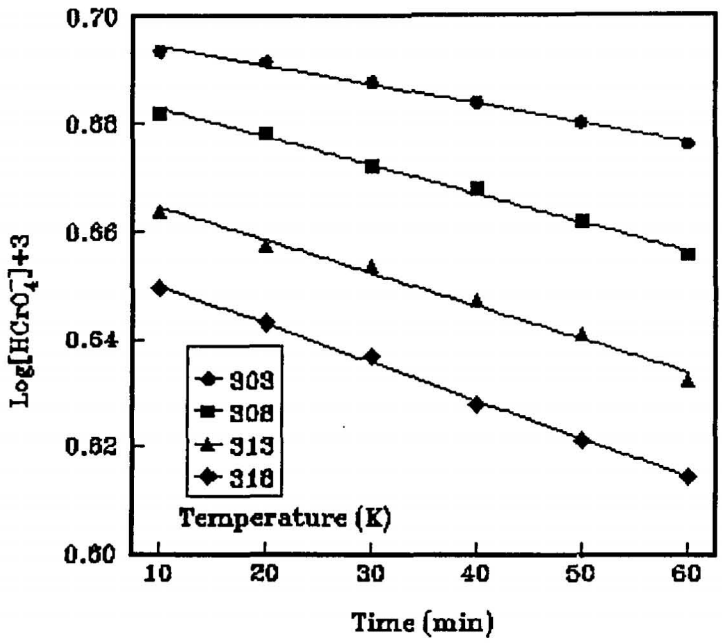


Fig.4.2.3.1(b). Effect of temperature on the rate of oxidation of 1-butanol.

PT catalyst -TBAB

4.2.3.3.2 Effect of temperature on the rate of oxidation of 1-pentanol

The effect of temperature on the rate of oxidation of 1-pentanol using phase transferred monochromate is presented in Table 4.2.3.2 and in Fig. 4.2.3.2(a) and (b).

Table 4.2.3.2 Effect of temperature on the rate of oxidation of 1-pentanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-pentanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	$k_{obs}x10^5$ (s^{-1})	$k_2 x10^5$ ($dm^3 mol^{-1}s^{-1}$)	$k_{obs}x10^5$ (s^{-1})	$k_2 x10^5$ ($dm^3 mol^{-1}s^{-1}$)
303	2.6814	13.4070	1.6954	8.4772
308	3.3766	16.8830	2.2175	11.0870
313	4.2638	21.3190	2.6781	13.3900
318	4.7486	23.7430	3.3350	16.6750

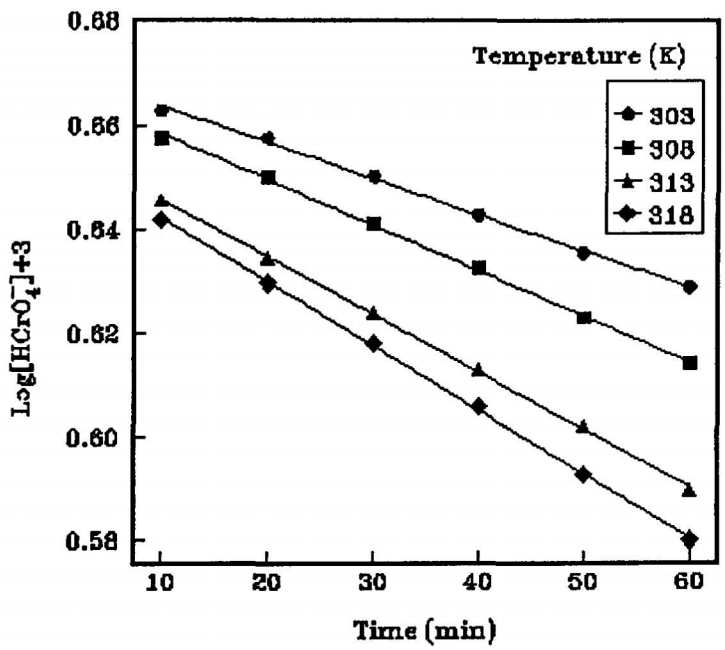


Fig.4.2.3.2(a). Effect of temperature on the rate of oxidation of 1-pentanol.

PT catalyst -TBPB

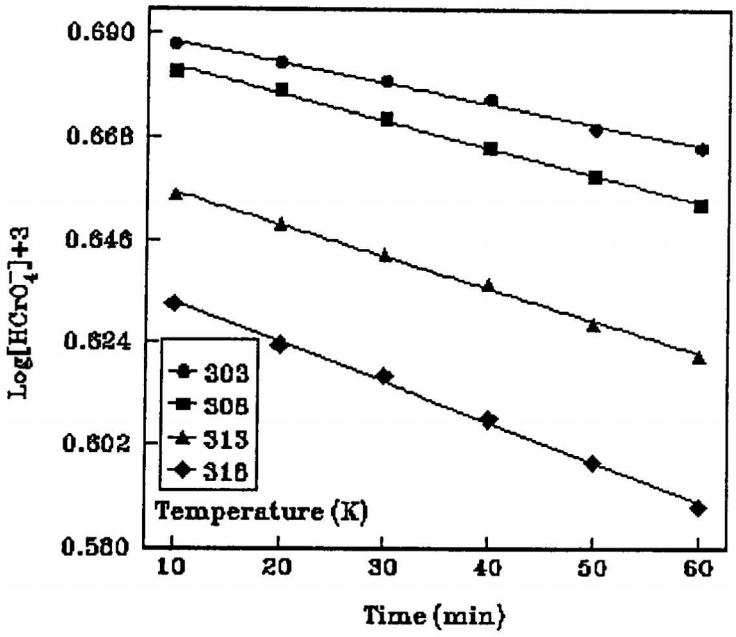


Fig.4.2.3.2(b). Effect of temperature on the rate of oxidation of 1-pentanol.

PT catalyst -TBAB

4.2.3.3.3. Effect of temperature on the rate of oxidation of 1-hexanol

The effect of temperature on the rate of oxidation of 1-hexanol using phase transferred monochromate is presented in Table 4.2.3.3 and in Fig. 4.2.3.3(a) and (b).

Table 4.2.3.3 Effect of temperature on the rate of oxidation of 1-hexanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-hexanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^5 ($dm^3 mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^5 ($dm^3 mol^{-1}s^{-1}$)
303	2.8963	14.4810	1.9784	9.8919
308	3.6091	18.0455	2.5377	12.6880
313	4.4525	22.2620	3.1913	15.9565
318	5.1083	25.5415	3.8318	19.1590

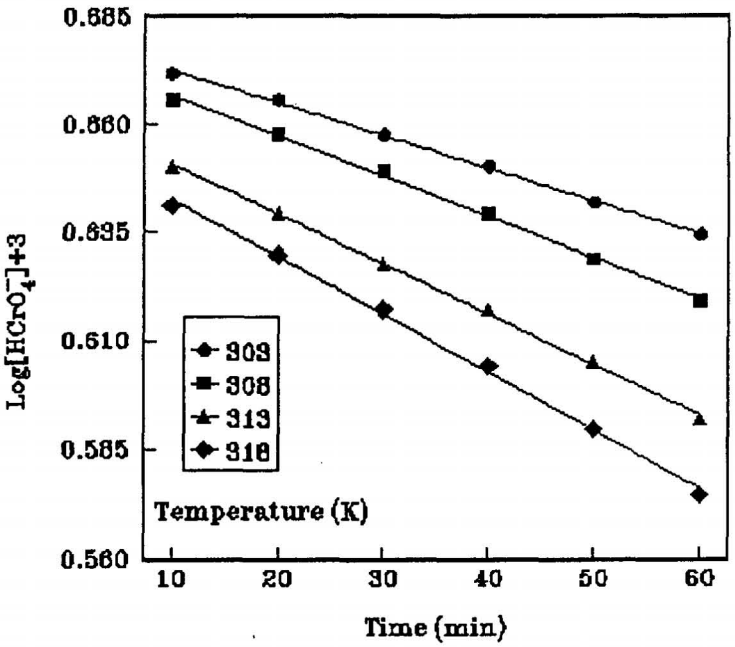


Fig.4.2.3.3(a). Effect of temperature on the rate of oxidation of 1-hexanol.

PT catalyst -TBPB

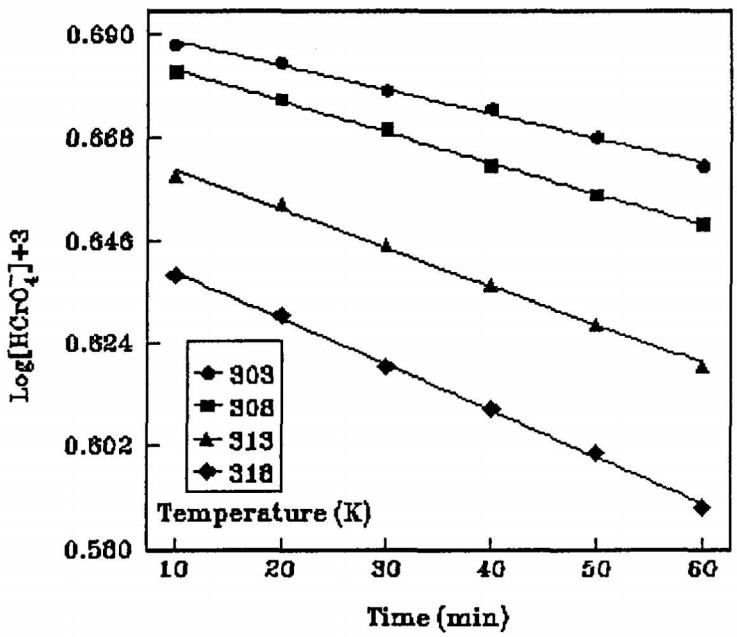


Fig.4.2.3.3(b). Effect of temperature on the rate of oxidation of 1-hexanol.

PT catalyst -TBAB

4.2.3.3.4. Effect of temperature on the rate of oxidation of 1-heptanol

The effect of temperature on the rate of oxidation of 1-heptanol using phase transferred monochromate is presented in Table 4.2.3.4 and in Fig. 4.2.3.4(a) and (b).

Table 4.2.3.4 Effect of temperature on the rate of oxidation of 1-heptanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-heptanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3\ mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3\ mol^{-1}s^{-1}$)
303	3.1167	1.5584	2.1879	1.0939
308	3.9327	1.9663	2.6912	1.3456
313	4.6367	2.3184	3.1957	1.5978
318	5.5020	2.7510	4.2748	2.1374

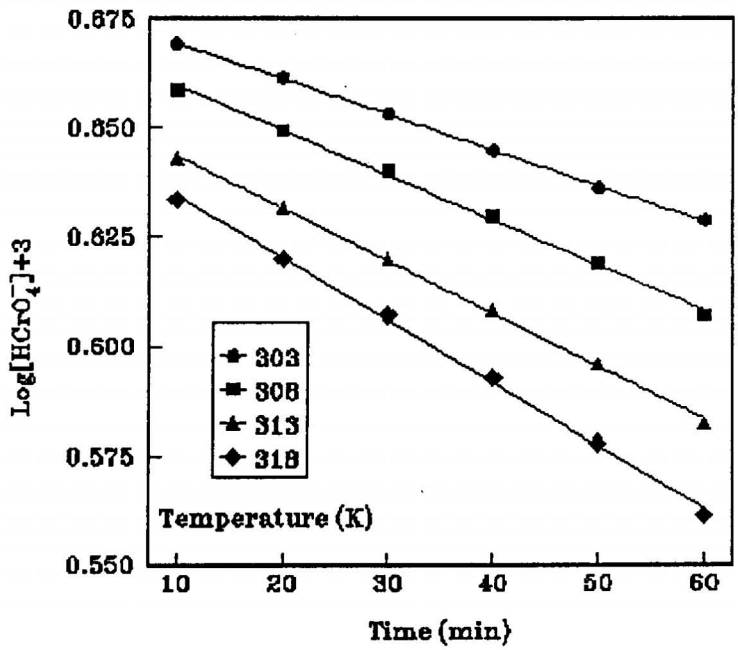


Fig.4.2.3.4(a). Effect of temperature on the rate of oxidation of 1-heptanol.

PT catalyst -TBPB

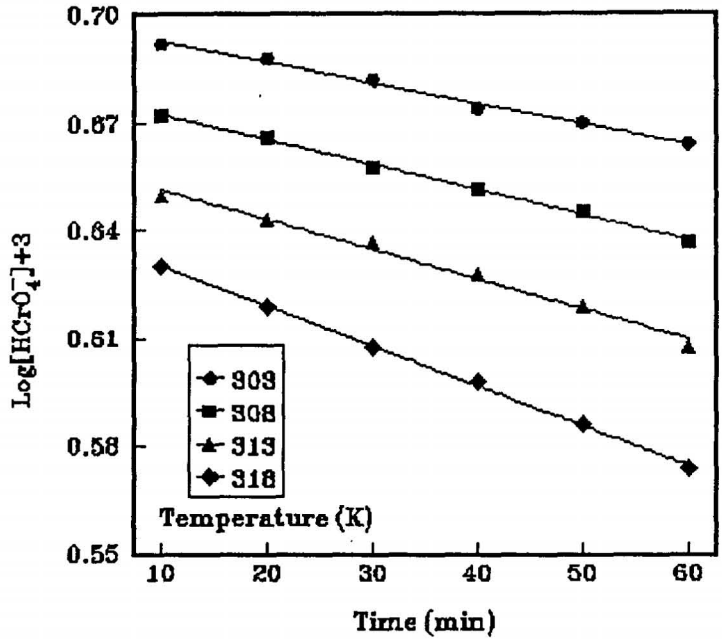


Fig.4.2.3.4(b). Effect of temperature on the rate of oxidation of 1-heptanol.

PT catalyst -TBAB

4.2.3.3.5. Effect of temperature on the rate of oxidation of 1-octanol

The effect of temperature on the rate of oxidation of 1-octanol by phase transferred monochromate is presented in Table 4.2.3.5 and in Fig. 4.2.3.5(a) and (b).

Table 4.2.3.5 Effect of temperature on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-octanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)
303	3.1444	1.5721	2.5508	1.2754
308	4.2825	2.1412	3.1573	1.5787
313	5.0008	2.5004	3.8570	1.9285
318	5.5689	2.7844	4.9372	2.4686

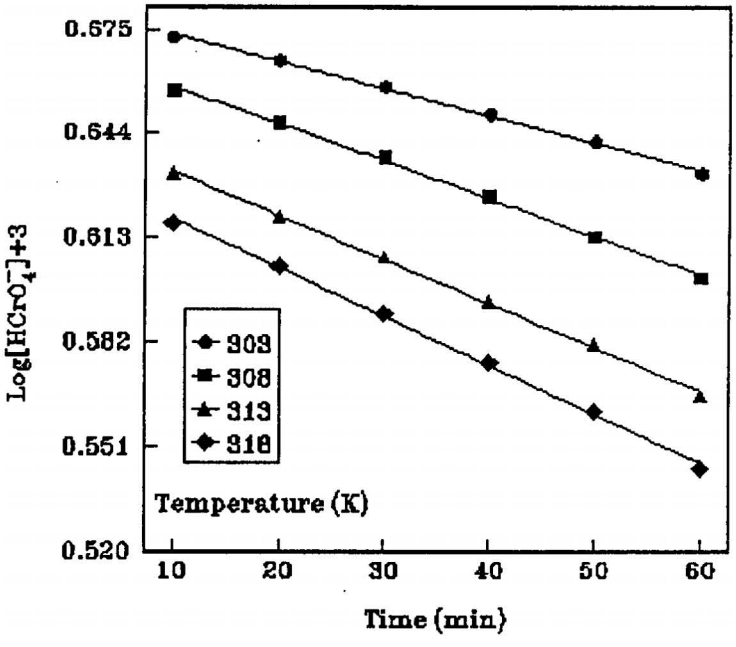


Fig.4.2.3.5(a). Effect of temperature on the rate of oxidation of 1-octanol.

PT catalyst -TBPB

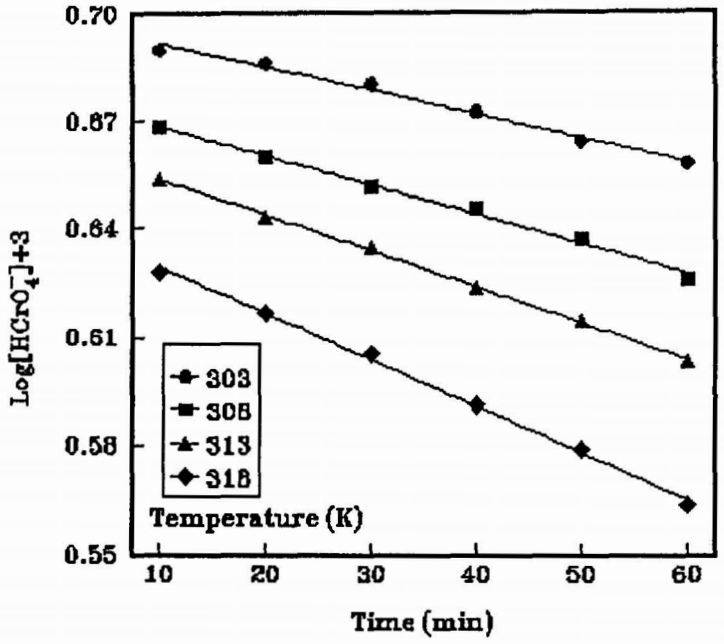


Fig.4.2.3.5(b). Effect of temperature on the rate of oxidation of 1-octanol.

PT catalyst -TBAB

4.2.3.3.6. Effect of temperature on the rate of oxidation of 1-nonanol

The effect of temperature on the rate of oxidation of 1-nonanol using phase transferred monochromate is presented in Table 4.2.3.6 and in Fig. 4.2.3.6(a) and (b).

Table 4.2.3.6 Effect of temperature on the rate of oxidation of 1-nonanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-nonanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)
303	3.3152	1.6576	2.7768	1.3884
308	4.2682	2.1341	3.1617	1.5808
313	5.1171	2.5585	4.2364	2.1182
318	5.8156	2.9078	5.1609	2.5805

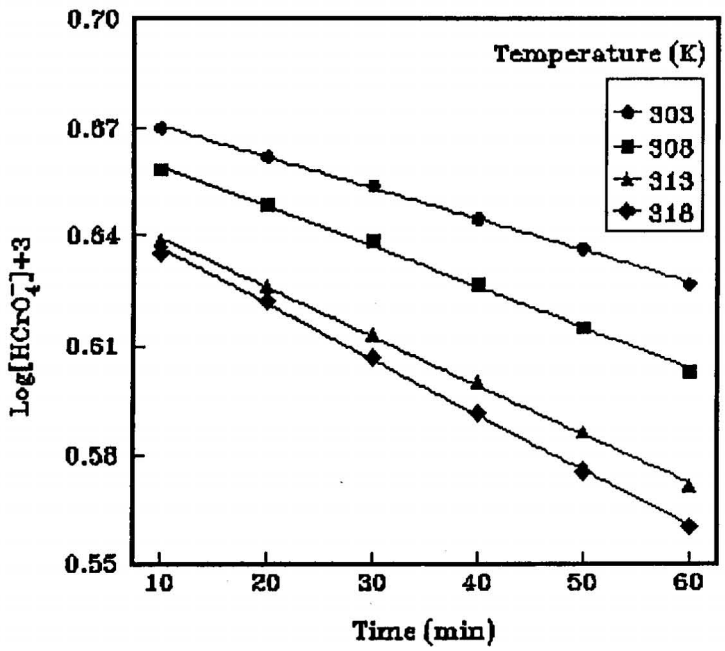


Fig.4.2.3.6(a). Effect of temperature on the rate of oxidation of 1-nonanol.

PT catalyst -TBPB

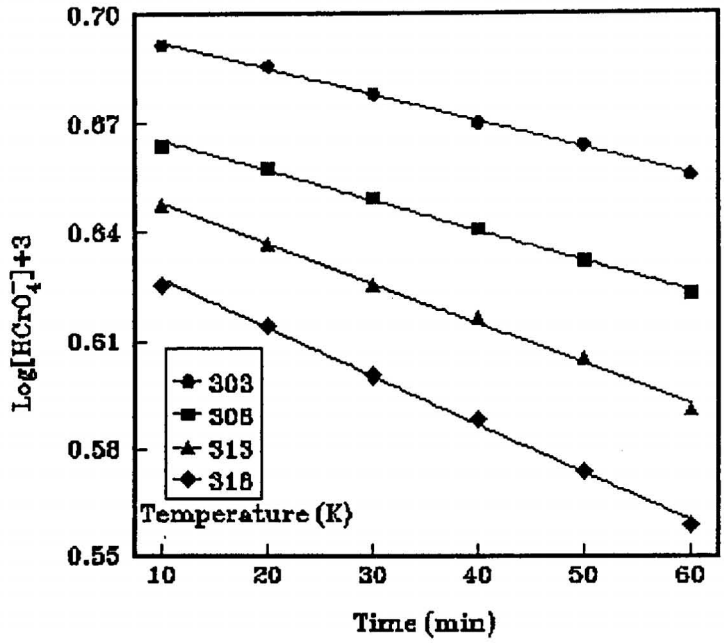


Fig.4.2.3.6(b). Effect of temperature on the rate of oxidation of 1-nonanol.

PT catalyst -TBAB

4.2.3.3.7. Effect of temperature on the rate of oxidation of 1-decanol

The effect of temperature on the rate of oxidation of 1-decanol using phase transferred monochromate is presented in Table 4.2.3.7 and in Fig. 4.2.3.7(a) and (b).

Table 4.2.3.7 Effect of temperature on the rate of oxidation of 1-decanol

$[Q^+HCrO_4^-]$ x10^3 = 5.0 mol dm^{-3} [1-decanol] x10^1 = 2.0 mol dm^{-3}

Medium - Benzene

Temperature (K)	TBPB		TBAB	
	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)	k_{obs} x10^5 (s^{-1})	k_2 x10^4 ($dm^3 mol^{-1}s^{-1}$)
303	3.4578	1.7289	2.8393	1.4196
308	4.2726	2.1363	3.8142	1.9071
313	5.2333	2.6167	4.6597	2.3299
318	6.0404	3.0202	5.4548	2.7274

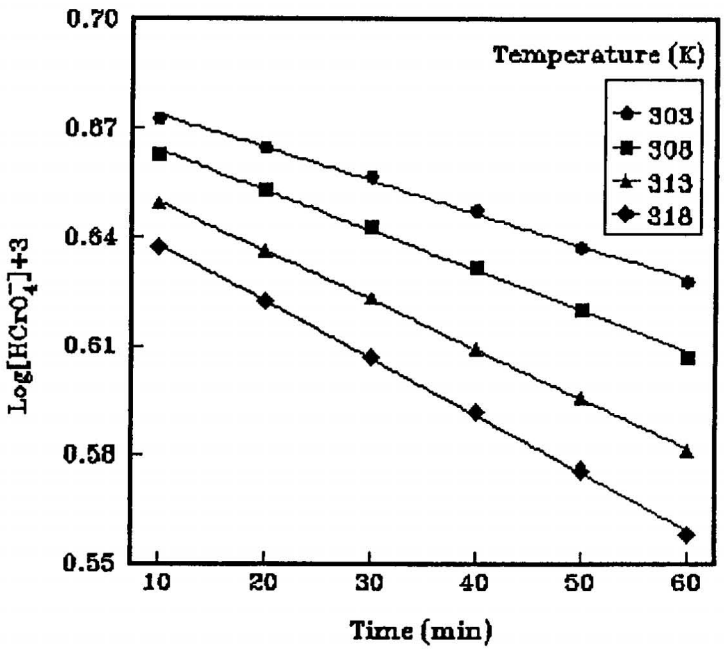


Fig.4.2.3.7(a). Effect of temperature on the rate of oxidation of 1-decanol.

PT catalyst -TBPB

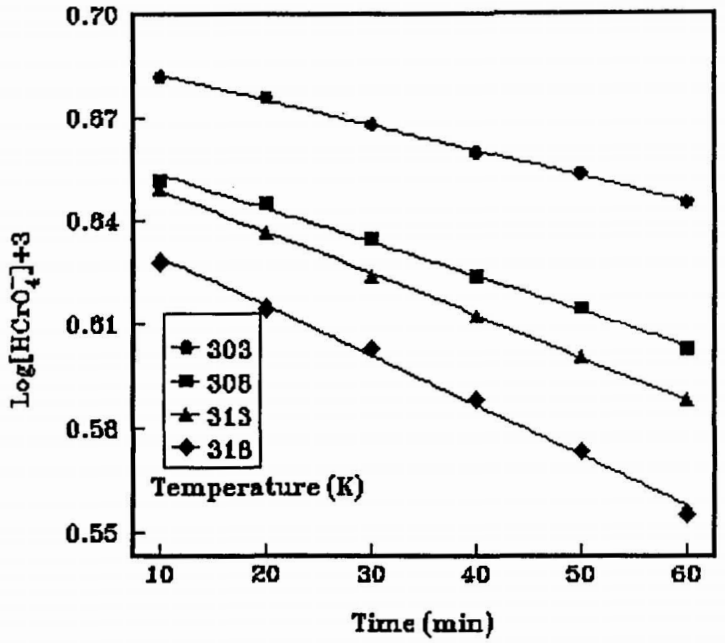


Fig.4.2.3.7(b). Effect of temperature on the rate of oxidation of 1-decanol.

PT catalyst -TBAB

The values of various thermodynamic parameters were calculated from the plot of log k_2Vs 1/T {Fig. 4.2.3.8(a) and (b)} and from plot of log k_2/T Vs 1/T {Fig. 4.2.3.9(a) and (b)}. The values of various thermodynamic parameters are presented in Table 4.2.3.8(a) and (b).

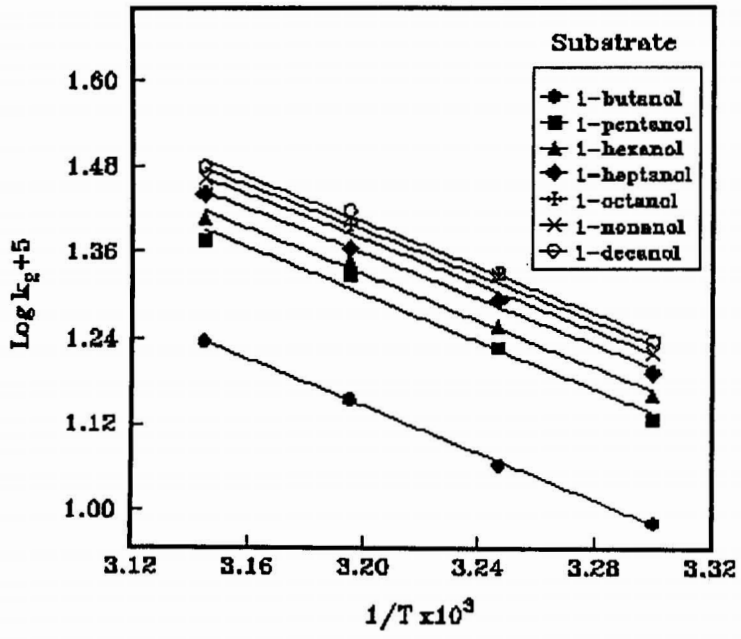


Fig.4.2.3.8(a). Plot of log k_2 Vs 1/T for the oxidation of aliphatic alcohols.

PT catalyst -TBPB

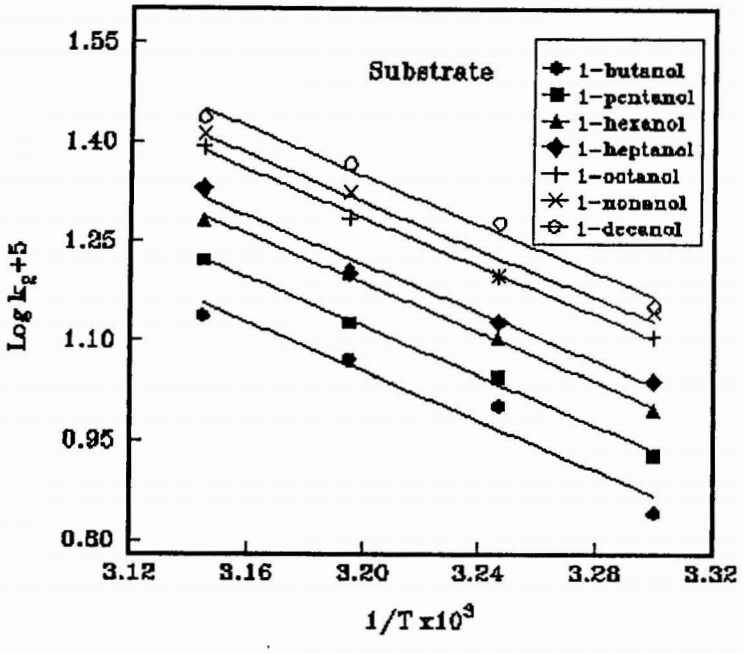


Fig.4.2.3.8(b). Plot of log k_2 Vs 1/T for the oxidation of aliphatic alcohols.

PT catalyst -TBAB

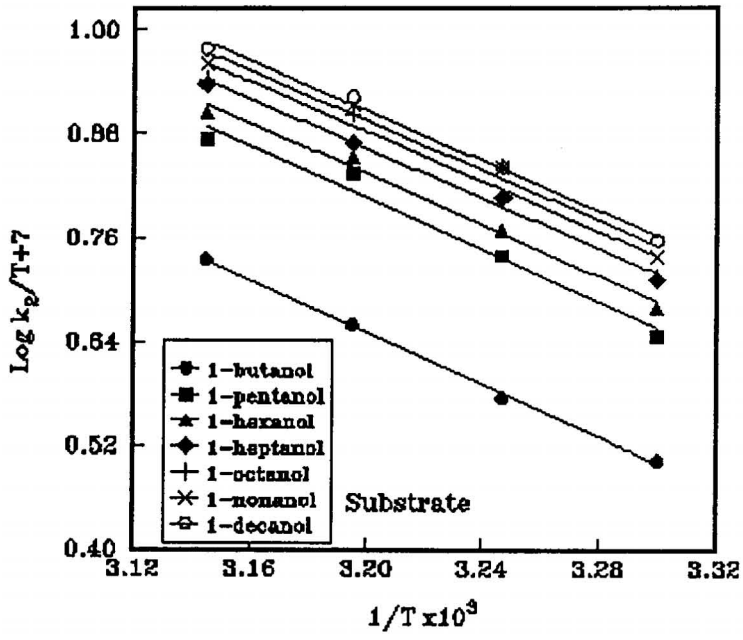


Fig.4.2.3.8(a). Plot of log k_2/T Vs 1/T for the oxidation of aliphatic alcohols.

PT catalyst -TBPB

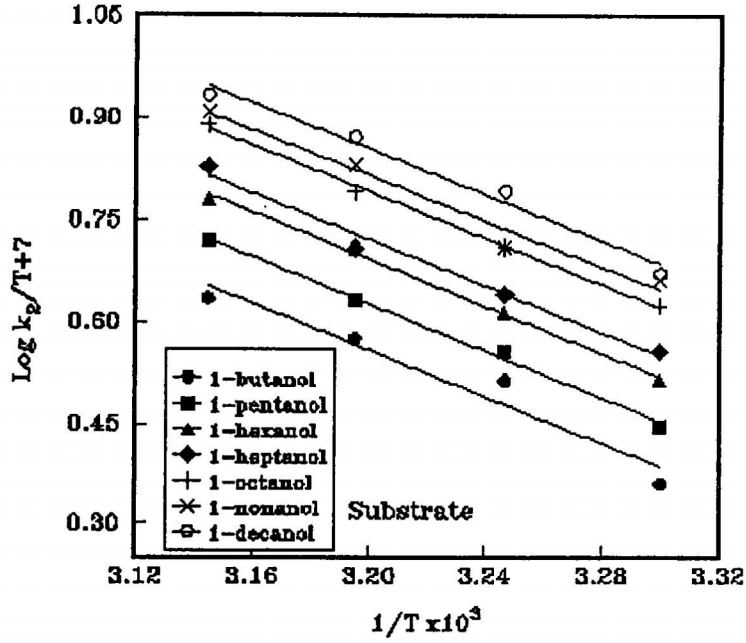


Fig.4.2.3.8(b). Plot of log k_2/T Vs 1/T for the oxidation of aliphatic alcohols.

PT catalyst -TBAB

Table 4.2.3.8(a) Activation parameters for the oxidation of aliphatic alcohols

Medium - Benzene PT catalyst -TBPB Temperature -303 K

Substrate	$k_2 x10^5$ ($dm^3 mol^{-1}s^{-1}$)	Ea ($kJmol^{-1}$)	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$-\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\neq}$ ($kJmol^{-1}$)
1-butanol	9.6342	31.41	28.83	226.83	97.56
1-pentanol	13.4070	31.28	28.70	224.52	96.73
1-hexanol	14.4815	30.69	28.11	225.82	96.53
1-heptanol	15.5835	30.00	27.42	227.49	96.35
1-octanol	15.7210	30.07	27.50	227.15	96.33
1-nonanol	16.5760	30.00	27.41	227.01	96.19
1-decanol	17.2890	30.10	27.53	226.26	96.09

Table 4.2.3.8(b) Activation parameters for the oxidation of aliphatic alcohols

Medium - Benzene PT catalyst -TBAB Temperature -303 K.

Substrate	$k_2 x10^5$ ($dm^3 mol^{-1} s^{-1}$)	Ea ($kJmol^{-1}$)	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$-\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\neq}$ ($kJmol^{-1}$)
1-butanol	6.9364	35.40	32.81	216.43	98.39
1-pentanol	8.4772	35.58	32.99	214.17	97.88
1-hexanol	9.8919	35.49	32.92	213.12	97.49
1-heptanol	10.9385	34.92	32.35	214.16	97.24
1-octanol	12.7540	34.94	32.36	212.85	96.85
1-nonanol	13.8840	34.46	31.88	213.73	96.64
1-decanol	14.1960	34.67	32.10	212.82	96.58

Discussion on the results obtained in the above investigation shows that the oxidation of all the aromatic as well as the aliphatic alcohols follow more or less the same path with similar stoichiometry. One mole of the

monochromate is equivalent to three moles of the alcohol. The product,viz the aldehydes were identified as their 2,4-dinitrophenylhydrozone (DNP) and yield of the products were around 90%. The sequential scan of the absorption spectra for the oxidation of primary alcohols using $Q^+HCrO_4^-$ ($Q=TBP^+$) in benzene at regular intervals of time {Fig. 4.1. (a) and (b)} showed isosbectic points at 321 nm and 394 nm for benzyl alcohol and at 333 nm and 394 nm for 1-octanol. This rules out the involvement of any complex events during the reaction and shows the formation a single product.[160-162, 166, 189-191]

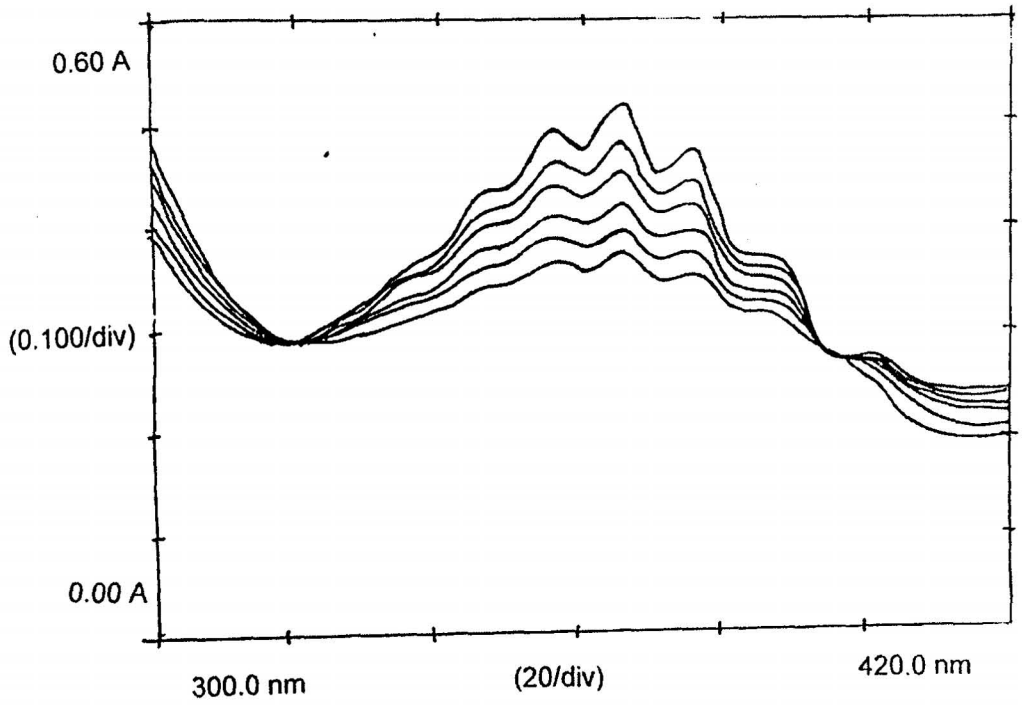


Fig. 4.1.(a). Absorption spectrum of the successive scans for the oxidation of benzyl alcohol by $Q^+HCrO_4^-$($Q=TBP^+$) in benzene at 308 K (isosbestic points at 321 nm and 394 nm).

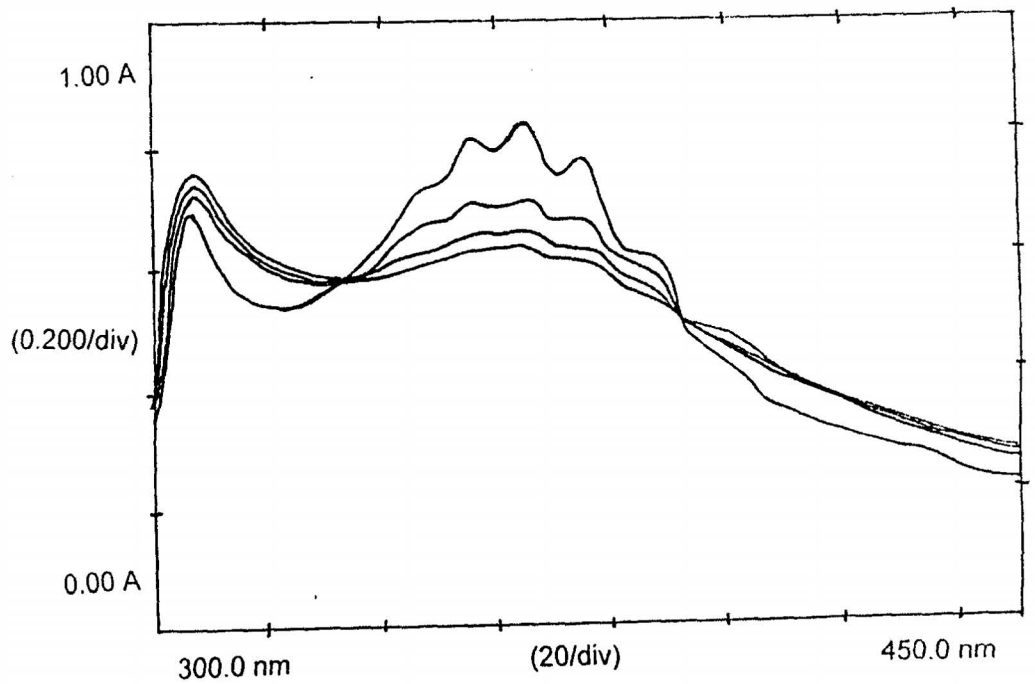


Fig. 4.1.(b). Absorption spectrum of the successive scans for the oxidation of 1-octanol by $Q^+HCrO_4^-$(Q=TBP^+) in benzene at 308 K (isosbestic points at 333 nm and 394 nm).

The reactions conformed to first order kinetics with respect to the concentration of the oxidant as well as that of the reactant. The rate of oxidation of alcohol in various solvents was found to increase with increase in dielectric constant of the medium. A plot of log k_2 versus 1/D, were D is dielectric constant of the medium is linear with a negative slope indicating interaction between a negative ion ($HCrO_4^-$) and a dipole[192] (alcohol). The reaction mixture failed to induce the polymerization of added acrylonitrile which rules out the involvement of any radical intermediate. This indicated

that a one electron oxidation is not possible and supports the interaction between an ion and a dipole.

The study of the influence of substituents at the para position of the benzene ring of benzyl alcohol showing rate acceleration of the oxidation by electron-releasing groups and the electron-withdrawing groups retard the process. The plots log k_2 versus σ, where σ is the substituent constant were found to be linear indicating the excellent correlation between the structure and the reactivity as given in the linear free energy relationships proposed by Hammet.[187] The polar reaction constant, ρ obtained were –0.4463 and −0.4396 for TBPB and TBAB respectively.

The activation enthalpies and entropies for the oxidation of benzyl alcohols are linearly related (r = 0.9981 and 0.9988 for TBPB and TBAB respectively). These plots are presented in Fig. 4.2.(a) and (b).

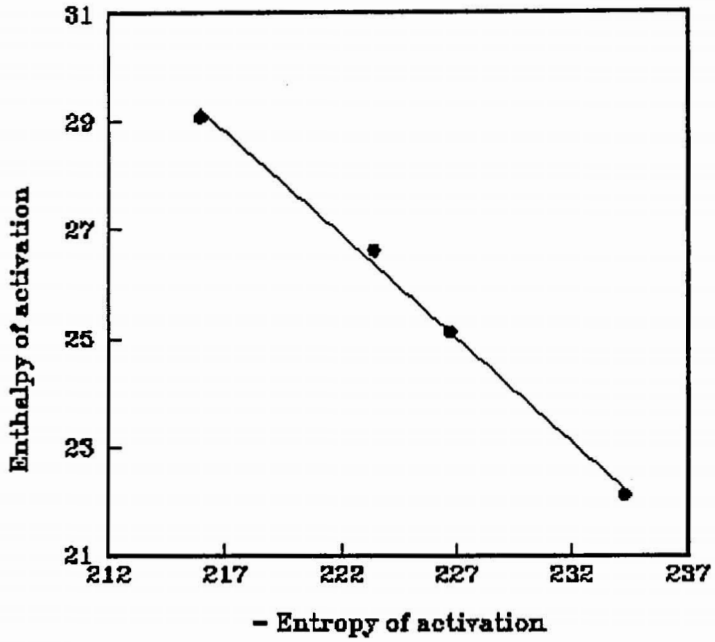


Fig.4.2(a). Isokinetic plot for the oxidation of benzyl alcohols.

PT catalyst -TBPB

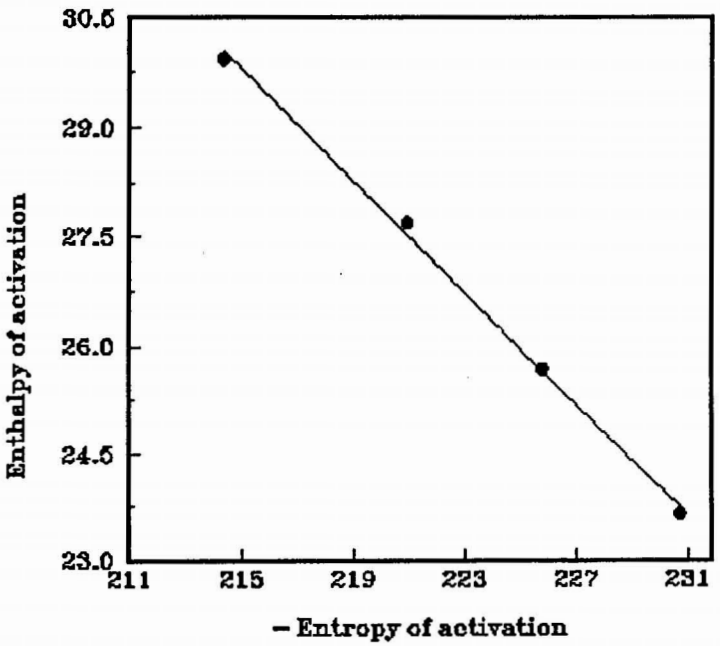


Fig.4.2(b). Isokinetic plot for the oxidation of benzyl alcohols.

PT catalyst -TBAB

The correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ was tested and found valid by applying Exner's criterion[194] by plotting log k_2 at 313 K and log k_2 at 303 K (r=0.9941 and 0.9946 for TBPB and TBAB respectively). These plots are presented in Fig. 4.3(a) and (b).

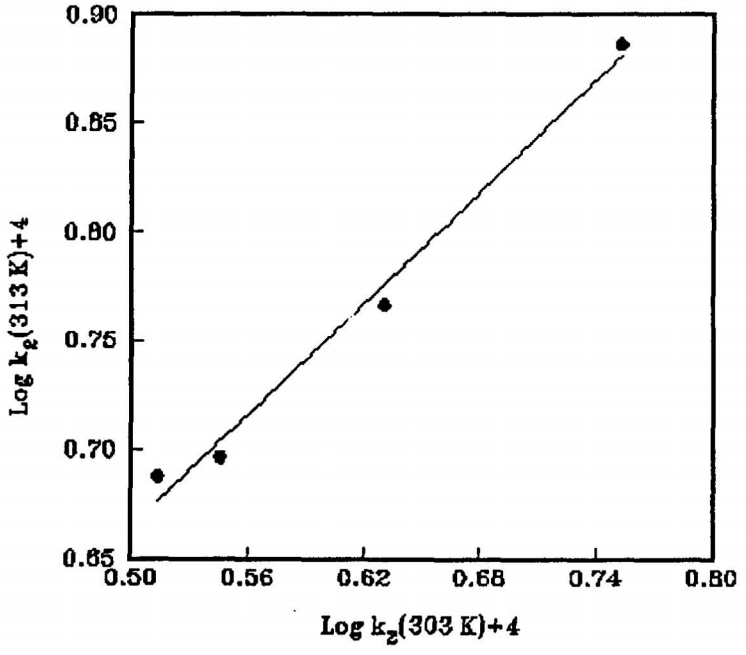


Fig.4.3(a). Exner's plot for the oxidation of benzyl alcohols.

PT catalyst -TBPB

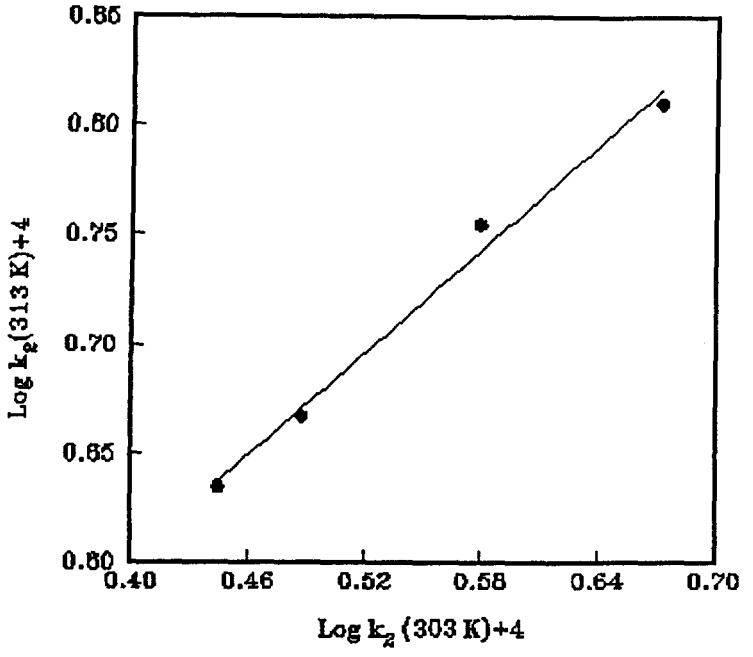


Fig.4.3(b). Exner's plot for the oxidation of benzyl alcohols.

PT catalyst -TBAB

The isokinetic temperature obtained from $\Delta H^{\neq}$ Vs $\Delta S^{\neq}$ plot is 381 K and 385 K for TBPB and TBAB respectively and from the Exner's plot the isokinetic temperature obtained is 387 K and 357 K for TBPB and TBAB respectively. These results suggest that similar mechanism operates for the oxidation of all the aromatic alcohols. This is further confirmed by the almost constant value of the free energy of activation ($\Delta G^{\neq} \approx 94$ for aromatic alcohols and $\Delta G^{\neq} \approx 97$ for aliphatic alcohols) {Table 4.1.5.5 (a) and (b) and Table 4.2.3.8(a) and (b)}.

Mechanism

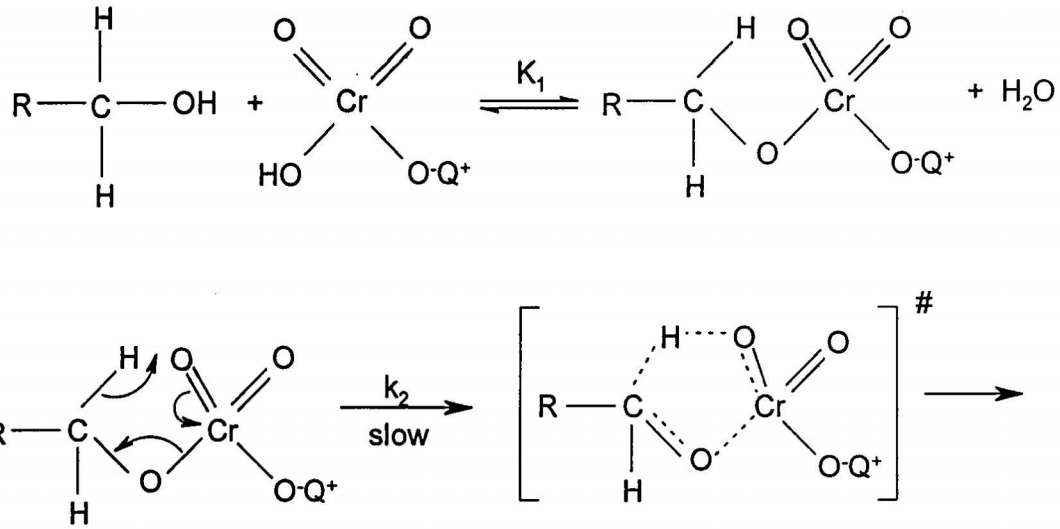
The anionic species,viz the $HCrO_4^-$ ions which is formed in the given aqueous acidic medium gets phase transferred to the organic medium as ion-pair ($Q^+HCrO_4^-$) in the presence of PT catalyst. The fact that a radical type mechanism is ruled out by the failure to induce the polymerization of acrylonitrile. The most probable route is through an interaction of the oxidant with the substrate alcohol to form a complex which subsequently disproportionate to the product. The observation of Michaelis - Menten type behaviour in the kinetics is a clear indication of this effect to generate an intermediate in a pre-equilibrium step and its subsequent disproportionation in the rate-determining step. It has been already established that oxidation of primary alcohols exhibits a substantial primary kinetic isotope effect.[195,196] This confirmed the clearage of an α-C-H bond in the rate-determining step. The negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a corbocation in character. Hence the transfer of hydride ion from the alcohol to the oxidant is suggested. The hydride ion transfer mechanism is also supported by the major role of cation solvating power of the solvents.

The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. It has been reported that the chromate ester has greater stability in organic solvents

than in water.[107, 197, 198] The negative $\Delta S^{\neq}$ values are in agreement with the formation of the chromate ester with a high degree of orderedness supporting cyclic intermediate formation. Bordwell has documented a cogent evidence against the occurrence of concerted one step bimolecular process by hydrogen transfer.[199] It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state are the only truly symmetrical processes involving linear hydrogen transfer.[200] Littler has also shown that a cyclic hydride transfer in the oxidation of alcohols by Cr(VI), involves six electrons and being a Huckel type system, is an allowed process.[201] Thus the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product. The mechanism proposed is presented as

$$[Q^+HCrO_4^-]_{H_2O} \rightleftharpoons [Q^+HCrO_4^-]_{org}$$

This phase transferred $Q^+HCrO_4^-$ reacts with alcohol in the organic medium as follows.



$$RCHO + Cr(IV) + Q^{+} + H^{+}$$

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

A suitable rate expression for the oxidation of primary alcohols using phase transferred monochromate in consistent with the above mechanism can be given by equation 4.1.

$$\frac{-d[HCrO_4^-]}{dt} = k_2[complex] \qquad (4.1)$$

$$= K_1k_2\,[RCH_2OH]\,[HCrO_4^-]$$

4.3. Oxidation of aromatic alcohols using potassium dichromate in aqueous acetic acid medium

The kinetics of the oxidation of benzyl alcohol and its para-substituted derivatives,viz p-OCH_3, p-CH_3,p-Cl and p-NO_2 using potassium dichromate were studied in 20% aqueous acetic acid with a view to compare the results with that of obtained by using phase transferred monochromate in benzene medium.

4.3.1. Stoichiometry and product analysis

Stoichiometry of the oxidation was established by equilibrating known excess concentration of potassium dichromate with known amount of benzyl alcohol. It was found that one mole of dichromate is equivalent to three moles of benzyl alcohol.

$$3PhCH_2OH + Cr(VI) \rightarrow 3PhCHO + Cr(IV) + 6H^+$$

The product, benzaldehyde was identified as its 2,4-dinitrophenylhydrazone (DNP). The yield of the product was above 85%.

4.3.2. Effect of addition of acrylonitrile

The oxidation of benzyl alcohol by potassium dichromate in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and rules out the involvement of any radical intermediate in the reaction.

4.3.3. Kinetic studies

The kinetic measurements were carried out under conditions where $[PhCH_2OH] >> [K_2Cr_2O_7]$. The progress of the reaction was followed by titrating aliquots of the reaction mixture with standard sodium thiosulphate at regular intervals of time. The experiments were repeated and pseudo-first order rate constants, k_{obs} were computed from the linear least square plots of log[oxidant] versus time.

4.3.3.1. Effect of added mineral acid on the rate of oxidation

The effect of H^+ on the rate of oxidation of benzyl alcohol was studied by varying the concentration of H_2SO_4 from $1.0x10^{-2}$ mol dm^{-3} to $2.5x10^{-2}$ mol dm^{-3} under pseudo-first order condition. These results are presented in Table 4.3.1 and in Fig. 4.3.1.1.

Table 4.3.1. Effect of $[H^+]$ on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v) Temperature - 308 K

$[H_2SO_4] \times 10^2$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)
1.0	1.7215	8.6077
1.5	2.1931	10.9655
2.0	2.4714	12.3570
2.5	3.0133	15.0665

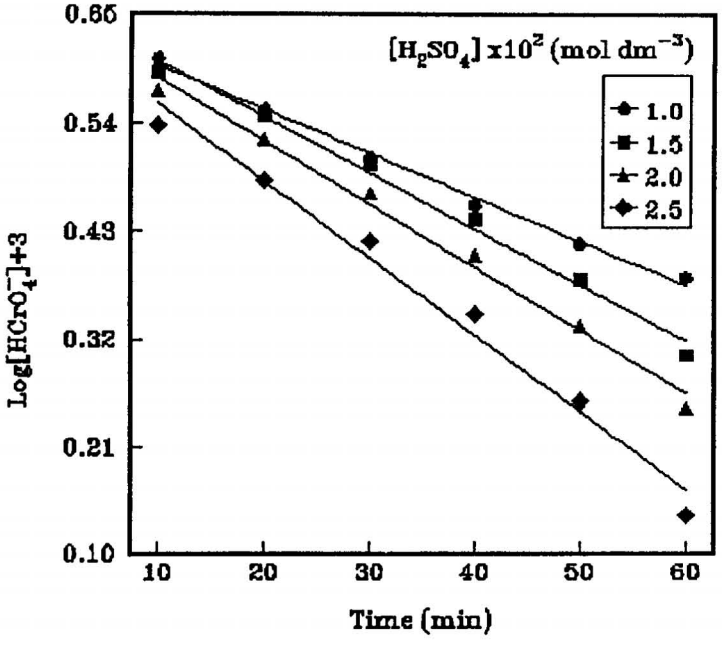


Fig.4. 3.1.1. Effect of $[H^+]$ on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium

The plot of log k_{obs} versus log $[H^+]$ (Fig. 4.3.1.2) was linear with a positive slope and the order with respect to $[H^+]$ is found to be fractional. The linear increase in the oxidation rate with acidity suggests the involvement of a protonated Cr(VI) species in the rate-determining step.

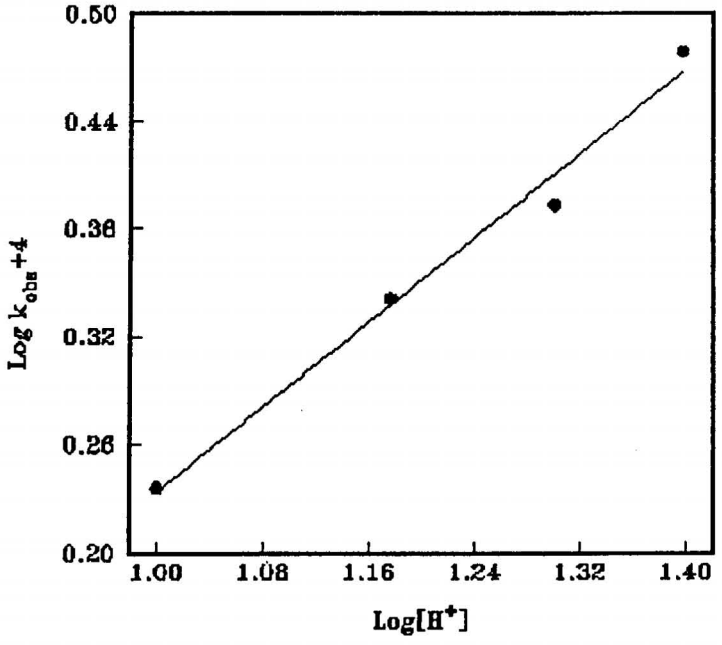


Fig.4.3.1.2. Plot of log k_{obs} Vs log$[H^+]$

4.3.3.2. Effect of added salt on the rate of oxidation

The effect of added salt on the rate of oxidation was studied by varying the concentration of NaCl from $2.0x10^{-1}$ mol dm^{-3} to $5.0x10^{-1}$ mol dm^{-3}. These results are presented in Table 4.3.2 and in Fig. 4.3.2.

Table 4.3.2. Effect of [NaCl] on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x 10^1 = 2.0 mol dm^{-3}
Medium - 20% aq. HOAc (v/v) Temperature - 308 K
$[H^+]$ x 10^2 = 1.0 mol dm^{-3}

[NaCl] x 10^1 (mol dm^{-3})	k_{obs} x 10^4 (s^{-1})	k_2 x 10^4 (dm^3 mol^{-1} s^{-1})
2.0	1.7095	8.5474
3.0	1.6983	8.4915
4.0	1.7152	8.5759
5.0	1.7338	8.6692

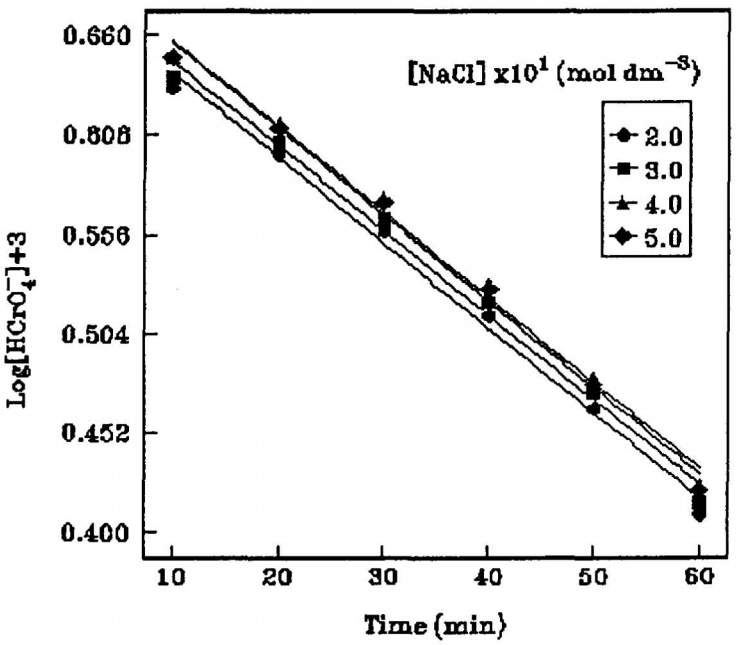


Fig.4.3.2. Effect of [NaCl] on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium.

The rate constant is found to be almost constant with different concentrations of NaCl. This ruled an ion-ion type interaction and suggests the interaction between an ion and a dipole or between two dipolar entities.[202,203]

4.3.3.3. Effect of concentration of the oxidant on the rate of oxidation

The oxidation of benzyl alcohol was carried out with different initial concentrations of the oxidant in 20% aq. acetic acid medium with $1.0x10^{-2}$mol dm^{-3} H_2SO_4 at 308 K and rates were measured. The plot of log [oxidant] versus time were found to be linear at various concentrations of the oxidant. This proved that the reaction is first order with respect to the concentration of the oxidant. This was further confirmed from the constancy in the values of specific rates (k_{obs}) for the different concentrations of the oxidant for a given concentration of the substrate. These results are consolidated in Table 4.3.3 and in Fig. 4.3.3.

Table 4.3.3. Effect of [oxidant] on the rate of oxidation of benzyl alcohol

$[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3} Temperature - 308 K
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

$[K_2Cr_2O_7] \times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^4$ (dm^3 mol^{-1} s^{-1})
4.0	1.7319	8.6593
5.0	1.7215	8.6077
6.0	1.7121	8.5606
8.0	1.7135	8.5677

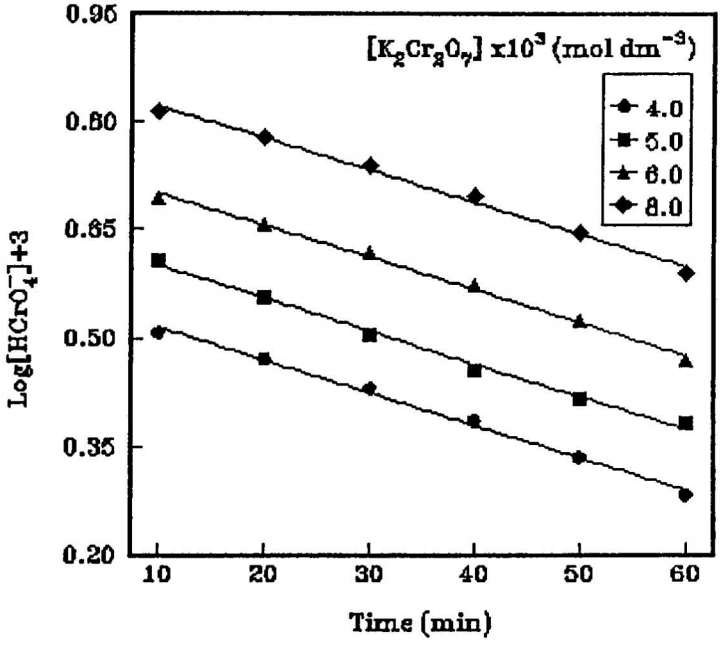


Fig.4.3.3. Effect of [oxidant] on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium.

4.3.3.4. Effect of concentration of the substrate on the rate of oxidation

The effect of concentration of the substrate on the rate of oxidation was studied with different initial concentrations of the substrate. The observed rate constant increased linearly with the increase in the concentration of benzyl alcohol. Further, the second order rate constants k_2, were found to be constant indicating first order dependence of the reaction with respect to [substrate]. These results are presented in Table 4.3.4 and in Fig. 4.3.4.1.

Table 4.3.4. Effect of [substrate] on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} Temperature - 308 K
Medium - 20% aq. HOAc (v/v) $[H^+]$ x 10^2 = 1.0 mol dm^{-3}

$[PhCH_2OH]$ x 10^1 (mol dm^{-3})	k_{obs} x 10^4 (s^{-1})	k_2 x 10^4 (dm^3 mol^{-1} s^{-1})
1.2	1.0444	8.7030
1.6	1.3929	8.7055
2.0	1.7215	8.6077
3.0	2.5919	8.6395

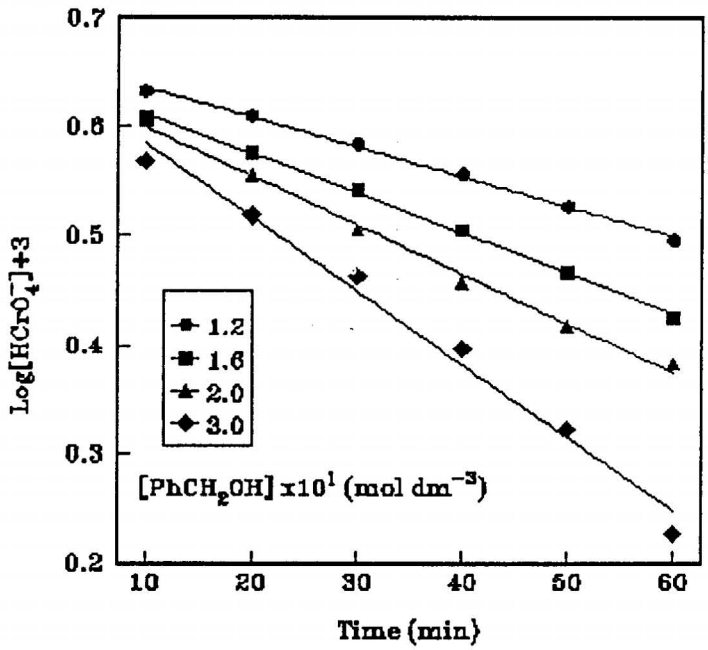


Fig.4.3.4.1. Effect of [substrate] on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium.

The first order dependence on [substrate] is further confirmed by the plot of log k_{obs} versus log[substrate] which is linear with a slope of unity (Fig. 4.3.4.2).

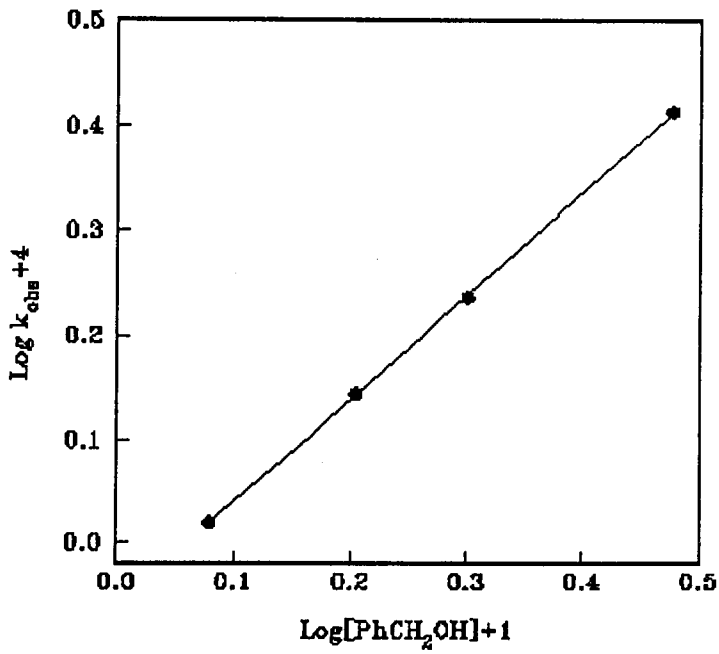


Fig.4.3.4.2. Plot of log k_{obs} Vs log [substrate]

The plot of $1/k_{obs}$ versus $1/[PhCH_2OH]$ is linear (r = 0.9999) with an intercept on the rate co-ordinate (Fig. 4.3.4.3). This proves the existence of a long lived intermediate and implies Michaelis-Menten type kinetics with respect to the benzyl alcohol.

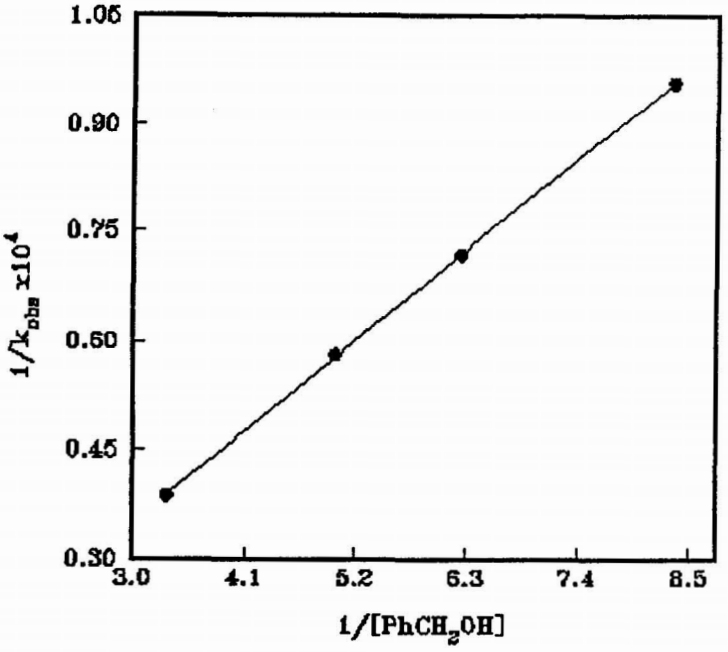


Fig.4.3.4.3. Plot of $1/k_{obs}$ Vs $1/[PhCH_2OH]$

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

The effect of polarity of the medium on the rate of oxidation of benzyl alcohol was investigated by varying the percentage of acetic acid in the reaction mixture. It has been observed that the reaction rate increases with increase in percentage of acetic acid (decrease in dielectric constant of the medium) suggesting more polar solvents may require larger reaction time. The dielectric constant values used were obtained from literature.[204] These results are presented in Table 4.3.5 and in Fig. 4.3.5.1.

Table 4.3.5. Effect of polarity of the medium on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x 10^1 = 2.0 mol dm^{-3}
$[H^+]$ x 10^2 = 1.0 mol dm^{-3} Temperature - 308 K

% of acetic acid (v/v)	Dielectric constant (D)	k_{obs} x 10^4 (s^{-1})	k_2 x 10^4 (dm^3 mol^{-1} s^{-1})
10	67.5	1.2013	6.0064
20	61	1.7215	8.6077
25	57	2.0593	10.2965
30	53	2.9067	14.5335

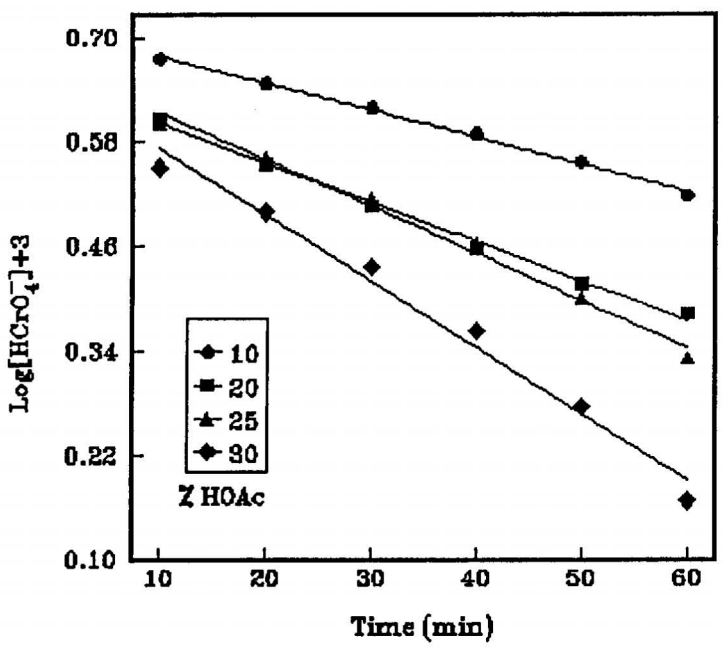


Fig.4.3.5.1. Effect of polarity of the medium on the rate oxidation of benzyl alcohol in 20% aq.HOAc medium.

The plot of log k_2 versus 1/D, where D is the dielectric constant of the medium is linear (r = 0.9978) with positive slope (Fig. 4.3.5.2). This implies

the occurrence of an interaction between a dipole and a positive ion and indicates the probable involvement of protonated Cr(VI) species in the reaction.

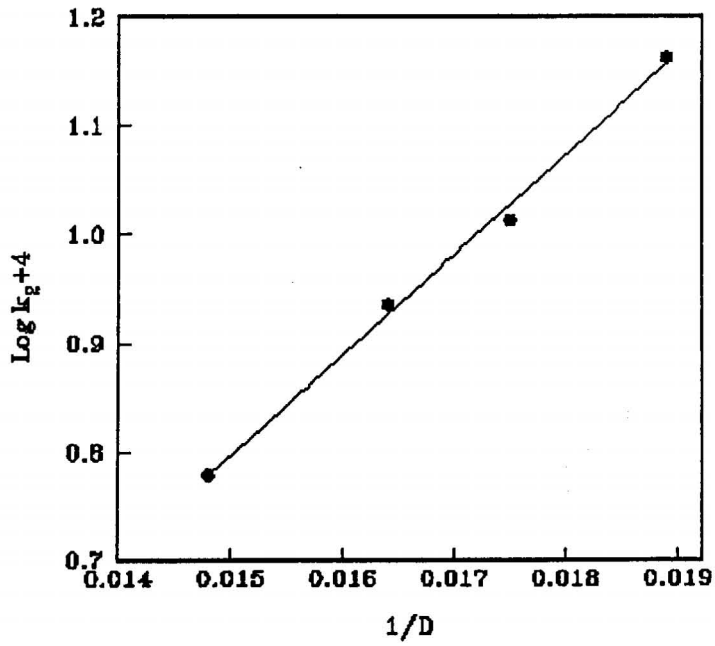


Fig.4.3.5.2. Plot of log k_2 Vs 1/D

4.3.3.6. Effect of substituents on the rate of oxidation to benzyl alcohol

The effect of substituents on the rate of oxidation of benzyl alcohol has been studied by using p-methoxy, p-methyl, p-chloro and p-nitro derivatives. These results are presented in Table 4.3.6 and in Fig. 4.3.6.1. The rate constants obtained for the oxidation of various substituted benzyl alcohols are found to be in the order of p-OCH_3 > p–CH_3 > $PhCH_2OH$ > p-Cl > p-NO_2.

The electron-releasing substituents accelerate the oxidation process while the electron-withdrawing substituents retard the process.

Table 4.3.6. Effect of substituents on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} [Substrate] x 10^1 = 2.0 mol dm^{-3}
Medium - 20% aq. HOAc (v/v) Temperature - 303 K

Substrate	k_{obs} x 10^5 (s^{-1})	k_2 x 10^4 ($dm^3 mol^{-1} s^{-1}$)
$PhCH_2OH$	15.4680	7.7342
p-OCH_3 BA	37.6000	18.800
p-CH_3 BA	27.3110	13.6555
p-Cl BA	12.9760	6.4879
p-NO_2 BA	5.5886	2.7943

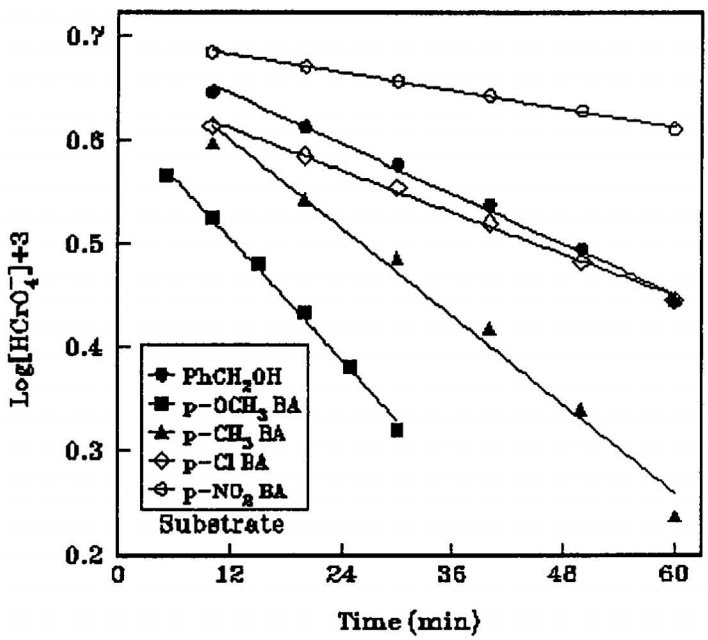


Fig.4.3.6.1. Effect of substituents on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium.

The plot of log k_2 versus σ (Fig. 4.3.6.2), where σ is the substituent constant was found to be linear indicating the excellent correlation between the structure and the reactivity as given in the linear free energy relationship proposed by Hammet.[187]

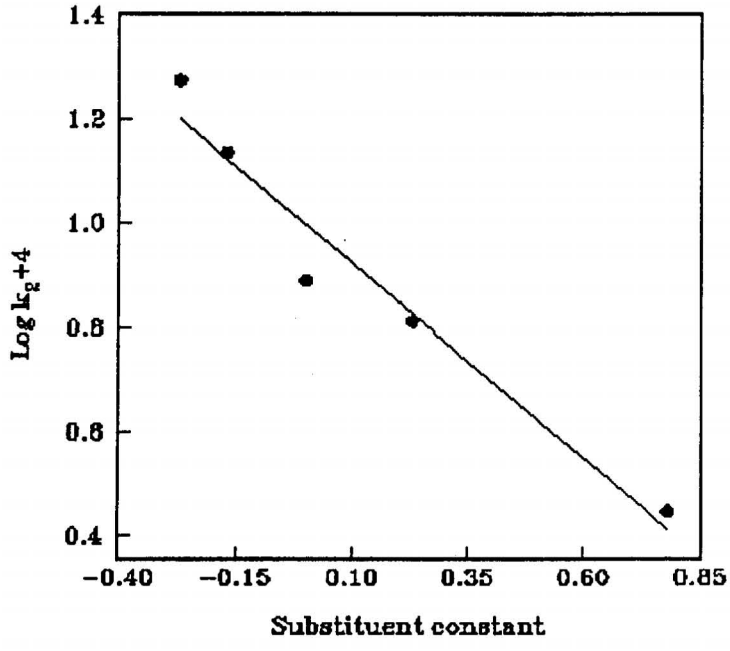


Fig.4.3.6.2. Hammet plot for the oxidation of benzyl alcohols in 20% aq.HOAc medium.

4.3.3.7. Effect of temperature on the rate of oxidation of benzyl alcohols

The effect of temperature on the rate of oxidation of benzyl alcohol and its p-OCH_3, p-CH_3, p-Cl and p-NO_2 derivatives using potassium dichromate in 20% aq. HOAc (v/v) in the presence of 1.0 x10^2 mol dm^{-3} H_2SO_4 were studied in the temperature range 303 K to 318 K. The activation

parameters for the oxidation of respective alcohols were determined using the Arrhenius equation $K = Ae^{-Ea/RT}$. The plots of log k_2 Vs 1/T and log k_2/T Vs 1/T were used for this purpose.[188]

4.3.3.7.1. Effect of temperature on the rate of oxidation of benzyl alcohol

The effect of temperature on the rate of oxidation of benzyl alcohol using potassium dichromate is presented in Table 4.3.7.1 and in Fig. 4.3.7.1.

Table 4.3.7.1. Effect of temperature on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^4$ ($dm^3 mol^{-1} s^{-1}$)
303	1.5468	7.7342
308	1.7215	8.6077
313	2.1420	10.7100
318	2.6370	13.1850

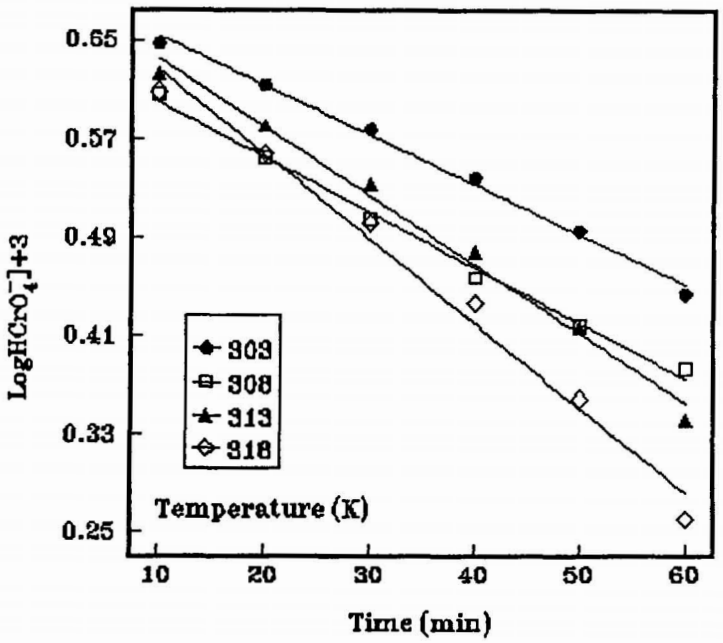


Fig.4.3.7.1. Effect of temperature on the rate of oxidation of benzyl alcohol in 20% aq.HOAc medium.

4.3.3.7.2. Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol

The effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol using potassium dichromate is presented in Table 4.3.7.2 and in Fig. 4.3.7.2.

Table 4.3.7.2. Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}OCH_3C_6H_4CH_2OH]x10^1$ = 2.0 mol dm^{-3}
Medium - 20% aq. HOAc (v/v) $[H^+]$ x 10^2 = 1.0 mol dm^{-3}

Temperature (K)	k_{obs} x 10^4 (s^{-1})	k_2 x 10^3 ($dm^3\ mol^{-1}\ s^{-1}$)
303	3.7600	1.8800
308	4.3687	2.1843
313	4.9999	2.4500
318	5.9292	2.9646

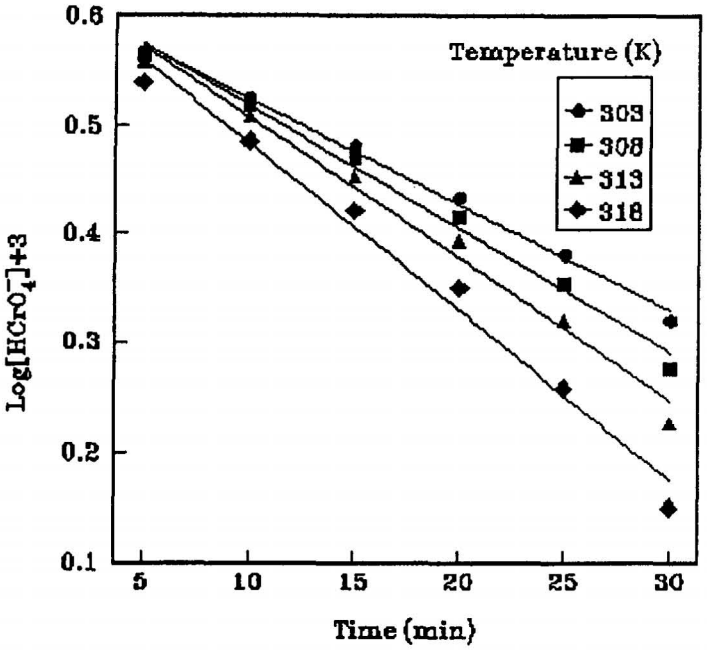


Fig.4.3.7.2. Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol in 20% aq.HOAc medium.

4.3.3.7.3. Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol

The effect of temperature on the rate of oxidation of P-methylbenzyl alcohol using potassium dichromate is presented in Table 4.3.7.3 and in Fig. 4.3.7.3.

Table 4.3.7.3. Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}CH_3C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^3$ ($dm^3 mol^{-1} s^{-1}$)
303	2.7311	1.3656
308	3.2390	1.6195
313	3.7010	1.8505
318	4.4062	2.2031

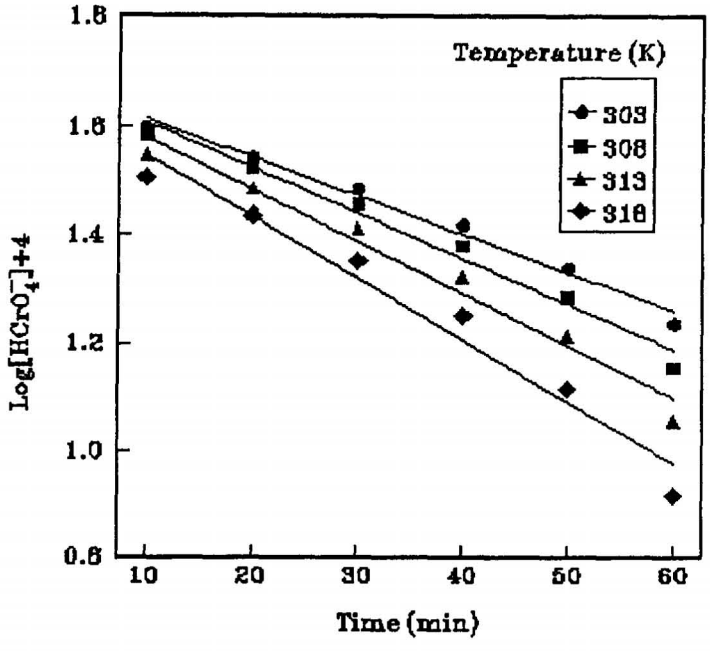


Fig.4.3.7.3. Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol in 20% aq.HOAc medium.

4.3.3.7.4. Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol

The effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol using potassium dichromate is presented in Table 4.3.7.4 and in Fig. 4.3.7.4.

Table 4.3.7.4. Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}ClC_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^4$ ($dm^3 mol^{-1} s^{-1}$)
303	1.2976	6.4879
308	1.6738	8.3692
313	1.9498	9.7488
318	2.2989	11.4945

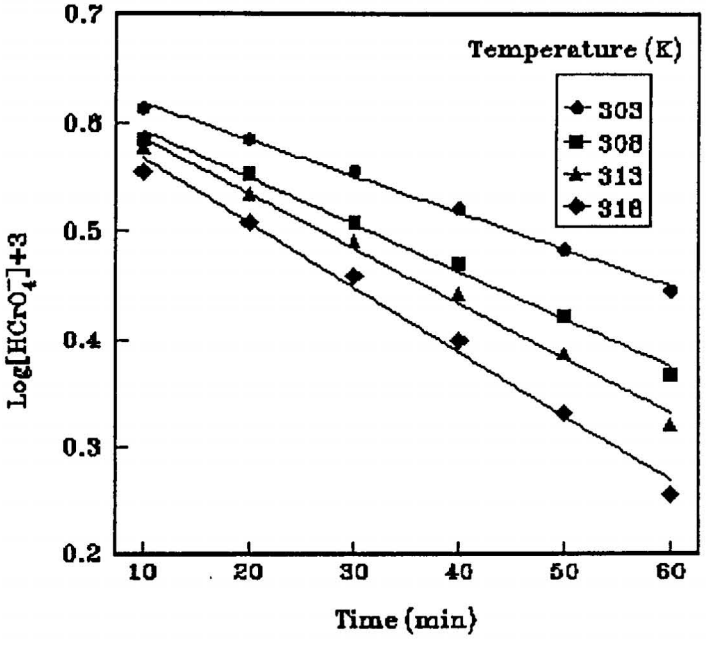


Fig.4.3.7.4. Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol in aq.HOAc medium.

4.3.3.7.5. Effect of temperature on the rate of oxidation of p-nitrobenzyl alcohol

The effect of temperature on the rate of oxidation of p-nitrobenzyl alcohol using potassium dichromate is presented in Table 4.3.7.5 and in Fig. 4.3.7.5.

Table 4.3.7.5. Effect of temperature on the rate of oxidation of p-nitrobenzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}NO_2C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	$k_{obs} \times 10^5$ (s^{-1})	$k_2 \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)
303	5.5886	2.7943
308	8.2469	4.1235
313	10.9600	5.4800
318	14.1670	7.0834

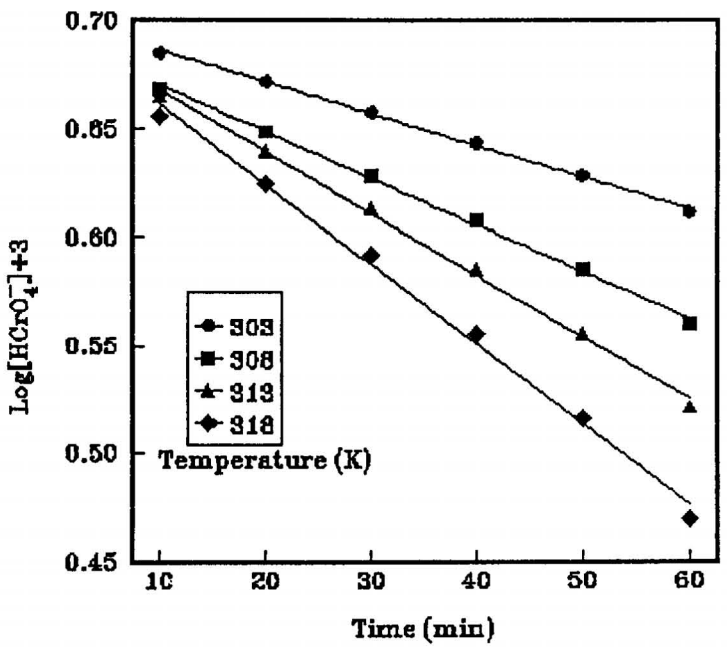


Fig.4.3.7.5. Effect of temperature on the rate of oxidation of p-nitrobenzyl alcohol in 20% aq.HOAc medium.

The values of various thermodynamic parameters were calculated from the plot of log k_2 Vs 1/T (Fig. 4.3.7.6) and from the plot of log k_2/T Vs 1/T (Fig. 4.3.7.7). The values of various thermodynamic parameters are presented in Table 4.3.7.6.

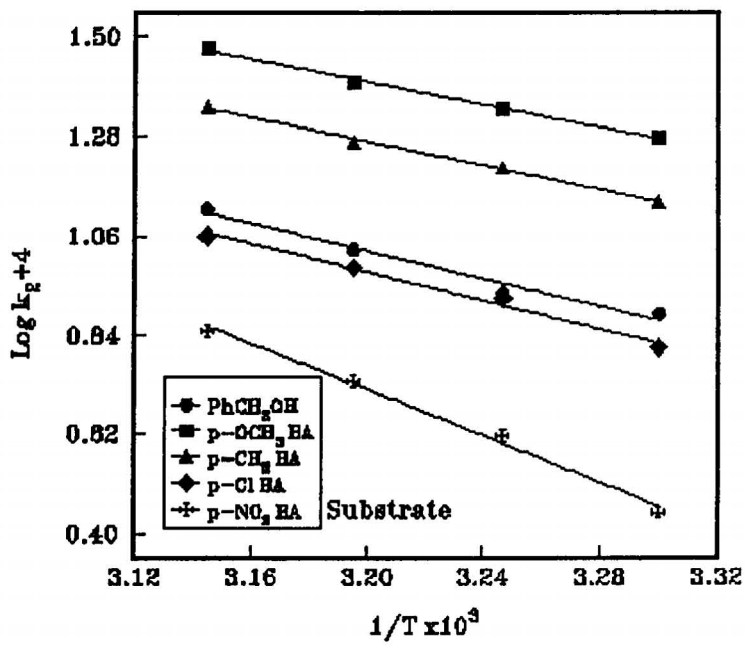


Fig.4.3.7.6. Plot of log k_2 Vs 1/T for the oxidation of benzyl alcohols in 20% aq.HOAc medium.

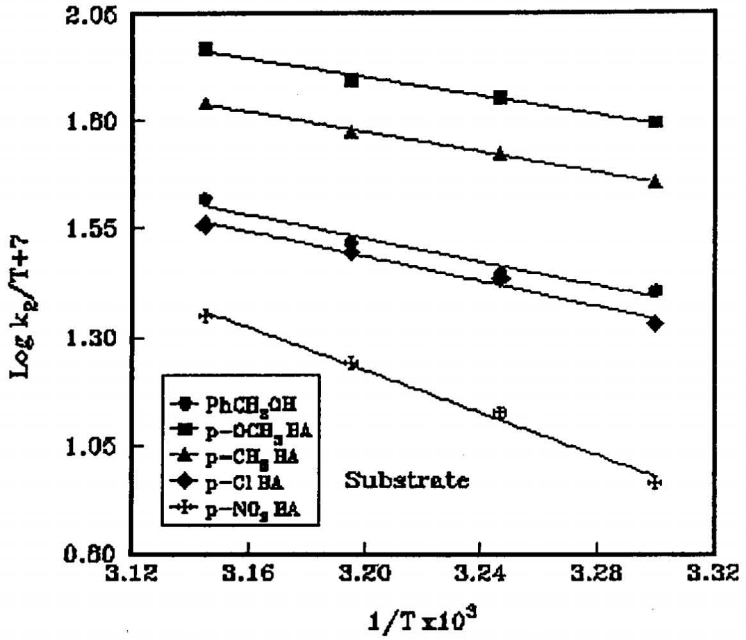


Fig.4.3.7.7. Plot of log k_2/T Vs 1/T for the oxidation of benzyl alcohols in 20% aq.HOAc medium.

Table 4.3.7.6. Activation parameters for the oxidation of benzyl alcohols

Medium - 20% aq. HOAc $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature-303 K

Substrate	$k_2 x 10^4$ ($dm^3 mol^{-1} s^{-1}$)	Ea ($kJmol^{-1}$)	$\Delta H^{\#}$ ($kJmol^{-1}$)	$-\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\#}$ ($kJmol^{-1}$)
$PhCH_2OH$	7.7342	29.11	25.87	219.28	92.31
p-OCH_3 BA	18.8000	24.05	21.13	227.54	90.07
p-CH_3 BA	13.6560	25.13	22.55	225.51	90.88
p-Cl BA	6.4879	30.00	27.41	215.67	92.76
p-NO_2 BA	2.7943	49.34	46.77	158.77	94.88

Discussion on the results obtained in the above investigation shows that the oxidation in aqueous medium follows more or less a similar path as in the case of reactions carried out in non-polar solvents under PTC. Stoichiometry of the oxidation of aromatic alcohols using potassium dichromate was found to be that one mole of dichromate is equivalent to three moles of alcohol. The product, benzaldehyde was identified as its 2,4-dinitrophenylhydrazone (DNP) and yield of the product was above 85%.

The reaction was found to show first order kinetics with respect to the concentration of the oxidant and the substrate. The effect of concentration of H^+ ion on the rate of oxidation was studied and is found that rate incrases as the concentration of H^+ ion increases. The plot of log k_{obs} Vs log $[H^+]$ was linear with a positive slope and the order with respect to $[H^+]$ is found to be fractional. The linear increase in the oxidation rate with acidity suggests the involvement of a protonated Cr(VI) species in the rate-determining step.

The rate constant is found to be constant with different concentrations of NaCl added. This ruled out the involvement of any ion-ion type interaction and hence the reaction may proceed through an ion-dipole or a dipole-dipole interactions.

The rate of oxidation of benzyl alcohol was found to decrease with increase in polarity of the medium. The plot of log k_2 Vs 1/D, where D is the dielectric constant of the medium is linear ($r = 0.9978$) with a positive slope.

This suggests an interaction between a positive ion and a dipole and indicates the probable involvement of a protonated Cr(VI) species.

The reaction mixture failed to induce the polymerization of added acrylonitrile which rules out the involvement of any radical intermediate. This indicated that a one electron oxidation is not possible and supports the interaction between an ion and a dipole.

The influence of substituents at the para position of the benzene ring of benzyl alcohol was studied and found that electron-releasing susbtituents accelerate the oxidation process while the electron-withdrawing groups retard the process. The plot of log k_2 versus σ, where σ is the susbtituent constant was found to be linear indicating the excellent correlation between the structure and the reactivity as given in the linear free energy relationship proposed by Hammet.[187] The polar reaction constant, ρ obtained was –0.7471.

The activation enthalpies and entropies for the oxidation of benzyl alcohols are linearly related (r = 0.9969) (Leffler Grunwald plot).[193] This is presented in Fig. 4.3.8.1.

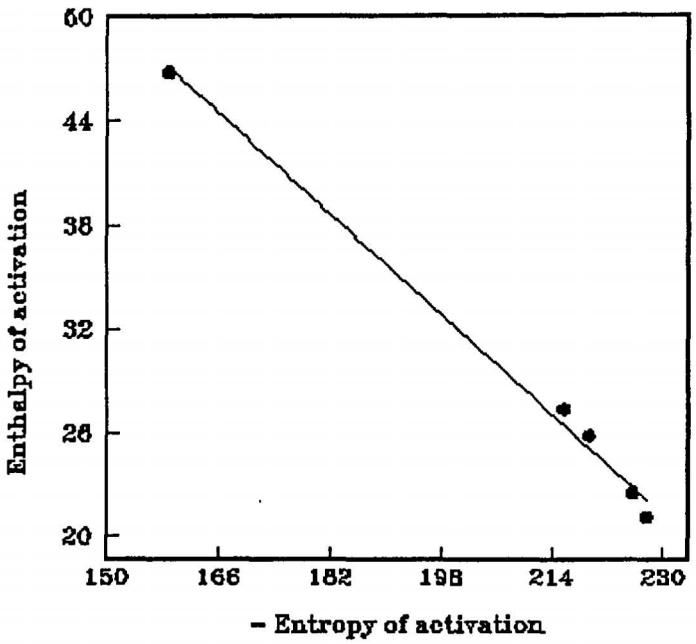


Fig.4.3.8.1. Isokinetic plot for the oxidation of benzyl alcohols in 20% aq.HOAc medium.

The correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ was tested and found valid by applying Exner's criterion[194] by plotting log k_2 at 303 K and log k_2 at 313 K ($r = 0.9946$). This plot is presented in Fig. 4.3.8.2.

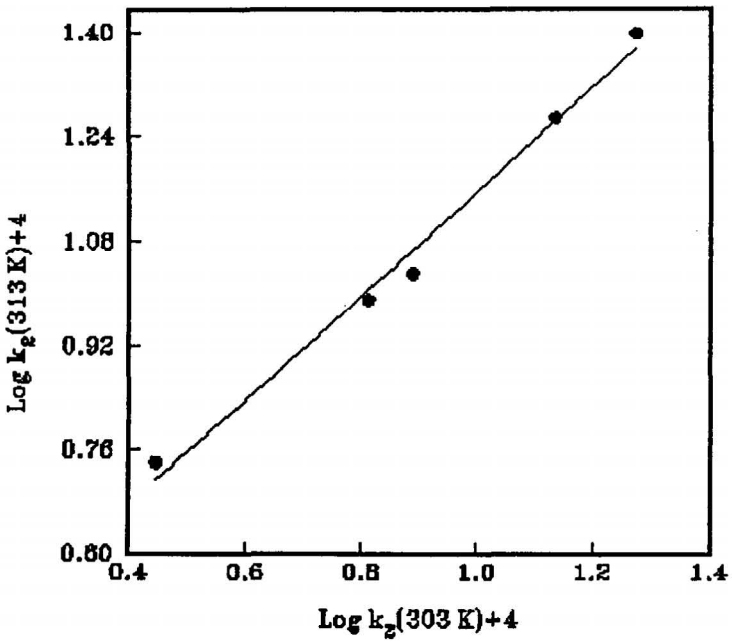


Fig.4.3.8.2. Exner's plot for the oxidation of benzyl alcohols in 20% aq.HOAc medium.

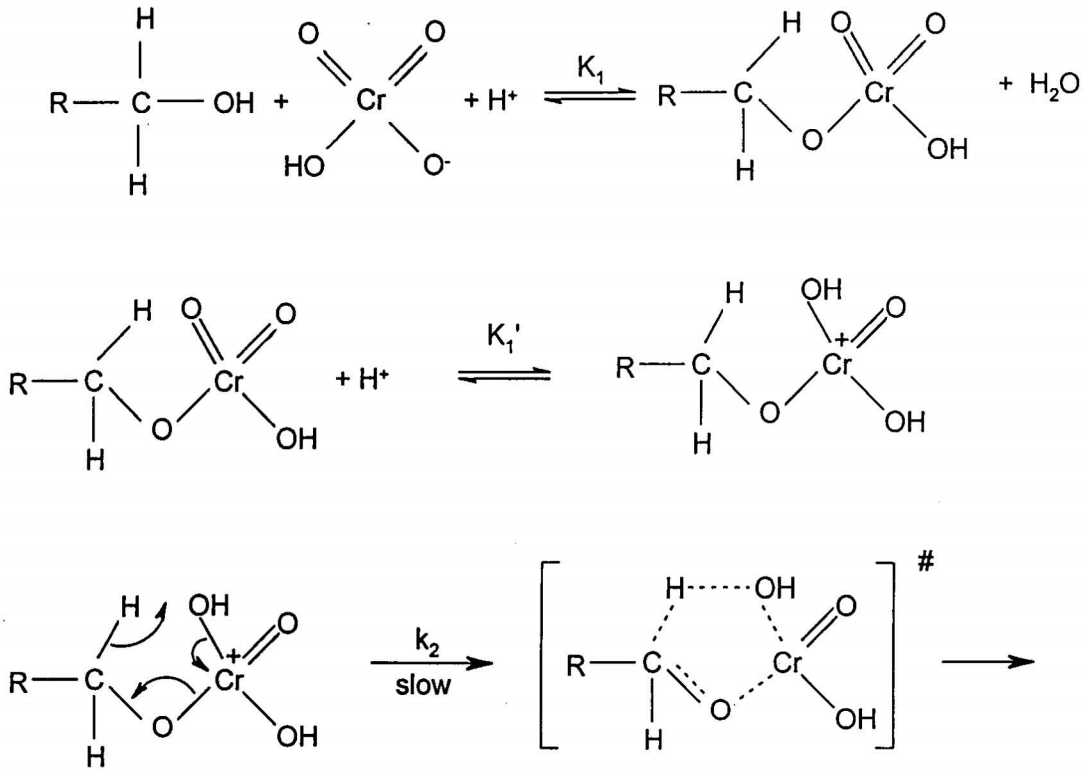
The isokinetic temperature obtained from $\Delta H^{\#}$ Vs $\Delta S^{\#}$ plot is 361 K and that from Exner's plot is 360 K. These results suggest that similar mechanism operates for the oxidation of all alcohols. This is further confirmed by the almost constant value of the free energy of activation ($\Delta G^{\#} \approx 92$ kJmol^{-1}) as given in Table 4.3.7.6.

Mechanism

It has been reported that the active species responsible for the oxidation of primary and secondary alcohols using Cr(VI) compound is $HCrO_4^-$.[205-207] A hydrogen abstraction mechanism leading to the formation of free radicals is ruled out in view of the failure to induce the polymerization of acrylonitrile. The reaction is first order with respect to [oxidant] and [substrate]. The observation of Michaelis-Menten type kinetics with respect to alcohols suggests the formation of an intermediate in a pre-equilibrium step and its subsequent disproportionation in the rate-determining step. It has been already established that oxidation of primary alcohols exhibits a substantial primary kinetic isotope effect.[195,196] This confirmed the cleavage of an α C–H bond in the rate-determining step. The negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a carbocation in character. Hence the transfer of hydride ion from the alcohol to the oxidant is suggested. The linear increase in the rate of oxidation with acidity suggests the involvement of protonated Cr(VI) species in the rate-determining step.

The hydride ion transfer may take place either by a cyclic process via an ester intermediate (scheme 1) or by an acyclic one step bimolecular process (scheme 2).

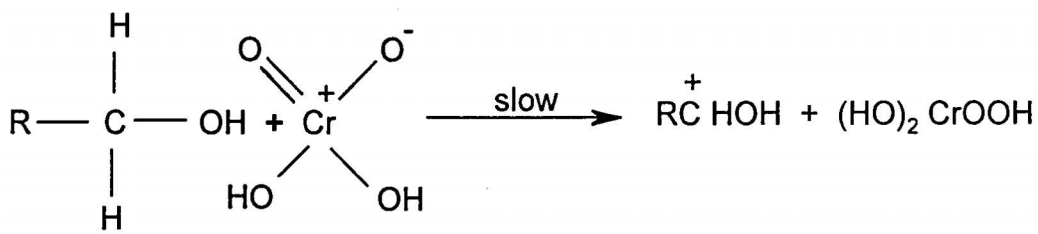
The negative $\Delta S^{\#}$ values are in agreement with the formation of a chromate ester. Bordwell has documented a cogent evidence against the occurrence of concerted one step bimolecular process by hydrogen transfer.[199] It is well established that intrinsically concerted sigmatropic reactions, characterised by transfer of hydrogen in a cyclic transition state are the only truly symmetrical processes involving a linear hydrogen transfer.[200] Littler has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and being a Huckel type system, is an allowed process. [201] The overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (scheme 1).The observed hydrogen ion dependence can be explained by assuming a rapid reversible protonation of the chromate ester and the protonated ester decomposing at a faster rate than the chromate ester (scheme 1).



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

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

Scheme 1. Mechanism involving a hydride ion transfer through an ester intermediate



$$RC^{+}HOH \xrightarrow{fast} RCHO + H^+$$

Scheme 2. Mechanism involving a direct hydride ion transfer

A suitable rate expression for the oxidation of primary aromatic alcohols using potassium dichromate in consistent with the above mechanism can be given by equation 4.2.

$$\frac{-d[HCrO_4^-]}{dt} = k_2[complex] = K_1k_2[RCH_2OH][HCrO_4^-] \qquad (4.2)$$

SUMMARY

Kinetics of the oxidation of benzyl alcohol, its para-substituted derivatives like p-methoxy, p-methyl and p-chloro and some aliphatic alcohols have been carried out in benzene using phase transferred monochromate as oxidant. Tetrabutylphosphonium bromide (TBPB) and tetrabutylammonium bromide (TBAB) were used as PT catalysts. The extraction of monochromate from aqueous phase to organic phase had occurred when the aqueous phase is acidic. The phase transferred monochromate called 'orange benzene' was found to be fairly stable over a period of more than five hours for effecting the oxidation of primary alcohols under homogenous condition.

Stoichiometry of the oxidation of primary alcohols using phase transferred monochromate has been determined. One mole of monochromate is equivalent to three moles of the alcohol. The product of the oxidation was found to be the corresponding aldehydes. The reaction mixture failed to induce the polymerization of added acrylonitrile. This rules out the involvement of any radical intermediates. The reaction was found to be first order each in [alcohol] and [chromate ions]. The rate of oxidation increased with increase in dielectric constant of the medium. The effect of substituents on the oxidation of benzyl alcohol is according to the demands of the

electronic environment at the seat of reaction. Electron-releasing substituents accelerate the reaction rate while the electron-withdrawing substituents retard the oxidation process. The Hammet plot is linear indicating the excellent correlation between the structure and the reactivity. The values of various thermodynamic parameters were calculated and these are comparable to oxidation studies in aqueous medium. The repetition of kinetic studies on the oxidation of primary aromatic alcohols using potassium dichromate in 20% v/v aqueous acetic acid has been done only to make a comparative study with the results obtained from the studies in the non-polar media.

The reaction of the selective oxidation of primary alcohols practically did not occur in non-polar organic solvents without the involvement of a PT catalyst. The PTC method offers a convenient route to study the kinetics and mechanism of the oxidation of these organic compounds in non-polar organic solvents apart from the synthetic importance.

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APPENDIX

KINETIC DATA

4.1. Oxidation of aromatic alcohols using phase transferred monochromate

Table 4.1.1(a). Effect of [oxidant] on the rate of oxidation of benzyl alcohol

$[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBPB

$[Q^+HCrO_4^-] \times 10^3$ (mol dm^{-3})	4.0	5.0	6.0	8.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	3.5651	4.4614	4.9493	6.9510
20	3.3859	4.2224	4.6904	6.5327
30	3.2066	3.9933	4.4414	6.2340
40	3.0473	3.8041	4.2323	5.9253
50	2.8879	3.6149	4.0033	5.6365
60	2.7585	3.4456	3.8240	5.3477
$k_{obs} \times 10^5$ (s^{-1})	8.6363	8.5979	8.6363	8.5979
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	4.3181	4.2989	4.3181	4.2989
Correlation coefficient (r)	0.9998	0.9996	0.9997	0.9994

Table 4.1.1(b). Effect of [oxidant] on the rate of oxidation of benzyl alcohol

$[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBAB

$[Q^+HCrO_4^-] \times 10^3$ (mol dm^{-3})	4.0	5.0	6.0	8.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	3.5922	4.4776	5.6160	7.9939
20	3.4151	4.2752	5.3630	7.6651
30	3.2633	4.0728	5.1353	7.3109
40	3.1116	3.8958	4.8824	6.9820
50	3.0104	3.7187	4.6800	6.6785
60	2.8333	3.5416	4.4523	6.3496
$k_{obs} \times 10^5$ (s^{-1})	7.6767	7.7919	7.7151	7.6767
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	3.8383	3.8959	3.8575	3.8383
Correlation coefficient (r)	0.9981	0.9999	0.9998	0.9997

Table 4.1.2(a). Effect of [substrate] on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBPB

$[PhCH_2OH] \times 10^1$ (mol dm^{-3})	1.2	1.6	2.0	3.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6904	4.5609	4.4614	4.2224
20	4.5112	4.4016	4.2224	3.9336
30	4.4116	4.2224	3.9933	3.6149
40	4.2522	4.0431	3.8041	3.3361
50	4.1527	3.8837	3.6149	3.0771
60	4.0431	3.7543	3.4456	2.8680
$k_{obs} \times 10^5$ (s^{-1})	4.9131	6.6403	8.5979	13.0887
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	4.0943	4.1502	4.2989	4.3629
Correlation coefficient (r)	0.9971	0.9994	0.9996	0.9997

Table 4.1.2(b). Effect of [substrate] on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBAB

$[PhCH_2OH] \times 10^1$ (mol dm^{-3})	1.2	1.6	2.0	3.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.9077	4.6547	4.4776	4.2499
20	4.8065	4.4776	4.2752	3.9464
30	4.6800	4.3258	4.0728	3. 6934
40	4.5535	4.1487	3.8958	3.4151
50	4.4270	4.0223	3.7187	3.2127
60	4.3258	3.8958	3.5416	2.9851
$k_{obs} \times 10^5$ (s^{-1})	4.2989	5 .9494	7.7919	11.7069
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	3.5824	3.7184	3.8959	3.9023
Correlation coefficient (r)	0.9992	0.9990	0.9999	0.9997

Table 4.1.3(a). Effect of polarity of the medium on the rate of oxidation benzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1=2.0 mol dm^3
Temperature -308 K PT catalyst - TBPB

Medium	Benzene	Toluene	Chloroform
Intrinsic dielectric constant	2.27	2.40	4.70
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})		
10	4.4614	4.8869	4.0793
20	4.2224	4.6647	3.8332
30	3.9933	4.3593	3.5772
40	3.8041	4.1372	3.3169
50	3.6149	3.8873	3.0835
60	3.4456	3.6929	2.8982
k_{obs} x 10^5 (s^{-1})	8.5979	9.5191	11.6302
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	4.2989	4.7595	5.815 1
Correlation coefficient (r)	0.9996	0.9992	0.9995

Table 4.1.3(b). Effect of polarity of the medium on the rate of oxidation benzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1=2.0 mol dm^{-3}
Temperature - 308 K PT catalyst - TBAB

Medium	Benzene	Toluene	Chloroform
Intrinsic dielectric constant	2.27	2.40	4.70
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})		
10	4.4776	4.9958	4.3896
20	4.2752	4.7183	4.1355
30	4.0728	4.4963	3.9135
40	3.8958	4.2742	3.6674
50	3.7187	4.0522	3.4165
60	3.5416	3.8301	3.1688
k_{obs} x 10^5 (s^{-1})	7.7919	8.7514	10.7857
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	3.8959	4.3757	5.3929
Correlation coefficient (r)	0.9999	0.9997	0.9983

Table 4.1.4(a). Effect of substituents on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} [Substrate] x $10^1 = 2.0$ mol dm^3
Medium - Benzene Temperature - 303 K PT catalyst - TBPB

[Substrate] x10^1 (mol dm^{-3})	$PhCH_2OH$	p-OCH_3 BA	p-CH_3 BA	p-Cl BA
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6008	4.2024	4.2224	4.1925
20	4.4215	3.9734	4.0232	4.0431
30	4.2224	3.7244	3.8340	3.8838
40	4.0531	3.4854	3.6448	3.7444
50	3.8838	3.2464	3.4556	3.5950
60	3.7344	2.9875	3.2664	3.4456
$k_{obs} \times 10^5$ (s^{-1})	7.0242	11.3310	8. 5299	6.5241
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	3.5121	5.6654	4.2649	3.2620
Correlation coefficient (r)	0.9998	0.9980	0.9995	0.9997

Table 4.1.4(b). Effect of substituents on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} [Substrate] x $10^1 = 2.0$ mol dm^3
Medium - Benzene Temperature - 303 K PT catalyst - TBAB

[Substrate] x10^1 (mol dm^{-3})	$PhCH_2OH$	p-OCH_3 BA	p-CH_3 BA	p-Cl BA
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.9835	4.7433	4.8949	4.9815
20	4.8318	4.5050	4.6783	4.8516
30	4.6800	4.2668	4.5050	4.6783
40	4.5029	4.0285	4.3101	4.5267
50	4.3258	3.8119	4.1152	4.3751
60	4.1487	3.5737	3.8769	4.2235
$k_{obs} \times 10^5$ (s^{-1})	6.1413	9.4072	7.5889	5.5656
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	3.0707	4.7036	3.7945	2.7828
Corr.coeft (r)	0.9980	0.9994	0.9974	0.9993

Table 4.1.5.1(a). Effect of temperature on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst -TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.6008	4.4614	4.4116	4.1825
20	4.4215	4.2224	4.1427	3.8141
30	4.2224	3.9933	3.9137	3.5551
40	4.0531	3.8041	3.6846	3.3062
50	3.8838	3.6149	3.4456	3.0473
60	3.7344	3.4456	3.2863	2.8979
k_{obs} x 10^5 (s^{-1})	7.0242	8.5979	9.9413	12.2827
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	3.5121	4.2989	4.9707	6.1414
Correlation coefficient (r)	0.9998	0.9996	0.9993	0.9975

Table 4.1.5.1(b). Effect of temperature on the rate of oxidation of benzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst -TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.9835	4.4776	4.4523	4.3764
20	4.8318	4.2752	4.1993	4.0981
30	4.6800	4.0728	3.9970	3.8452
40	4.5029	3.8958	3.7693	3.5922
50	4.3258	3.7187	3.5669	3.3645
60	4.1487	3.5416	3.3645	3.1622
k_{obs} x 10^5 (s^{-1})	6.1413	7.7918	9.2888	10.8625
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	3.0707	3.8959	4.6444	5.4312
Correlation coefficient (r)	0.9980	0.9999	0.9998	0.9999

Table 4.1.5.2(a).Effect of temperature on the rate of oxidation p-methoxybenzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}OCH_3C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.2024	4.1128	3.9634	3.8639
20	3.9734	3.8340	3.6547	3.5153
30	3.7244	3.5651	3.3161	3.2066
40	3.4854	3.3161	3.0473	2.9079
50	3.2464	3.0672	2.7784	2.5892
60	2.9875	2.7884	2.4896	2.2406
$k_{obs} \times 10^5$ (s^{-1})	1.1331	1.2793	1.5392	1.7809
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	5.6654	6.3963	7.6959	8.9044
Correlation coefficient (r)	0.9980	0.9985	0.9991	0.9959

Table 4.1.5.2(b).Effect of temperature on the rate of oxidation p-methoxybenzyl alcohol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}OCH_3C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.7433	4.6783	4.7649	4.6133
20	4.5050	4.3967	4.4617	4.3101
30	4.2668	4.1585	4.1368	3.8986
40	4.0285	3.8986	3.8336	3.5954
50	3.8119	3.6170	3.5520	3.2488
60	3.5737	3.3355	3.2270	2.9023
$k_{obs} \times 10^5$ (s^{-1})	9.4072	11.1490	12.9030	15.4640
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	4.7036	5.5744	6.4517	7.7321
Correlation coefficient (r)	0.9994	0.9975	0.9985	0.9975

Table 4.1.5.3(a). Effect of temperature on the rate of oxidation p-methylbenzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}CH_3C_6H_4CH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.2224	4.1527	4.1029	4.0730
20	4.0232	3.9936	3.8539	3.7942
30	3.8340	3.7145	3.6049	3.4954
40	3.6448	3.4854	3.3659	3.2166
50	3.4556	3.2564	3.1269	2.9178
60	3.2664	3.0274	2.8879	2.6191
k_{obs} x 10^5 (s^{-1})	8.5299	10.5270	11.6760	14.6640
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	4.2649	5.2635	5.8381	7.3318
Correlation coefficient (r)	0.9995	0.9984	0.9991	0.9972

Table 4.1.5.3(b). Effect of temperature on the rate of oxidation p-methylbenzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}CH_3C_6H_4CH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.8949	4.7866	4.6566	4.5483
20	4.6783	4.5484	4.3967	4.2451
30	4.5050	4.3318	4.1152	3.9636
40	4.3101	4.0935	3.8553	3.6820
50	4.1152	3.8553	3.5737	3.3788
60	3.8769	3.6170	3.3138	3.0972
k_{obs} x 10^5 (s^{-1})	7.5889	9.2997	11.3760	12.7630
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	3.7945	4.6499	5.6879	6.3815
Correlation coefficient (r)	0.9974	0.9987	0.9987	0.9985

Table 4.1.5.4(a). Effect of temperature on the rate of oxidation p-chlorobenzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}ClC_6H_4CH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.1925	4.1427	4.0630	4.0132
20	4.0431	3.9734	3.8639	3.7842
30	3.8838	3.7942	3.6547	3.5452
40	3.7444	3.6149	2.4456	3.3062
50	3.5950	3.4456	3.2365	3.0672
60	3.4456	3.2664	3.0373	2.8182
k_{obs} x 10^5 s^{-1})	6.5241	7.9256	9.7417	11.7530
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	3.2620	3.9628	4.8708	5.8765
Correlation coefficient (r)	0.9997	0.9993	0.9991	0.9981

Table 4.1.5.4(b). Effect of temperature on the rate of oxidation p-chlorobenzyl alcohol

$[Q^+HCrO_4^-]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}ClC_6H_4CH_2OH]$ x10^1 = 2.0 mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.9815	4.7866	4.6350	4.5483
20	4.8516	4.6133	4.4401	4.3318
30	4.6783	4.4401	4.2235	4.0935
40	4.5267	4.2451	4.0069	3.8336
50	4.3751	4.0719	3.8119	3.5954
60	4.2235	3.8769	3.5737	3.3571
k_{obs} x 10^5 (s^{-1})	5.5656	7.0143	8.6231	10.2100
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	2.7828	3.5071	4.3115	5.1050
Correlation coefficient (r)	0.9993	0.9988	0.9983	0.9984

4.2. Oxidation of aliphatic alcohols using phase transferred monochromate.

Table 4.2.1(a). Effect of [oxidant] on the rate of oxidation of 1-octanol

[1-octanol] x 10^1 = 2.0 mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBPB

$[Q^+HCrO_4^-]$ x 10^3 (mol dm^{-3})	4.0	5.0	6.0	8.0
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	3.8020	4.5360	5.5618	7.3404
20	3.7173	4.4325	5.4394	7.1710
30	3.6326	4.3290	5.3077	6.9922
40	3.5385	4.2160	5.1854	6.8134
50	3.4538	4.1031	5.0536	6.6440
60	3.3597	3.9902	4.4218	6.4652
k_{obs} x 10^5 (s^{-1})	4.1191	4.2825	4.0752	4.2364
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	2.0595	2.1412	2.0376	2.1182
Correlation coefficient (r)	0.9994	0.9992	0.9996	0.9998

Table 4.2.1(b). Effect of [oxidant] on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-]$ x 10^1 = 2.0 mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBAB

$[Q^+HCrO_4^-]$ x 10^3 (mol dm^{-3})	4.0	5.0	6.0	8.0
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	3.9852	4.6566	5.9562	7.7105
20	3.9419	4.5700	5.8695	7.5806
30	3.8769	4.4834	5.7612	7.4506
40	3.8119	4.4184	5.6529	7.2990
50	3.7253	4.3318	5.5447	7.1691
60	3.6387	4.2235	5.4364	7.0391
k_{obs} x 10^5 (s^{-1})	3.0586	3.1573	3.0794	3.0652
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	1.5293	1. 5787	1.5397	1.5326
Correlation coefficient (r)	0.9921	0.9972	0.9990	0.9997

Table 4.2.2(a). Effect of [substrate] on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBPB

$[PHCH_2OH] \times 10^1$ (mol dm^{-3})	1.2	1.6	2.0	3.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.7148	4.7054	4.5360	4.5172
20	4.6583	4.6207	4.4325	4.3760
30	4.6019	4.5360	4.3290	4.2349
40	4.5548	4.4607	4.2160	4.0483
50	4.4984	4.3760	4.1031	3.9525
60	4.4419	4.2913	3.9902	3.8020
$k_{obs} \times 10^5$ (s^{-1})	1.9652	3.0498	4.2825	5.7333
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.6377	1.9061	2.1412	1.9111
Correlation coefficient (r)	0.9996	0.9998	0.9992	0.9995

Table 4.2.2(b). Effect of [substrate] on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K
Medium - Benzene PT catalyst - TBAB

$[PHCH_2OH] \times 10^1$ (mol dm^{-3})	1.2	1.6	2.0	3.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8949	4.7649	4.6566	4.5700
20	4.8516	4.7000	4.5700	4.4617
30	4.8083	4.6350	4.4834	4.3318
40	4.7449	4.5483	4.4184	4.2235
50	4.7216	4.4834	4.3318	4.1152
60	4.6566	4.4184	4.2235	4.0069
$k_{obs} \times 10^5$ (s^{-1})	1.6154	2.5618	3.1573	4.4064
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.3462	1.6011	1.5787	1.4688
Correlation coefficient (r)	0.9964	0.9991	0.9972	0.9998

Table 4.2.3.1(a). Effect of temperature on the rate of oxidation of 1-butanol.

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-butanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.7901	4.6489	4.5831	4.5172
20	4.7525	4.6019	4.5172	4.4231
30	4.7054	4.5548	4.4419	4.3478
40	4.6395	4.4890	4.3667	4.2631
50	4.5831	4.4137	4.2913	4.1690
60	4.5266	4.3384	4.2066	4.0655
$k_{obs} \times 10^5$ (s^{-1})	1.9268	2.3162	2.8612	3.4512
$k_2 \times 10^5$ ($dm^3mol^{-1}s^{-1}$)	9.6342	11.5810	14.3060	17.2560
Correlation coefficient (r)	0.9963	0.9932	0.9989	0.9981

Table 4.2.3.1(b). Effect of temperature on the rate of oxidation of 1-butanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-butanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.9832	4.8033	4.6133	4.4617
20	4.9165	4.7649	4.5484	4.3967
30	4.8732	4.7000	4.5050	4.3318
40	4.8299	4.6566	4.4401	4.2451
50	4.7866	4.5917	4.3751	4.1801
60	4.7433	4.5267	4.2884	4.1152
$k_{obs} \times 10^5$ (s^{-1})	1.3873	2.0102	2.3535	2.7417
$k_2 \times 10^5$ ($dm^3mol^{-1}s^{-1}$)	6.9364	10.0510	11.7670	13.7080
Correlation coefficient (r)	0.9959	0.9972	0.9940	0.9990

Table 4.2.3.2(a). Effect of temperature on the rate of oxidation of 1-pentanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-pentanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6019	4.5454	4.4231	4.3854
20	4.5454	4.4701	4.3101	4.2631
30	4.4701	4.3760	4.2066	4.1502
40	4.3948	4.2913	4.1031	4.0372
50	4.3196	4.1972	3.9996	3.9149
60	4.2537	4.1031	3.8867	3.8020
$k_{obs} \times 10^5$ (s^{-1})	2.6814	3.3766	4.2638	4.7486
$k_2 \times 10^5$ ($dm^3mol^{-1}s^{-1}$)	13.4070	16.8830	21.3190	23.7430
Correlation coefficient (r)	0.9989	0.9994	0.9997	0.9997

Table 4.2.3.2(b). Effect of temperature on the rate of oxidation of 1-pentanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-pentanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8732	4.8083	4.5267	4.2684
20	4.8299	4.7649	4.4617	4.2018
30	4.7866	4.7000	4.3967	4.1368
40	4.7433	4.6350	4.3318	4.0502
50	4.6783	4.5700	4.2451	3.9636
60	4.6350	4. 5050	4.1801	3.8769
$k_{obs} \times 10^5$ (s^{-1})	1.6954	2.2175	2.6781	3.3350
$k_2 \times 10^5$($dm^3mol^{-1}s^{-1}$)	8.4772	11.0870	13.3900	16.6750
Correlation coefficient (r)	0.9970	0.9979	0.9984	0.9986

Table 4.2.3.3(a). Effect of temperature on the rate of oxidation of 1-hexanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-hexanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6960	4.6301	4.4701	4.3760
20	4.6301	4.5454	4.3572	4.2631
30	4.5454	4.4607	4.2443	4.1408
40	4.4701	4.3572	4.1408	4.0184
50	4.3854	4.2537	4.0278	3.8867
60	4.3101	4.1596	3.9055	3.7549
$k_{obs} \times 10^5$ (s^{-1})	2.8963	3.6091	4.4525	5.1083
$k_2 \times 10^5$ ($dm^3mol^{-1}s^{-1}$)	14.4810	18.0455	22.2620	25.5415
Correlation coefficient (r)	0.9993	0.9986	0.9993	0.9987

Table 4.2.3.3(b). Effect of temperature on the rate of oxidation of 1-hexanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-hexanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8732	4.8083	4.5700	4.3534
20	4.8299	4.7433	4.5050	4.2668
30	4.7649	4.6783	4.4184	4.1585
40	4.7216	4.5917	4.3318	4.0719
50	4.6566	4.5267	4.2451	3.9852
60	4.5917	4.4401	4.1585	3.8769
$k_{obs} \times 10^5$ (s^{-1})	1.9784	2.5377	3.1913	3.8318
$k_2 \times 10^5$ ($dm^3mol^{-1}s^{-1}$)	9.8919	12.6880	15.9565	19.1590
Correlation coefficient (r)	0.9973	0.9992	0.9985	0.9991

Table 4.2.3.4(a). Effect of temperature on the rate of oxidation of 1-heptanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-heptanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6678	4.5548	4.3948	4.3007
20	4.5831	4.4607	4.2819	4.1690
30	4.4984	4.3666	4.1690	4.0466
40	4.4137	4.2631	4.0561	3.9149
50	4.3290	4.1596	3.9431	3.7831
60	4.2537	4.0655	3.8208	3.6420
$k_{obs} \times 10^5$ (s^{-1})	3.1167	3.9327	4.6367	5.5020
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.5584	1.9663	2.3184	2.7510
Correlation coefficient (r)	0.9999	0.9987	0.9995	0.9990

Table 4.2.3.4(b). Effect of temperature on the rate of oxidation of 1-heptanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-heptanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.9166	4.6996	4.4617	4.2668
20	4.8732	4.6350	4.3967	4.1858
30	4.8083	4.5483	4.3318	4.0502
40	4.7216	4.4834	4.2451	3.9636
50	4.6783	4.4184	4.1585	3.8553
60	4.6133	4.3318	4.0510	3.7470
$k_{obs} \times 10^5$ (s^{-1})	2.1879	2.6912	3.1957	4.2748
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.0939	1.3456	1.5978	2.1374
Correlation coefficient (r)	0.9963	0.9988	0.9937	0.9994

Table 4.2.3.5(a). Effect of temperature on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-octanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.7054	4.5360	4.2819	4.1408
20	4.6301	4.4325	4.1596	4.0184
30	4.5454	4.3290	4.0466	3.8961
40	4.4607	4.2160	3.9243	3.7643
50	4.3760	4.1031	3.8114	3.6420
60	4.2819	3.9902	3.6890	3.5008
$k_{obs} \times 10^5$ (s^{-1})	3.1444	4.2825	5.0008	5.5689
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.5721	2.1412	2.5004	2.7844
Correlation coefficient (r)	0.9989	0.9992	0.9993	0.9990

Table 4.2.3.5(b). Effect of temperature on the rate of oxidation of 1-octanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-octanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8949	4.6566	4.5050	4.2451
20	4.8516	4.5700	4.3967	4.1368
30	4.7866	4.4834	4.3101	4.0285
40	4.6996	4.4184	4.2018	3.8986
50	4.6133	4.3318	4.1152	3.7903
60	4.5484	4.2235	4.0069	3.6603
$k_{obs} \times 10^5$ (s^{-1})	2.5508	3.1573	3.8570	4.9372
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.2754	1. 5787	1.9285	2.4686
Correlation coefficient (r)	0.9944	0.9972	0.9993	0.9987

Table 4.2.3.6(a). Effect of temperature on the rate of oxidation of 1-nonanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-nonanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.6772	4.5548	4.3478	4.3196
20	4.5925	4.4513	4.2255	4.1878
30	4.5078	4.3478	4.1031	4.0466
40	4.4137	4.2349	3.9808	3.9055
50	4.3290	4.1219	3.8584	3.7643
60	4.2349	4.0090	3.7267	3.6325
$k_{obs} \times 10^5$ (s^{-1})	3.3152	4.2682	5.1171	5.8156
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.6576	2.1341	2.5585	2.9078
Correlation coefficient (r)	0.9995	0.9992	0.9994	0.9996

Table 4.2.3.6(b). Effect of temperature on the rate of oxidation of 1-nonanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-nonanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.9166	4.6133	4.4401	4.2235
20	4.8516	4.5483	4.3318	4.1152
30	4.7649	4.4617	4.2235	3.9852
40	4.6783	4.3751	4.1368	3.8769
50	4.6133	4.2884	4.0285	3.7470
60	4.5267	4.2018	3.8986	3.6170
$k_{obs} \times 10^5$ (s^{-1})	2.7768	3.1617	4.2364	5.1609
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.3884	1.5808	2.1182	2.5805
Correlation coefficient (r)	0.9990	0.9985	0.9979	0.9988

Table 4.2.3.7(a). Effect of temperature on the rate of oxidation of 1-decanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-decanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBPB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.7054	4.6019	4.4607	4.3384
20	4.6207	4.4984	4.3290	4.1878
30	4.5360	4.3948	4.1972	4.0466
40	4.4419	4.2819	4.0655	3.9055
50	4.3384	4.1690	3.9431	3.7643
60	4.2443	4.0466	3.8114	3.6138
$k_{obs} \times 10^5$ (s^{-1})	3.4578	4.2726	5.2333	6.0404
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.7289	2.1363	2.6167	3.0202
Correlation coefficient (r)	0.9986	0.9988	0.9999	0.9996

Table 4.2.3.7(b). Effect of temperature on the rate of oxidation of 1-decanol

$[Q^+HCrO_4^-] \times 10^3 = 5.0$ mol dm^{-3} $[1\text{-decanol}] \times 10^1 = 2.0$ mol dm^{-3}
Medium - Benzene PT catalyst - TBAB

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8083	4.4834	4.4617	4.2451
20	4.7433	4.4184	4.3318	4.1152
30	4.6566	4.3101	4.2018	4.0069
40	4.5700	4.2018	4.0935	3.8769
50	4.5050	4.1152	3.9852	3.7470
60	4.4184	4.0069	3.8769	3.5954
$k_{obs} \times 10^5$ (s^{-1})	2.8393	3.8142	4.6597	5.4548
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	1.4196	1.9071	2.3299	2.7274
Correlation coefficient (r)	0.9989	0.9974	0.9996	0.9975

4.3. Oxidation of aromatic alcohols using potassium dichromate in aqueous acetic acid medium

Table 4.3.1. Effect of $[H^+]$ on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq.HOAc (v/v) Temperature - 308 K

$[H^+] \times 10^2$ (mol dm^{-3})	1.0	1.5	2.0	2.5
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.0333	3.9108	3.7367	3.4517
20	3.5833	3.5308	3.3408	3.0400
30	3.2000	3.1508	2.9450	2.6283
40	2.8667	2.7708	2.5492	2.2167
50	2.6167	2.4067	2.1533	1.8050
60	2.4167	2.0108	1.7733	1.3775
$k_{obs} \times 10^4$ (s^{-1})	1.7215	2.1931	2.4714	3.0133
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	8.6077	10.9655	12.3570	15.0665
Correlation coefficient (r)	0.9974	0.9950	0.9948	0.9903

Table 4.3.2. Effect of [NaCl] on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq.HOAc (v/v) Temperature - 308 K

[NaCl] $\times 10^1$ (mol dm^{-3})	2.0	3.0	4.0	5.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.2900	4.3450	4.4550	4.4550
20	3.9600	4.0150	4.1067	4.0883
30	3.6117	3.6667	3.7583	3.7400
40	3.2633	3.3183	3.3917	3.3733
50	2.9150	2.9700	3.0250	3.0067
60	2.5667	2.6033	2.6583	2.6400
$k_{obs} \times 10^4$ (s^{-1})	1.7095	1.6983	1.7152	1.7338
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	8.5474	8.4915	8.5759	8.6692
Correlation coefficient (r)	0.9967	0.9961	0.9962	0.9966

Table 4.3.3. Effect of [oxidant] on the rate of oxidation of benzyl alcohol

$[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3} Temperature - 308 K
Medium - 20% aq. HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

$[K_2Cr_2O_7] \times 10^3$ (mol dm^{-3})	4.0	5.0	6.0	8.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	3.2167	4.0333	4.9333	6.5167
20	2.9667	3.5883	4.5333	5.9833
30	2.7000	3.2000	4.1333	5.4667
40	2.4333	2.8667	3.7333	4.9500
50	2.1667	2.6167	3.3333	4.4167
60	1.9167	2.4167	2.9500	3.8833
$k_{obs} \times 10^4$ (s^{-1})	1.7319	1.7215	1.7121	1.7135
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	8.6593	8.6077	8.5606	8.5677
Correlation coefficient (r)	0.9972	0.9974	0.9976	0.9968

Table 4.3.4. Effect of [substrate] on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} Temperature - 308 K
Medium - 20% aq.HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

$[PhCH_2OH] \times 10^1$ (mol dm^{-3})	1.2	1.6	2.0	3.0
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.2833	4.0500	4.0333	3.7000
20	4.0667	3.7667	3.5833	3.3000
30	3.8333	3.4833	3.2000	2.9000
40	3.6000	3.2000	2.8667	2.5000
50	3.3667	2.9333	2.6167	2.1000
60	3.1333	2.6667	2.4167	1.6833
$k_{obs} \times 10^4$ (s^{-1})	1.0444	1.3929	1.7215	2.5919
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	8.7030	8.7055	8.6077	8.6395
Correlation coefficient (r)	0.9985	0.9989	0.9974	0.9927

Table 4.3.5. Effect of polarity of the medium on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[PhCH_2OH]$ x10^1 = 2.0 mol dm^{-3}
$[H^+]$ x10^2 =1.0 mol dm^{-3} Temperature - 308 K

% HOAc	10	20	25	30
Dielectric constant	67.5	61	57	53
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.7367	4.0333	3.9900	3.5467
20	4.4333	3.5833	3.6400	3.1500
30	4.1533	3.2000	3.2667	2.7300
40	3.8733	2.8667	2.8933	2.3100
50	3.5933	2.6167	2.5200	1.8900
60	3.2900	2.4167	2.1467	1.4700
k_{obs} x 10^4 (s^{-1})	1.2013	1.7215	2.0593	2.9067
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	6.0064	8.6077	10.2965	14.5335
Correlation coefficient (r)	0.9983	0.9974	0.9953	0.9910

Table 4.3.6. Effect of substituents on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} [Substrate] x $10^1 = 2.0$ mol dm^3
Medium -20% aq.HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^3 Temperature - 303 K

[substrate] x10^1 (mol dm^{-3})	$PhCH_2OH$	p-OCH_3 BA	p-CH_3 BA	p-Cl BA	p-NO_2 BA
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})				
5	-	3.6850	-	-	-
10	4.4333	3.3550	3.9600	4.1067	4.8400
15	-	3.0250	-	-	-
20	4.1067	2.7133	3.5017	3.8500	4.6933
25	-	2.4017	-	-	-
30	3.7800	2.0900	3.0617	3.5933	4.5467
40	3.4533	-	2.6217	3.3183	4.4000
50	3.1267	-	2.1817	3.0433	4.2533
60	2.7767	-	1.7233	2.7867	4.0883
$k_{obs} \times 10^5$ (s^{-1})	15.4680	37.6000	27.3110	12.9760	5.5886
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	7.7342	18.8000	13.6555	6.4879	2.7943
Correlation coefficient (r)	0.9969	0.9995	0.9924	0.9980	0.9991

Table 4.3.7.1.Effect of temperature on the rate of oxidation of benzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[PhCH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq.HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.4333	4.0333	4.2000	4.0600
20	4.1067	3.5833	3.8033	3.6167
30	3.7800	3.2000	3.4067	3.1733
40	3.4533	2.8667	3.0100	2.7300
50	3.1267	2.6167	2.6133	2.2867
60	2.7767	2.4167	2.1933	1.8200
$k_{obs} \times 10^4$ (s^{-1})	1.5468	1.7215	2.1420	2.6370
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	7.7342	8.6077	10.7100	13.1850
Correlation coefficient (r)	0.9969	0.9974	0.9946	0.9922

Table 4.3.7.2.Effect of temperature on the rate of oxidation of p-methoxybenzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}OCH_3C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq.HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
5	3.6850	3.6667	3.6117	3.4650
10	3.3550	3.3000	3.2267	3.0617
15	3.0250	2.9517	2.8417	2.6400
20	2.7133	2.6033	2.4750	2.2367
25	2.4017	2.2550	2.0900	1.8150
30	2.0090	1.8883	1.6887	1.4117
$k_{obs} \times 10^4$ (s^{-1})	3.7600	4.3687	4.9999	5.9292
$k_2 \times 10^3$ ($dm^3mol^{-1}s^{-1}$)	1.8800	2.1843	2.4500	2.9646
Correlation coefficient (r)	0.9975	0.9951	0.9928	0.9916

Table 4.3.7.3. Effect of temperature on the rate of oxidation of p-methylbenzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[p\text{-}CH_3C_6H_4CH_2OH]$ x 10^1 = 2.0 mol dm^{-3}
Medium - 20% aq.HOAc (v/v) $[H^+]$ x 10^2 = 1.0 mol dm^{-3}

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	3.9600	3.8500	3.5383	3.2083
20	3.5017	3.3550	3.0617	2.7317
30	3.0617	2.8783	2.5850	2.2550
40	2.6217	2.4017	2.1083	1.7783
50	2.1817	1.9250	1.6317	1.3017
60	1.7233	1.4300	1.1367	0.8250
k_{obs} x 10^4 (s^{-1})	2.7311	3.2390	3.7010	4.4062
k_2 x 10^3 ($dm^3mol^{-1}s^{-1}$)	1.3656	1.6195	1.8505	2.2031
Correlation coefficient (r)	0.9924	0.9894	0.9855	0.9809

Table 4.3.7.4. Effect of temperature on the rate of oxidation of p-chlorobenzyl alcohol

$[K_2Cr_2O_7]$ x 10^3 = 5.0 mol dm^{-3} $[P\text{-}ClC_6H_4CH_2OH]$ x 10^1 = 2.0 mol dm^{-3}
Medium - 20% aq.HOAc (v/v) $[H^+]$ x 10^2 = 1.0 mol dm^{-3}

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-]$ x10^3 (mol dm^{-3})			
10	4.1067	3.8500	3.7767	3.5933
20	3.8500	3.5750	3.4283	3.2267
30	3.5933	3.2267	3.0983	2.8783
40	3.3183	2.9517	2.7683	2.5117
50	3.0433	2.6400	2.4383	2.1450
60	2.7867	2.3283	2.0900	1.7967
k_{obs} x 10^4(s^{-1})	1.2976	1.6738	1.9498	2.2989
k_2 x 10^4 ($dm^3mol^{-1}s^{-1}$)	6.4879	8.3692	9.7488	11.4945
Correlation coefficient (r)	0.9980	0.9968	0.9961	0.9951

Table 4.3.7.5. Effect of temperature on the rate of oxidation of p-nitrobenzyl alcohol

$[K_2Cr_2O_7] \times 10^3 = 5.0$ mol dm^{-3} $[p\text{-}NO_2C_6H_4CH_2OH] \times 10^1 = 2.0$ mol dm^{-3}
Medium - 20% aq.HOAc (v/v) $[H^+] \times 10^2 = 1.0$ mol dm^{-3}

Temperature (K)	303	308	313	318
Time (min)	$[HCrO_4^-] \times 10^3$ (mol dm^{-3})			
10	4.8400	4.6567	4.6200	4.5283
20	4.6933	4.4550	4.3633	4.2167
30	4.5467	4.2533	4.1067	3.9050
40	4.4000	4.0517	3.8500	3.5933
50	4.2533	3.8500	3.5933	3.2817
60	4.0883	3.6300	3.3183	2.8917
$k_{obs} \times 10^5$ (s^{-1})	5.5886	8.2469	10.9600	14.1670
$k_2 \times 10^4$ ($dm^3mol^{-1}s^{-1}$)	2.7943	4.1235	5.4800	7.0834
Correlation coefficient (r)	0.9991	0.9988	0.9983	0.9975