Exploring The Kinetics of Alcohol Oxidizing Employing Metavanadate Compounds as Oxidizing Agents.

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Abstract—**Kinetic studies were conducted to investigate the oxidation of sevaluabl alcohols using Oxidant. The reaction rate was determined by observing changes in the concentrations of Reactants and products over time. Through the derivation of a rate law, the relationship between the reaction rate and the concentrations of reactants was established, allowing for the Determination of the reaction order. Cyclohexanol, nbutanol, Cyclohexanol & Cinnamyl Alcohol which are commonly used in industries, were the specific secondary alcohols Examined. Ammonia metavanadate & Potassium metavanadate was employed as the oxidizing Agent to facilitate the oxidation process. By combining the kinetic and thermodynamic data, a Comprehensive understanding of the oxidation process was achieved, enabling the optimization of reaction conditions, catalyst design, and predictions of reaction behaviour under diffierent Circumstances. These findings contribute to the broader field of catalysis and provide valuable Insights into the Ammonia metavanadate & Potassium metavanadate as an oxidizing agent for the oxidation of secondary alcohols. To monitor the progress of the reaction, the oxidant was Periodically estimated using an iodometric method.**

I. INTRODUCTION

Chemical kinetics is the study of the rates of chemical reactions and the different factors, which affect the rates of reactions. It also gives information about the reaction mechanism responsible for the conversion of reactants into products. On the other hand, Thermodynamics gives the reasons why chemical reactions take place and tells with precision, to what extent a chemical reaction takes place. It investigates the conditions prevalent when the reaction reaches equilibrium. Thus, Chemical Kinetics and Thermodynamics complement each other in furnishing complete information about a chemical reaction.

According to the law of mass action, the rate of a reaction is directly proportional to the active masses of the reacting substances at any given instant. The active masses of the reacting substances decrease with time hence the reaction proceeds rapidly at first but slows down with time. For a chemical reaction, the rate at any instant is given by

$-\frac{dc}{} = kc^n dt$ (1.1)

where, c is the concentration of the reactant at time t, n is the quotient to which the concentration has to be raised and is called the "Order of reaction" and k is the rate constant (also known as specific reaction rate.

1.1 Rate Equations

The rate of a chemical reaction can be found by measuring the concentration of one of the reactants (or products) as a function of time. The integrated rate equations derived for different orders of a reaction are given below:

- First order reaction

$k = 1t \ln (aa-x)$

$k = 2.303. 1t \log (\frac{}{}aa-x)$ (1.4)

- Second order reaction

1. Equal concentrations

$k = at1\ (a-xx)$ (1.5)

2. Unequal concentrations

$k = t\frac{}{}2(a.303-b) \log ba((ab--xx))$ (1.6)

- Third order reaction

$$k = \frac{1}{2a^2t}\frac{x(2a-x)}{(a-x)^2} \quad (1.7)$$

In general, for nth order reaction (n > 0, n ≠ 1),

$k = (\frac{}{}\frac{}{}n-11)\ t\ [\ (a-x1)\ n-1 - (a)1n-1]$ (1.8)

In these equations, a and b are the initial concentrations of the reactants and x is the amount of reactant which has reacted in time t (or the amount of product formed in time t). The concentrations are expressed in moles per unit volume.

1.1.1 Graphical Method to determine rate constant k

The rate constant can be conveniently determined using the graphical method. In this method, the integrated rate equation is put in such a form that a linear plot can be obtained. For the first order reaction, the plot of log $\frac{a}{(a-x)}$ against t will give a straight line passing

through the origin and whose slope is equal to k/2.303. Alternatively, the plot of log (a-x) against t will be a straight line whose slope is equal to -k/2.303 and with an intercept equal to log(a) on the log(a-x) axis.

1.2 Kinetics Theories of Chemical Kinetics

1.2.1 Collision Theory

The collision theory9-11 tries to explain the reaction rates on the basis that a chemical reaction is the result of collisions between the reactant molecules. In 1918 W.C.McC Lewis9 identified the frequency factor A of Arrhenius equation with the collision number i.e. the total number of collisions per ml per sec. He calculated the value of the collision number using the kinetic theory of gases in which molecules are assumed to behave like hard spheres.

For a reaction involving two identical molecules, the total number of collisions per ml per sec is given by

ZAA = $\sqrt{\frac{\pi \kappa T}{m}}$ 2n2d2 (1.13)

Were

ZAA is called the collision frequency,

n is the number of molecules per mL,

m is the mass of a single molecule,

d is the distance between the centers of colliding molecules, and ● κ is the Boltzmann constant.

The rate of reaction in molecular units is then given by

Rate = $2n^2d^2\sqrt{\frac{\pi KT}{m}}\, e^{-E/KT}$ molecules mL-1s-1

For a reaction involving two dissimilar molecules, A and B, the collision frequency ZAB is given by

ZAB = $n_A n_B d^2_{AB}\sqrt{8\,\pi KT\,\frac{m_A + m_B}{m_A m_B}}$ (1.14)

were

$$d_{AB} = \frac{d_A + d_B}{2}$$

is the mean molecular diameter and is called the collision cross section.

The rate of reaction between A and B is then given by,

$$\text{rate} = n_A n_B d_{AB}^2 \sqrt{\frac{8\pi kT(m_A + m_B)}{m_A m_B}}\, e^{-E/kT} \quad (1.15)$$

Equation 1.15 can be modified to give

$$k' = \frac{\text{rate}}{n_A n_B} = d_{AB}^2 \sqrt{\frac{8\pi kT(m_A + m_B)}{m_A m_B}}\, e^{-E/kT} \quad (1.16)$$

where k′ is the rate constant in molecular units, i.e.

$$k' \ (\text{mL molecule}^{-1}\ \text{s}^{-1})$$

Multiplying Equation 1.16 by N, the Avogadro's number, we get,

$$k = Nk' = Nd_{AB}^2 \sqrt{\frac{8\pi kT(m_A + m_B)}{m_A m_B}}\, e^{-E/kT} \quad (1.17)$$

Where k is the rate constant in mL mol-1 s-1

A comparison of equation 1.17 with equation 1.12 indicates that

$\sqrt{8\,\pi KT\,\frac{m_A + m_B}{m_A m_B}}$ A = Nd2AB (1.18)

Hence the expression on the right hand of Equation 1.18 is the same as the frequency factor of the Arrhenius equation. The expression is known as the collision number and is represented by the symbol Z.

In case of reaction involving two identical molecules, the corresponding relation is

$$\sqrt{\frac{\pi \kappa T}{m}} \quad A = 2\ Nd2 \qquad (1.19)$$

Comparison of equation 1.12 and 1.19 leads us to the equation,

$$k = Ze\text{-}E/RT \qquad (1.20)$$

1.3 Reactions in Solutions

The study of the kinetics of reactions occurring in the gaseous or liquid phase is relatively easy.

In the gaseous state, the interaction between the individual molecules is relatively unimportant.

The molecules behave in a random manner and can be treated in terms of the kinetic theory. Liquids, on the other hand, have neither a completely random structure of a gas nor the completely regular structure of a solid and as a result, the kinetics of reactions occurring in the liquid phase cannot be easily studied. But still, a lot of work has been done on reactions in solutions. In many such reactions, the solvent plays a relatively unimportant role in the reaction. It merely provides the physical environment for the reaction by acting as space filler. Such reactions are not affected by changes in the solvent and give the same rate in the gaseous phase as well as in solution20. The thermal decomposition of nitrogen pentoxide21 is an example of such a reaction. But in some reactions, the rate is found to be different in different solvents e.g.

the rate of reaction between ethyl iodide and triethylamine22 is influenced by the solvent. (The rate of reaction is proportional to the concentrations of the activated complexes [X•] i.e.

$$\text{rate } \alpha\ [X\bullet] \qquad (1.37)$$

For the reaction $A + B \leftrightarrow X\bullet \rightarrow$ products

$$[X\bullet] = K\bullet\ [A]\ [B]\ \alpha A\ \alpha B \qquad (1.38)$$

$\alpha\bullet$

where K• is the true equilibrium constant and the α's are the activity coefficients. These activity coefficients were previously neglected as they are close to unity in the gas phase.

rate constant k is given by

$$k\ \alpha\ K\bullet\ \alpha A\ \alpha B$$

1.4 Factors that influence the Reaction Rates

The important factors which influence reactions rates are:

Temperature

Catalyst

Solvent

Ionic Strength

Substituent's

Most reaction rates are profoundly influenced by temperature changes.

1.4.1 Influence of Temperature

As a general rule, the rate of a reaction increases with temperature. The influence of temperature on the rate of a reaction is given by the Arrhenius equation k = Ae-E/RT. In 1884,

Van't Hoff gave the relation,

$$\frac{d(\ln Kc)}{dT} = \frac{\Delta E}{RT2}$$

were

kc is the equilibrium constant and ΔE is the energy change involved in the reaction. For a reversible reaction, the rate constants of the forward and reverse reactions are related to the equilibrium constant by the expression,

$Kc = kf / kr$

If Ef and Er are the energy changes associated with the forward and the reverse reactions respectively, then ΔE= Ef – Er. The Van't Hoff's equation can be split into two component equations:

$$\frac{d(\ln kf)}{dT} = \frac{Ef + I}{RT2}$$

$$d(\ln kr) = Er + I\ dT\ RT2$$

The constant I have been experimentally found to be zero.

In general,

$$\frac{d(\ln k)}{dT} = \frac{E}{RT2} \qquad (1.43)$$

1.4.2 Influence of Catalyst

Ostwald26 defined a catalyst as a substance, which changes the velocity of a chemical reaction without appearing in the end product of the reaction. Earlier, it was thought that a catalyst does not enter into chemical reaction but later studies have revealed that a catalyst does take active part in the chemical reaction by forming a complex with the reactant (i.e. the substrate). This complex is an intermediate and decomposes to give the products. e.g. in a reaction catalysed by hydrogen ions, an intermediate complex involving the substrate and the hydrogen ion is formed. This complex reacts further (e.g. with the solvent) with the liberation of the hydrogen ion to give

the products. Since a catalyst is unchanged at the end of the reaction, it gives no energy to the reacting system and hence, according to thermodynamics, it has no influence on the position of equilibrium. Since the equilibrium constant is the ratio of the rate constants of the forward and reverse reactions, i.e. K = kf/kr, the catalyst influences the forward and reverse rates in the same proportion.

Homogeneous catalyst reacts with the substrate to form an intermediate in the first step of a sequence of several reaction steps leading to the products. Another type of homogeneous catalysis of an organic reaction is nucleophilic catalysis29, 30, in which a nucleophile attacks a carbon atom. It is sometimes difficult to distinguish between base catalysis and nucleophilic catalysis. If the organic compound can form a complex with metal ions, its reaction may be metal ion catalysed.

1.4.3 Metal Ion Catalysis

Many organic reactions are catalysed by metal ions. One of the earliest studies was the metal ion catalysed decarboxylation of acetone dicarboxylic acid45. The catalysis was affected by bivalent transition metal ions as well as La+3, Al+3 and Be+2 ions. The reactive intermediate is probably a chelate complex with one carboxylate group and keto oxygen as ligands. The electron withdrawing effect of the metal ion in the complex facilitates the rupture of the bond between methylene carbon and free carboxylate group. The sequence of the catalytic powers of the metal ions is reverse of that found by Irving and Williams46 for the equilibrium constants of complex formation. Ni+2, Zn+2 and Co+2 were found to be more active catalysts than Cu+2. A similar reaction is the catalytic decarboxylation of dimethyl oxaloacetic acid47 using Zn+2 and Mn+2 catalysts. Metal ions have been used to catalyze the hydrolysis of Schiff bases48. The role of metal ions in the catalysis of organic reactions has been reviewed49.

Metal ions catalyze a number of hydrolytic reactions. In phenanthroline-1-nitrile, the hydration of the nitrile group (to form the amide group) is catalysed by Cu+2, Zn+2 and Ni+2 ions, which form complexes with the substrate50.

Rate = k [Ni-phenanthroline+2] [OH-]

The alkaline hydrolysis of the nitrile is accelerated by a factor of 107 if catalysed by Ni+2 of by 109 if catalysed by Cu+2. The mechanism of metal ion catalysed reaction probably involves external attack of hydroxyl ion at the nitrile carbon. It is unlikely that the strong acceleration caused by the metal ion is solely due the field effect of the positive charge. The metal ion probably interacts (weakly) with the π electrons of C≡N multiple bonds. The basic hydrolysis of the amide is also catalysed by transition metal ions, but the acceleration of the reaction rate is much smaller. Similarly, the transition metals catalyze the basic hydrolysis of the esters of αamino acids51. The rate law52, 53 is analogous to that observed in the hydration of phenanthroline-nitrile. Complex formation takes place at the amino group of the substrate. In some examples, the increase of hydrolysis rate of the ester group in the complexed substrate is of the same order of magnitude as in the N protonated substrate. It can be quantitatively understood because of electrostatic effect, which facilitates attack of the OH- on the carboxyl group52. On the other hand, it may be expected that the metal ions form a chelate complex with the substrate, which involves the amino group as well as the carbonyl oxygen. In the pathway, the attack of OH- on the carbonyl carbon is facilitate even more by the electron withdrawing effect of the metal ion. Furthermore, this assumption leads to a better understanding of the differences in the catalytic actions of the various metal ions, as far as these are not caused by the differences in the equilibrium constants of complex formation, The mechanism of metal ion catalysis in these systems is similar to that of acid catalysis in so far as the metal ion is bonded to a basic site of the substrate to form an intermediate, which readily undergoes nucleophilic attack at a neighboring position. Other reactions that have been catalysed by metal ions include the hydrolysis of Schiff bases54, the decarboxylation of β-keto acid55 and the carboxylation of primary nitro compounds and the methyl ketones56, 57.

1.4.4 Influence of Ionic Strength

The influence of ionic strength on the rate of reactions between ions has been studied by

Bronsted63, Bjerrum64, Christiansen65, Scatchard66.

Applying the simple limiting form of the

Debye-Huckel equation of dilute solutions, it can be shown that

$$\log k = \log k_o + 2QZ_AZ_B\mu \qquad (1.61)$$

where ko is the rate constant at infinite dilution in a given solvent, Q is a constant for a given solvent and

temperature, ZA and ZB are the valencies of the ions and μ is the ionic strength. The above equation has been tested a number if times by several workers. The variation of the rate constant k with the ionic strength depends on the magnitude and sign of ZAZB.

- Case (i) ZAZB is positive and hence k increases with increasing concentration of ions (i.e. increasing ionic strength)
- Case (ii) ZAZB is negative and hence k decreases with increasing ionic strength.
- Case (iii) ZAZB is zero. In this case, the ionic concentration has virtually no effect on the rate constant. This is observed at least in the case of dilute solutions.

The effect of ionic strength on the activity coefficient is termed as Primary Salt Effect. For reactions catalysed by acids or bases, there is a Secondary Salt Effect. The secondary salt effect deals with the effect of a salt on the concentration of the reactants and not with the effect on the rate of a reaction. These salt effects are produced by foreign salts as well as salts involved in the reaction. Bronsted and his co-workers have done a lot of work on primary and secondary salt effects. Positive secondary salt effects have been observed in acid-catalysed reactions involving weak and uncharged acids, since salts increase the degree of dissociation and hence the hydrogen ion concentration. Similarly, in base-catalysed reactions involving weak uncharged bases, the addition of salts increases the degree of dissociation and hence the hydroxyl ion concentration. But if the acid or base is charged, the results are altogether different. The secondary salt effects are small in case of strong acids and bases, which are completely dissociated under all conditions.

1.4.5 Influence of Substituent

The effect of substituents on reaction rates is best quantified by the use of the equation proposed by Hammett67 which relates the equilibrium and rate constants for the reactions of meta and para substituted benzene derivatives. The Hammett relationship is given by the equation.

$$\log k = \log k_o + \sigma\rho \qquad (1.62)$$

$$\log K = \log K_o + \sigma\rho \qquad (1.63)$$

where k or K is the rate constant or equilibrium constant respectively for the reaction involving the substituted compound, ko or Ko that for the reaction involving the unsubstituted compound (parent compound) and σ and ρ are constants.

σ depends only on the substituent and ρ is a reaction constant, which varies with the reaction and the external conditions such as the solvent. Electron withdrawing substituents such as Cl have positive σ values whereas electron-releasing substituents like CH3 have negative σ values.

Substituent with positive σ values are stronger electron attracters than hydrogen and substituents with negative σ values repel electrons more strongly than hydrogen i.e. they attract electrons weeklies than hydrogen. Reactions with positive σ values are accelerated by electron withdrawal from the benzene ring, whereas those with negative σ values are retarded by electron withdrawal from the benzene ring. The free energy activation ΔG* is related to the rate constant k by the equation,

$$k = \frac{\kappa T}{h} e^{-\Delta G^{\bullet}/RT}$$

$$\frac{\kappa T}{h} - \frac{\Delta G^{\bullet}}{2.303\ RT}$$

where κ is the Boltzmann constant. Taking logarithm of the above equation, we get, log k = log

Equation 1.62 can therefore be written a

$$\Delta G^* = \Delta G^*o - 2.303\ RT\ \sigma\rho \qquad (1.64)$$

Equation 1.64 with a particular value of ρ applies to any reaction involving a reactant having a series of substituents. For a given reaction, under a given set of conditions, ΔG*, R, T and ρ are constants and hence σ is linear with ΔG*.

The Hammett equation does not satisfactorily explain the reactions of aliphatic compounds as there is some steric effect between the substituents and the reaction site. Taft proposed an equation analogous to Hammett's equation.

$$\log k = \log k_o + \rho^*\sigma^* \qquad (1.65)$$

where, ρ* is the reaction constant and σ* is the polar substituent constant. σ* is a measure of the electron – attracting ability of the substituents, the effect being a purely polar (inductive) one since it is transmitted through an aliphatic chain. The Taft equation is useful to study the reactions of aliphatic compounds and ortho – substituted benzene derivatives.

It has been argued that linear free energy relationship such as those of Hammett and Taft are associated with the existence of linear relationship between energies of activation and energies of reaction, the entropies remaining constant within a homologous series69. It has now become apparent, on the contrary, that free energies are much simpler functions than energies, which are most sensitive to extreme factors, such as brought about by the solvent.

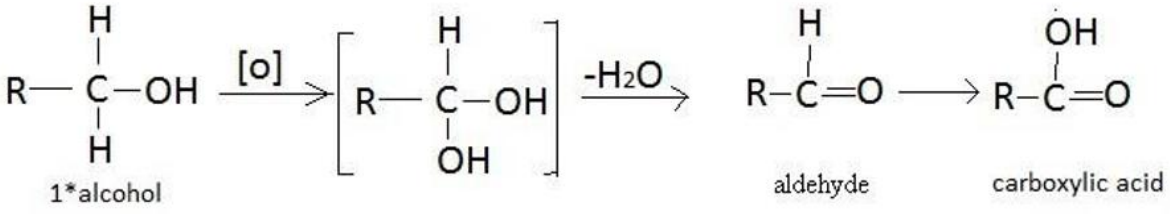
Examples are known in which free energies show linear relationship and show addivity but in which the corresponding energy and enthalpy changes do not show relationships. This is possible because there is a general tendency in processes in solution for heats and entropies to compensate each other, so that changes in free energy are much smaller. In a number of cases70, the plots of TΔS* against ΔH• have been found to be straight lines. This means that the dependence of ΔG* on solvent or substituent is much smaller than that of ΔH• or TΔS*. A similar compensation effect has been found between ΔH* and TΔS* for overall processes in solution. Therefore, the compensation between ΔH*• and TΔS* cannot be explained in terms of purely kinetic effects. The correct explanation is given in terms of solvent – solute interaction. A strong binding between solvent and solute molecules will lower the enthalpy. It will also lower the entropy due to the restriction of the freedom of vibration and rotation of solvent molecules. The application of more exact theories to these effects leads to the result that these effects will give rise to a fairly exact compensation between ΔH and TΔS and therefore to a very small effect on ΔG. Though the changes of substituent and solvent frequently exert their influence on ΔH* in a rather complex manner, the partial compensation between ΔH* and TΔS* in such that their influence on ΔG* is of a much simpler nature. It is for this reason that simple concepts have been very successful in explaining the effects of solvents and substituents on the rates, i.e. on ΔG*, whereas much more complicated explanations, involving detailed consideration of solvent-solute interactions are required to explain the effects on heats and entropies. Not much progress has yet been made in this field.

II. OXIDATION OF ALCOHOLS

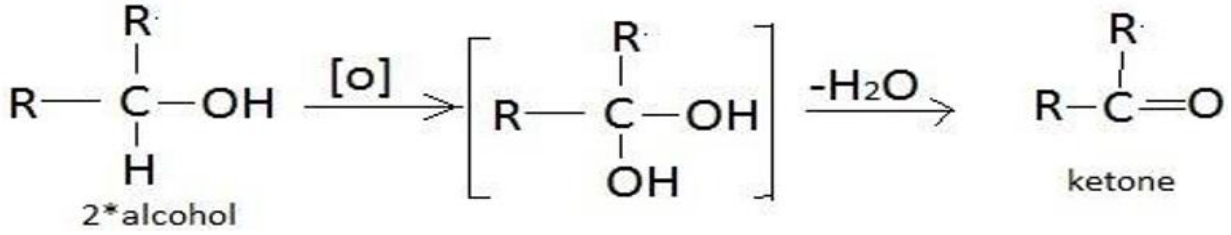
The oxidation of alcohols is a reaction of great industrial importance and several industrially important compounds are obtained as products of oxidation.

The nature of the product depends on whether the alcohol is primary, secondary or tertiary alcohol.

A primary alcohol on oxidation first gives an aldehyde which is oxidized to carboxylic acid containing the same number of carbon atoms. During oxidation, the hydrogen atoms attached to the carbon atom carrying the -OH group are successively oxidized



A secondary alcohol on oxidation gives a ketone containing the same number of carbon atoms. The subsequent oxidation of the ketone to a carboxylic acid containing the same number of carbon atoms takes place only under very vigorous conditions since it helps in the breaking of the C – C bond.



A tertiary alcohol is not oxidized easily in neutral or alkaline medium. The oxidation requires very strong oxidizing agents. e.g. acidic KMnO4.
Under such vigorous conditions, the 3 alcohol gets oxidized to a mixture of ketone and acid, each containing fewer carbon atoms than the alcohol, e.g. tertiary butyl alcohol gives a mixture of acetone and acetic acid.
Thus, we see that the conditions for oxidation become more vigorous as we go from 1 to 2
to 3 to alcohols.

Oxidizing agents for oxidation of alcohols
The oxidizing agents commonly used for the oxidation of alcohols are:
1. KMnO4 it is probably the most powerful of the oxidizing agents.
2. MnO2 used to oxidize α, β unsaturated alcohols to α, β unsaturated carbonyl compounds.
3. Ruthenium Tetraoxide RuO4…. it is a vigorous oxidant for the oxidation of secondary alcohols to ketones1-4 but it is a poor oxidant as far as primary alcohols are concerned5.
4. Platinum and Oxygen primary and secondary alcohols are oxidized by oxygen in the presence of platinum6 with the primary alcohols being more readily oxidized than the secondary alcohols. Under neutral conditions, primary alcohols are converted into aldehydes7; while in alkaline aqueous medium carboxylic acids are formed. Platinum is a specific catalyst for the oxidation of hydroxyls at the 3 positions of poly hydroxy steroids8-12.
5. Cerric ion Ce (IV) is one of the most widely used oxidizing agents for the preparation of aldehydes and ketones13-15.
6. Chromium Tetraoxide CrO3 (or chromic acid H2CrO4). is one of the most versatile oxidizing agents for all types of oxidizable substances in the chemical industry. The oxidation can be controlled to give one product and this makes oxidation by chromic acid a very useful tool in synthetic organic chemistry. Cr (VI) compounds can act as oxidizing agents in a variety of solvents-water, glacial acetic acid, acetone, petroleum ether, benzene, CCl4, pyridine and dimethyl formamide (DMF). Several organic solvents can be used as co solvents with water. The major application of chromic acid in synthetic chemistry is in the oxidation of primary and secondary alcohols to aldehydes and ketones respectively.
7. Ammonium metavanadate is the inorganic compound with formula NH4VO3. It is a white solid, although all samples are yellow owing to impurities V2O5.It is important intermediate in the purification of vanadium.

Present work on the Oxidation of Alcohols
The kinetics of the oxidation of the Aliphatic & Cyclic alcohol n-butanol, 2-chloroethanol, cyclohexanol, cinnamyl alcohol has been investigated using a variety of oxidizing agents:
1. Ammonium metavanadate & Potassium metavanadate in H2SO4. The oxidation was studied by varying the following parameters: 1. concentration of alcohol
2. concentration of the oxidizing agent
3. ionic strength using Na2SO4
4. temperature in the range of 300 to 315 k
5. Catalytic activity of Ni (II), Co (II), Mn (II) ions on the oxidation of the alcohols using Ammonium metavanadate & Potassium metavanadate as oxidizing agent in acidic medium.
The Arrhenius energy of activation E was determined from the linear plots of logk v/s T-1. The thermodynamic parameters k•, ΔG•, ΔH• and ΔS• have been evaluated. Suitable mechanism and rate laws have been suggested for the oxidation reactions under study.

III. EXPERIMENTAL

The rate of a reaction can be measured by determining the change in concentration with time of one of the reactants (or products) of the reaction. The concentration changes can be measured by using either chemical or physical methods of analysis.
In the chemical method, a known volume of the reaction mixture is withdrawn at regular time intervals, the reaction is arrested and the concentration of the unreacted reactant (or product formed) is determined by titrimetric methods of analysis. The reaction is arrested by (i) sudden cooling of the reaction mixture and (ii) addition of a substance which immediately reacts with one of the reactants and thus removes it from the field of chemical action. Chemical methods permit the direct measurement of the concentrations of reactants (or products) but continuous measurement is not possible.

In a physical method, a change in some physical property of one of the reactants (or products) is measured at regular time intervals. Some of the commonly used physical methods to monitor the progress of a reaction are measurement of

1. intensity of the light absorbed
2. electrical conductance
3. pH
4. optical activity

The physical methods permit the continuous measurement of the concentrations of reactants (or products) without disturbing the equilibrium of the system.

Physical methods of analysis are faster and more convenient to use than chemical methods. In the present investigation, the rate of oxidation of alcohols has been determined by titrimetric methods of analysis.

3.1 Materials used

All chemicals used in the oxidation study were of Analytical Grade (AR)

1) Alcohols – The perfumery alcohols were procured from (i) S.H. Kelkar and Co. Ltd. Mumbai, (ii)Yasho Industries Pvt. Ltd. Mumbai.

Uses:

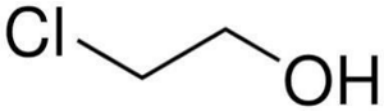
1. N-butanol – It is commonly use as solvent in industries like Paints,Coating & Varnishes. It is also utilized in the production of plastics, textiles, and personal care products.
2. Cyclohexanol - Cyclohexanol is often used as an antiseptic and disinfectant due to its antimicrobial properties. It is commonly found in healthcare settings and personal care products like hand sanitizers and soaps.
3. 2-chloroethanol - 2-chloroethanol is primarily used in the production of pharmaceuticals and pesticides. It acts as a key intermediate in the synthesis of various chemicals.
4. Cinnamyl alcohol - cinnamyl alcohol is a compound with a sweet, floral scent often used in the fragrance industry. It is a common ingredient in perfumes, soaps, and other scented products.

These Alcohol find applications in various industries such as pharmaceutical, chemical, plastic, fragrance & food.

N-BUTANOL

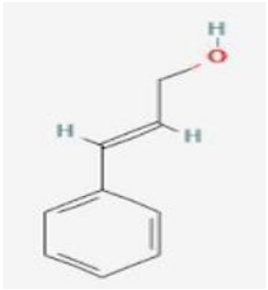
Molecular weight=74.12g/mol

2-CHLORO ETHANOL



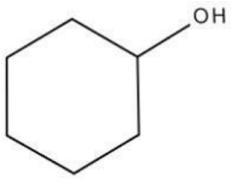
Molecular weight=80.51 g/mol

Cinnamyl Alcohol



Molecular weight=134.18 g/mol

Cyclohexanol

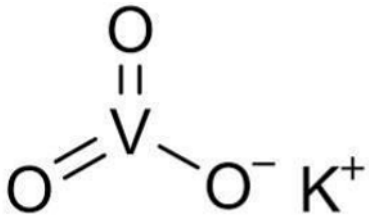


Molecular weight = 100.16 g/mol.

Oxidising agent

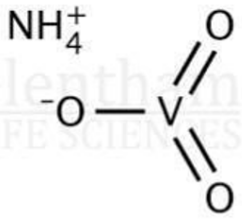
1) Ammonium metavanadate

Molecular weight=116.98 g/mol



2) Potassium metavanadate

Molecular weight =138.04 g/mol



3) To study the effect of ionic strength on the rate of oxidation, Analytical Grade (AR) Na2SO4 was used.
4) The titrants used were standard solution of Na2S2O3 for estimation of unreacted oxidants.

3.2 Preparation of Solutions
Sulphuric Acid Solution
A.R. Grade H2SO4 was suitably diluted to obtain the acid solutions of desired concentrations. These acid solutions were then standardized using the above prepared standard NaOH solution.
Alcohol Solutions
The required amount of alcohol was weighed out by difference method and suitably diluted to get the alcohol solutions of desired concentrations.
Solutions of Oxidising agents were prepared as follows:
Ammonium metavanadate - 0.05 M Ammonium metavanadate & Potassium metavanadate – 0.05 M in 2 M H2SO4

3.3 Apparatus
Borosil brand glassware was used throughout and calibration was done in accordance with the methods described by Vogel. The glassware was thoroughly cleaned with dichromate- sulphuric acid mixture, washed with distilled water and dried before use.

3.4 Kinetic Measurements
A. Kinetics of Oxidation of Alcohols
The solutions of alcohol and oxidizing agent in required amounts were allowed to equilibrate in a thermostat, previously adjusted to the required temperature. After the temperature equilibrium was attained, the solutions were mixed to initiate the reaction. Aliquots of the reaction mixture were withdrawn at regular intervals from the start and the reaction was arrested using ice. The unreacted oxidising agent was then estimated titrimetrically.
Unreacted Ammonium metavanadate were treated with ice cold 10% KI and dilute H2SO4 and the liberated iodine was titrated against standard Na2S2O3 using starch as indicator towards the end.
The reaction was studied in the temperature range 303K to 318K. The plots of log (a-x) versus time were found to be straight lines and the pseudo first order rate constants were calculated from the slopes of the graphs. From the effect of temperature on reaction rate, the energy of activation (E), the probability factor (PZ) and the thermodynamic activation parameters like equilibrium constant (K*), heat of activation (ΔH*), free energy of activation (ΔG*) and entropy of activation (ΔS*) have been evaluated.
The effect of ionic strength μ on the reaction rate was studied by using Na2SO4 in dilute solution in accordance with the Bronsted-Bjerrum equation
$\log k = \log k0 + 1.02\ ZAZB.\ \sqrt{\mu}$

B. Kinetics of transition metal ion catalysed oxidation of alcohols by Oxidant in
H2SO4 medium
The pseudo first order rate constants were determined from the straight-line plots of log (a-x) versus time. From the effect of temperature on oxidation rate, the energy of activation and other thermodynamic activation parameters were determined.

3.4.1 Oxidising agent – Ammonium metavanadate & Potassium metavanadate.
Preparation of solutions
1. 0.2M Alcohol
2. 0.05M ammonium metavanadate & Potassium metavanadate in 2M H2SO4: 5.84 g/L & 6.924 g/L.
3. N/60 Na2S2O3: 4.133g/L
4. 2M H2SO4: 56 ml of conc. H2SO4 / L
5. Starch indicator
6. For ionic strength study 0.333M Na2SO4 (μ=1) : 58.009g/L [MW of Na2SO4 = 142.04

Experimental sets

Set -A [Alc.] is constant and [Oxidant] is variable

Set	Vol. of 0.2M Alcohol (mL)	[Alc] x101 mol dm-3	Vol. of 0.05M Oxidant in 2M H2SO4 x102(mL)	Vol. of 2M H2SO4 (mL)	[Oxidant] x103 mol dm-3	Total volume (mL)
A1	50	1.0	5	45	2.5	100
A2	50	1.0	10	40	5.0	100
A3	50	1.0	20	30	10.0	100
A4	50	1.0	30	20	15.0	100
A5	50	1.0	40	10	20.0	100
A6	50	1.0	50	-	25.0	100

Concentration:
[Alc.] = 0.1M in all sets
[Oxidant] = 2.5 to 25.0 x 10-3 mol dm3
[H2SO4] = 1M in all sets
Temp. = 300 to 315 K

Method: For sets A1, A2, A3, A4, A5, A6, titrate 5ml reaction mixture against N/60 Na2S2O3 at regular time intervals from the start using starch as indicator.
One set is carried out at different temperatures to study temperature dependence of oxidation rate.

Set -B [Oxidant] is constant and [Alc] is variable

SET	Vol. of 0.2M Alcohol (mL)	Vol. of solvent (mL)	[Alc] x102 mol dm-3	Vol. of 0.05M Oxidant in 2M H2SO4 (mL)	Vol.of 2M H2SO4 (mL)	[Oxidant] x103 mol dm-3	Total volume (mL)
B1	12.5	37.5	2.50	10	40	5.0	100
B2	25.0	25.0	5.00	10	40	5.0	100
B3	31.3	18.7	6.25	10	40	5.0	100
B4	37.5	12.5	7.50	10	40	5.0	100
B5	43.8	6.2	8.75	10	40	5.0	100
B6	50.0	-	10.00	10	40	5.0	100

Concentrations:
[Alc.] = 2.5 to 10.0 x 10-2 mol.dm3
[Oxidant] = 5.0 x10-3 mol.dm-3in all sets
[H2SO4] =1M in all sets

Method: For all the sets titrate 5ml reaction mixture against N/60
Na2S2O3 at regular time intervals from the start using starch as indicator

Set-I Effect of ionic strength(μ):

[Alc.] is constant,
[Oxidant] is constant,
Ionic strength μ is variable.
Ionic strength μ=1 using 0.333M Na2SO4 $\mu=1/2 \sum CiZi^2$
$=1/2[0.333(1)2+0.333(1)2+0.333(2)2]$
$=1/2[0.333+0.333+1.332]$
$=1/2[2]$
$=1$

Set	Vol. of 0.2M Alcohol (mL)	[Alc.] x101 mol dm-3	Vol. of 0.333M K2SO4 (mL)	Vol. of water (mL)	μ mol dm-3	Vol. of 0.05M Oxidant in 2M H2SO4 (mL)	Vol. of 2M H2SO4 (mL)	[Oxidant] x103 mol dm-3	Total vol. (mL)
I1	50	1.0	5	20	0.05	10	15	5.0	100
I2	50	1.0	10	15	0.10	10	15	5.0	100
I3	50	1.0	15	10	0.15	10	15	5.0	100

I4	50	1.0	20	5	0.20	10	15	5.0	100
I5	50	1.0	25	-	0.25	10	15	5.0	100

Concentrations:
[Alc.] =0.1M in all sets
[Oxidant]= 5.0 x10-3 mol.dm-3in all sets μ= 0.05 to 0.25M

Method: For all the sets titrate 5ml reaction mixture against N/60
Na2S2O3 at regular time intervals from the start using starch as indicator

IV. RESULTS AND DISCUSSION

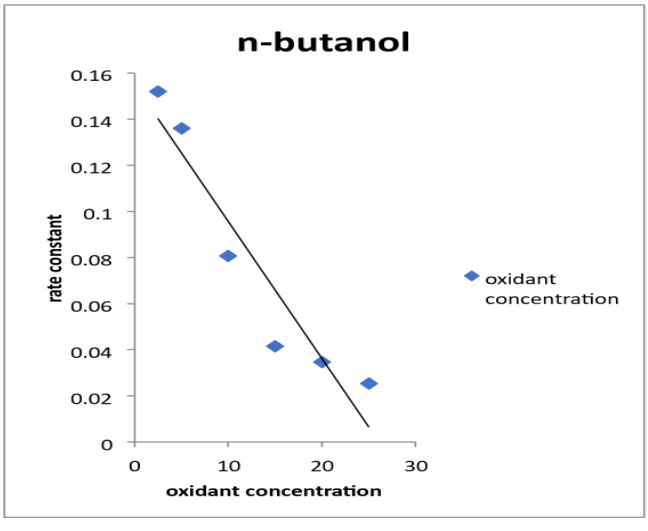
4.1 OXIDISING AGENT –AMMONIUM METAVANADATE in acidic medium

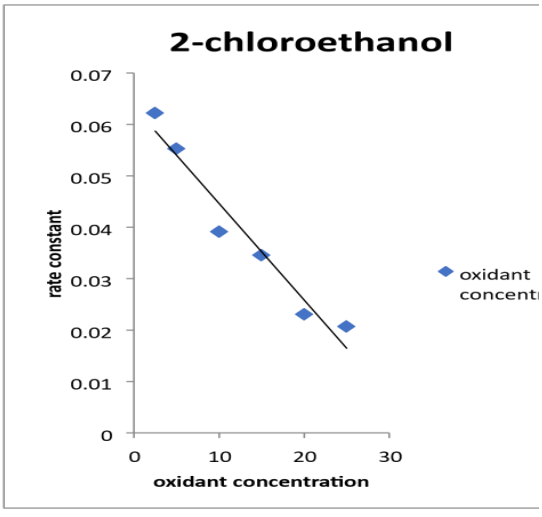
4.1.1 Effect of concentration of alcohol and oxidizing agent on oxidation rate of alcohol the rate of oxidation of alcohol has been studied using pseudo first order kinetics. The validity of the pseudo unimolecular reaction has been confirmed by linear relationship obtained when log(a-x) was plotted against time.
From the slopes of the linear plots, the rate constant (k) has been determined.
Table 4.1.1to 4.1.2 give the experimental data of log(a-x) v/s time for Alcohol for Set A[Alc]=constant, [Ammonium metavanadate] is variable at 303K.
The alcohol oxidized to corresponding aldehyde or ketone. The rate constant k increases with alcohol concentration as expected (Figure) but decreases with the concentration of Ammonium metavanadate for all alcohols.

Effect of Oxidant concentration:

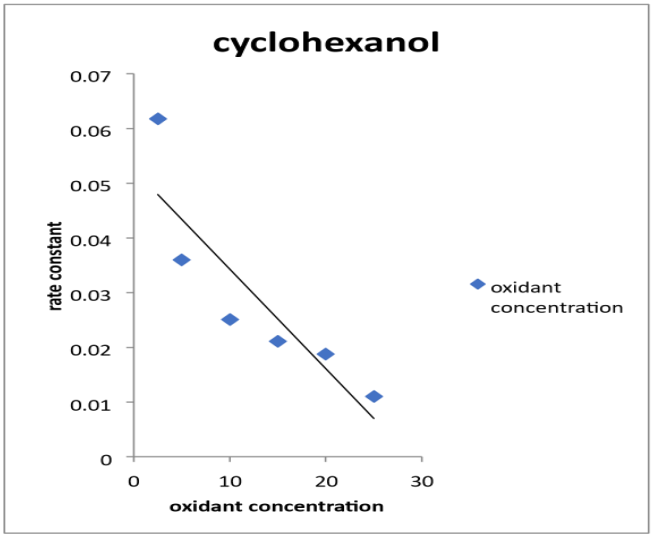
Table: 4.1.1

[Alcohol] mol dm-3	[Ammonia metavanadate] mol dm-3	n-butanol	2chloroethanol	Cyclohexenol	Cinnamyl alcohol
		s^-1	s^-1	s^-1	s^-1
1	2.5	0.15199	0.062181	0.0618	0.06909
1	5	0.1359	0.055272	0.03598	0.036948
1	10	0.0806	0.039151	0.02512	0.036849
1	15	0.0414	0.03454	0.02114	0.029939
1	20	0.03454	0.02303	0.0188	0.027636
1	25	0.02533	0.020727	0.01101	0.013818





Effect of Substrate concentration:



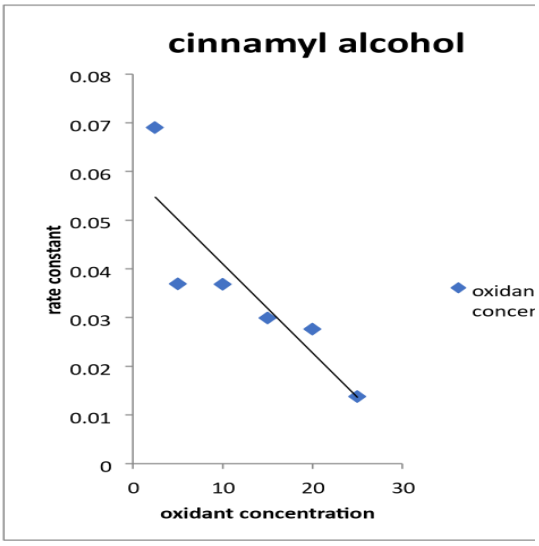
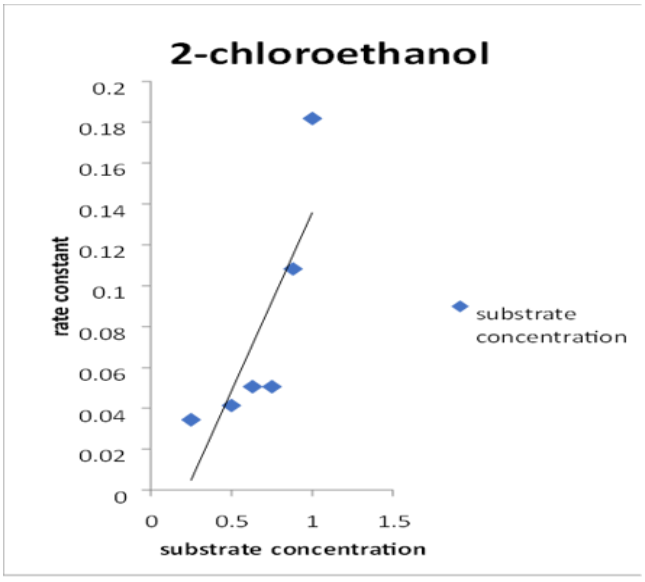
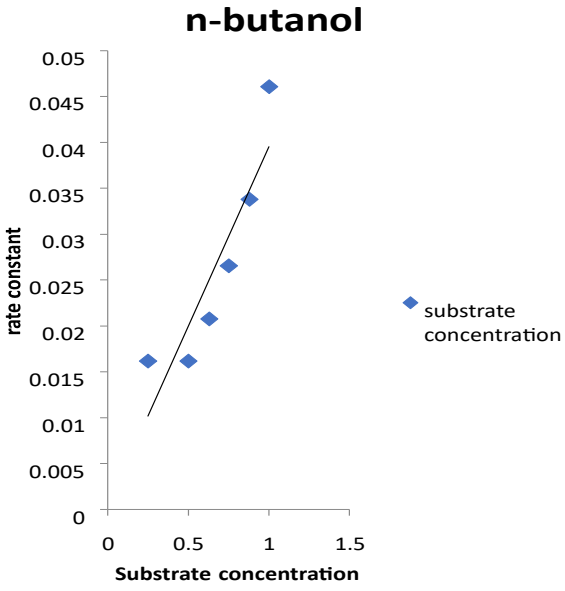


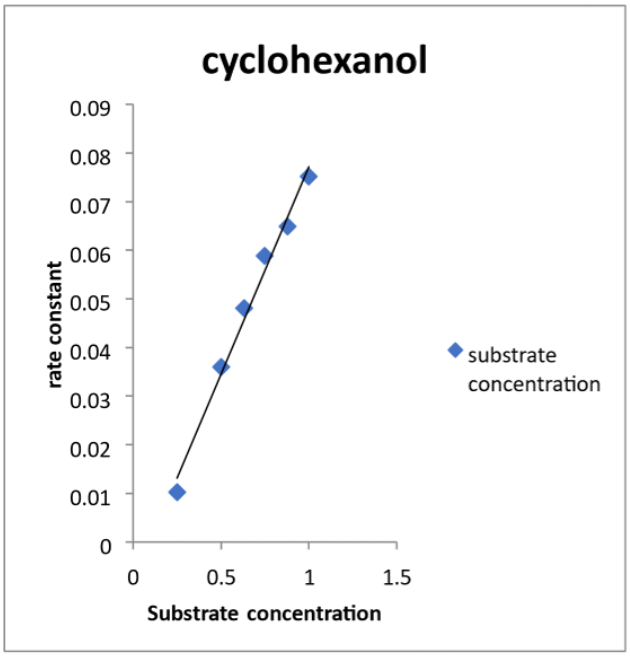
Table: 4.1.2

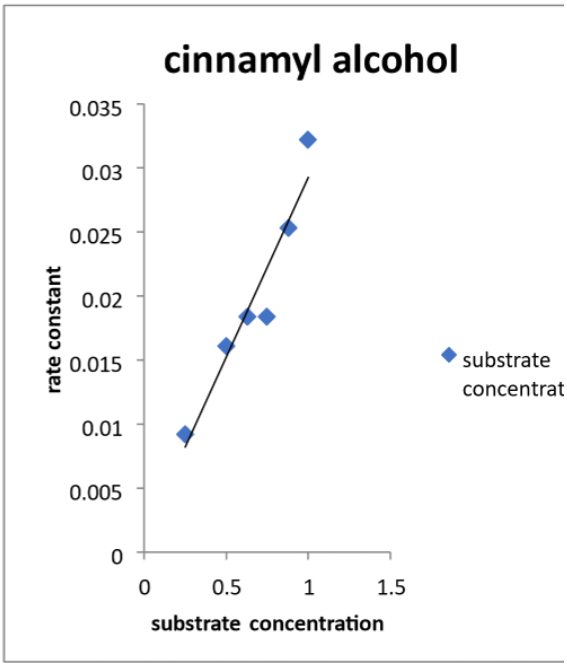
[Alcohol] mol dm -3	[Ammonia Metavanadate] mol dm-3	n-butanol	2- Chloroethanol	Cyclohexanol	Cinnamyl alcohol
		s^-1	s^-1	s^-1	s^-1
0.25	5	0.016121	0.03454	0.0102	0.009212
0.5	5	0.016122	0.0414	0.03601	0.016121
0.63	5	0.020727	0.0506	0.04812	0.018424
0.75	5	0.02654	0.0506	0.05887	0.018424
0.88	5	0.03375	0.1082	0.06481	0.025333
1	5	0.04606	0.1819	0.07512	0.032242



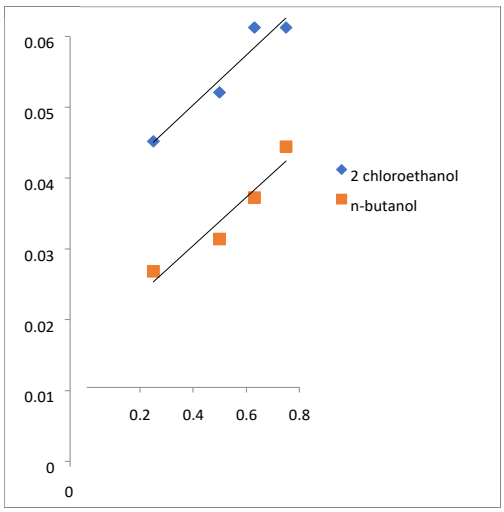


- It was noted that the oxidation rate exhibited of proportional increase corresponding to the concentration to alcohol. For all the alcohol examined, while it decreases with an increasing concentration of the oxidant.
- It was observed that the series of alcohol oxidation rate follows the sequence



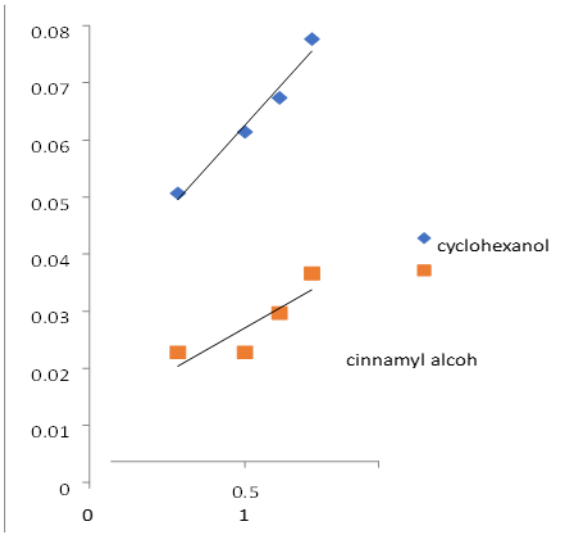


1. Cyclic Alcohol: cyclohexanol > Cinnamyl alcohol
2. Aliphatic Alcohol: 2-chloroethanol > n-butanol.



Aliphatic alcohol
Cyclic alcohol

4.1.2 Effect of ionic strength on oxidation rate of alcohols.



The effect of ionic strength on the rate of reaction between ions has been studied in detail by Scatchard. The several deviations observed due to high concentration and multiple charged ions were explained by taking into account the Debye Huckel theory of activity coefficient and the following equation was proposed

$$\text{Log } k = \log k0 + 1.02ZAZB\sqrt{\mu} \ldots (4.1)$$

where k0 is the rate constant at infinite dilution in a given, ZA and ZB are the valencies of the ions and √μis the ionic strength. This equation was tested by Davies for its linear relationship when logk is plotted against √μ. For reaction involving neutral molecules,

the effect of ionic strength on rate constant is negligible.

In the presence study the reaction is between a neutral molecule (alcohol) and another neutral molecule (Ammonium metavanadate). Hence the rate constant should be independent of ionic strength since ZA and ZB is zero in sufficiently diluted solution for Debye Huckel limiting law to be applicable. In the present studied in dilute solution in the range μ = 5 to 25 x 10-2 mol.dm3 using Na2SO4.

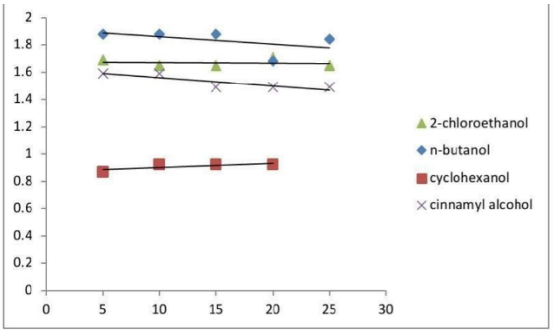
The effect of ionic strength on the activity coefficient is called the primary salt effect. Since in the present study, the solutions are dilute, no primary salt effect can be expected. Table 4.1.2 illustrates the effect of ionic strength on the oxidation rates of alcohols by Ammonium metavanadate in H2SO4 data indicates that the rate of oxidation of alcohols is practically constant and independent of ionic strength.

The graph of log k v/s √μwhich are parallel for the √μaxis indicating that the rate of oxidation is independent of ionic strength.

Table: Effect of ionic strength on the oxidation rates on alcohols by Ammonium metavanadate in H2SO4. [Alc.] = 0.1M, [H2SO4] = 2.5 x 10-2 M, [Ammonium metavanadate] = 2.5 x 10-3, Temperature = 313 K

$\mu \times 10^2$ mol dm^{-3}	K x 10^3 s^{-1}			
	n-butanol	2-chloroethanol	cyclohexanol	Cinnamyl alcohol
5		1.69	0.868	1.59
10	1.88	1.65	0.921	1.59
15	1.88	1.65	0.921	1.49
20	1.681	1.71	0.921	1.49
25	1.842	1.65	1.842	1.49

Plot of √μ v/s log k is shown below for effect of ionic strength:



4.1.3 Effect of temperature on oxidation rate of alcohols.

The rate of oxidation was studied in the temperature range 300-315 K. For all the alcohols under study, the oxidation rate increases with temperature. The energy of activation Ea of the oxidation reaction was calculated from the slopes of the linear plots of log k v/s 1/T. The thermodynamic parameters K*, ΔH*, ΔG* and ΔS* were evaluated from the formula.

Effect of temperature on rate constant of alcohols,

Alcohols	ΔE kJmol^{-1}	ΔH kJmol^{-1}	ΔG kJmol^{-1}	ΔS K^{-1} kJmol^{-1}
2-chloroethanol	9.65	7.1308	-93.96	-0.28657
n-butanol	21.1	18.5808	-80.0376	-0.20283
cyclohexanol	62.88	60.3608	-88.1729	-0.09179
cinnamyl alcohol	71.76	69.2408	-83.1816	-0.04601

The important findings from the data are:

1. The rate of oxidation of alcohol increases with temperature as expected.
2. The equilibrium constant K* increases with temperature. Since the rate constant is directly proportional to K*, K* is also a function of temperature.
3. For each alcohol under study, there is a slight increase in ΔG* with temperature and slight decrease in ΔH* with temperature.
4. For each alcohol under study, the entropy of activation ΔS* is almost constant at all temperatures indicating that the site of oxidation is the same at all temperatures.

4.2 OXIDISING AGENT –POTASSIUM METAVANADATE in acidic medium:

4.2.1 Effect of concentration of alcohol and oxidizing agent on oxidation rate of alcohol-

The rate of oxidation of alcohol has been studied using pseudo first order kinetics. The validity of the pseudo unimolecular reaction has been confirmed by linear relationship obtained when log(a-x) was plotted against time. From the slopes of the linear plots, the rate constant (k) has been determined.

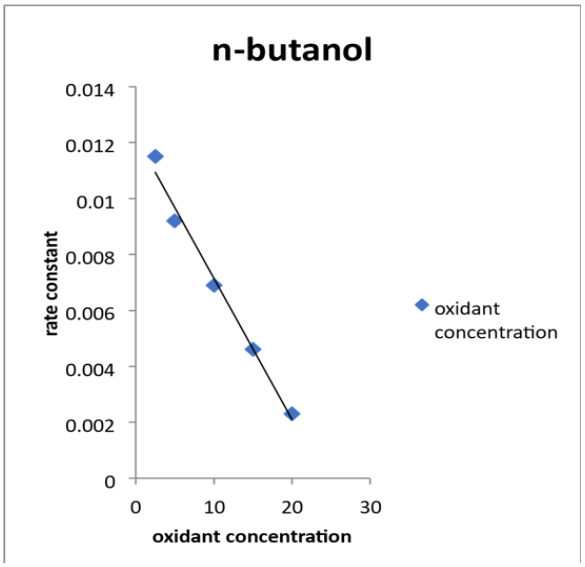
Table 4.2.1 to 4.2.2 give the experimental data of log(a-x) v/s time for Alcohols for Set

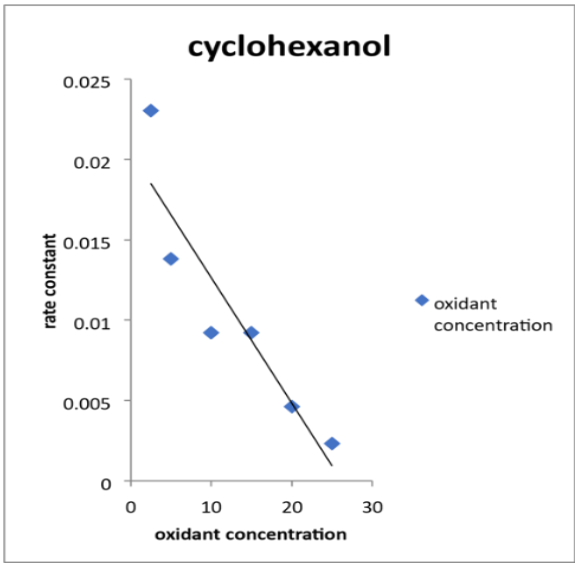
A[Alc]=constant, [Ammonium metavanadate] is variable at 303K.give the corresponding linear plots of log(a-x) v/s time at 303K.

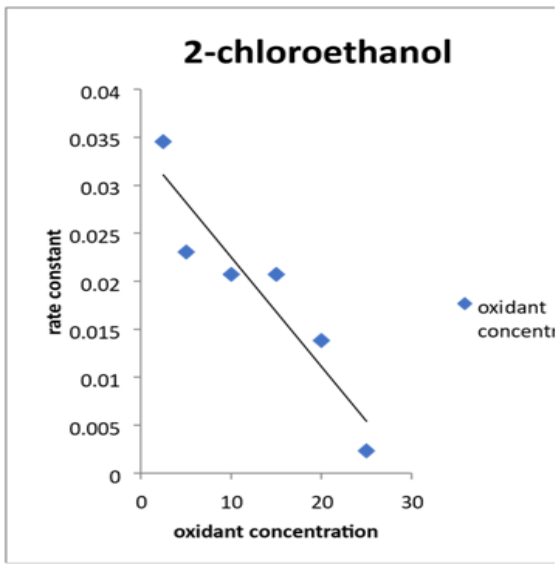
The alcohol oxidized to corresponding aldehyde or ketone. The rate constant k increases with alcohol concentration as expected (Graphs) but decreases with the concentration of Potassium metavanadate for all alcohols.

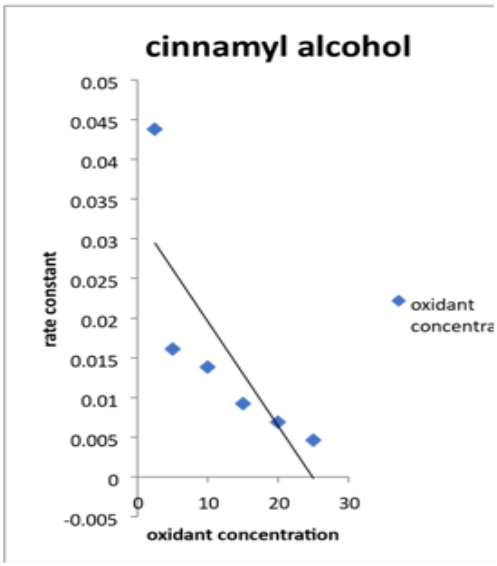
Effect of Oxidation concentration:

[Alcohol]	[Potassium metavanadate]	nbutanol	2 chloroethanol	Cyclohexanol	Cinnamyl alcohol
mol dm-3	mol dm-3	s^-1	s^-1	s^-1	s^-1
1	2.5	0.0276	0.034545	0.02303	0.0438
1	5	0.0115	0.02303	0.013818	0.0161
1	10	0.0092	0.020727	0.009212	0.0138
1	15	0.0069	0.020727	0.009212	0.0092
1	20	0.0046	0.013838	0.004606	0.0069
1	25	0.0023	0.002303	0.002303	0.0046



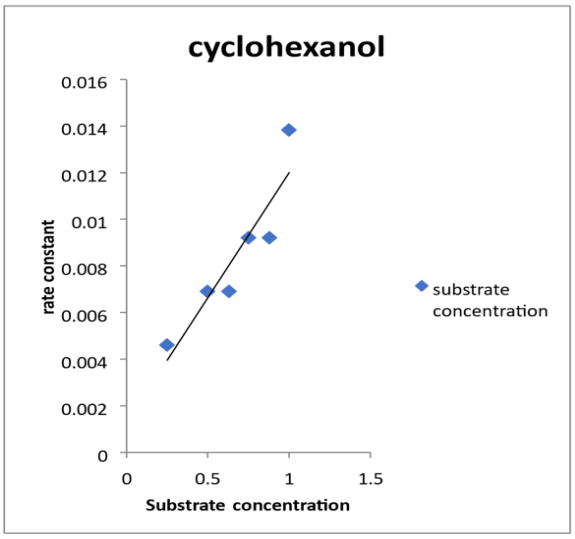


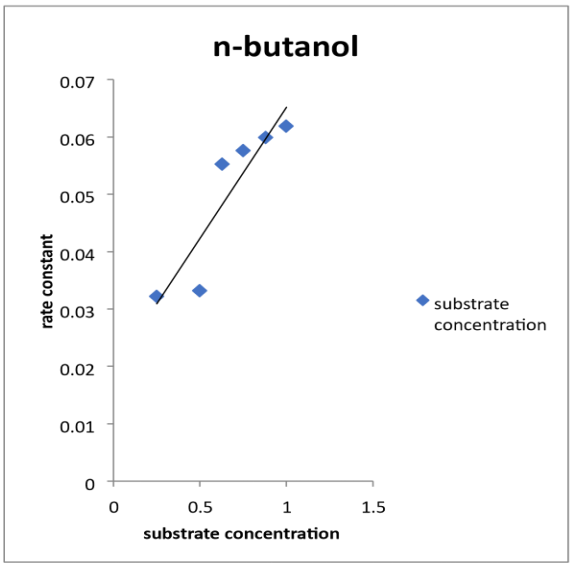


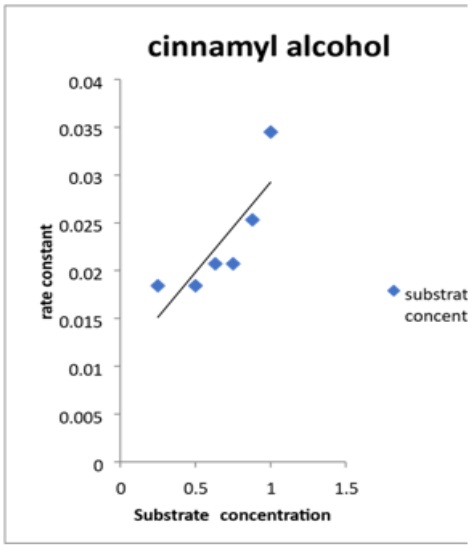


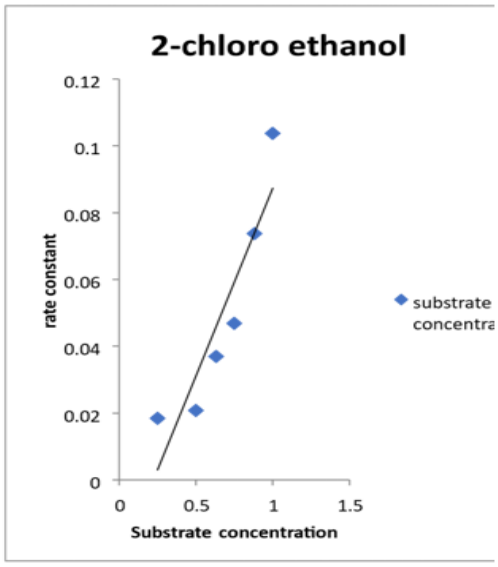
Effect of Substrate concentration:

[Alcohol]	[Potassium metavanadate]	n-butanol	2-chlorohexanol	Cyclohexanol	Cinnamyl alcohol
mol dm-3	mol dm-3	s^-1	s^-1	s^-1	s^-1
0.25	5	0.0322	0.018424	0.004606	0.0184
0.5	5	0.0322	0.020727	0.006909	0.0184
0.63	5	0.0553	0.036848	0.006909	0.0207
0.75	5	0.0576	0.046848	0.009212	0.0207
0.88	5	0.0599	0.073696	0.009212	0.0253
1	5	0.0619	0.103635	0.013818	0.0345







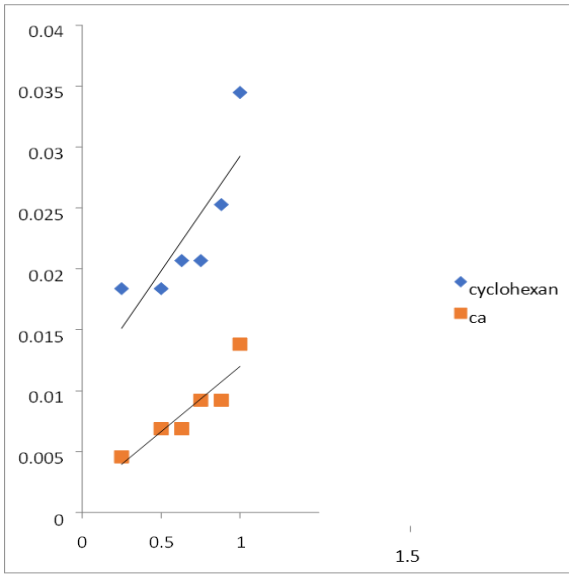


It was noted that the oxidation rate exhibited of proportional increase corresponding to the concentration to alcohol. For all the alcohol examined,

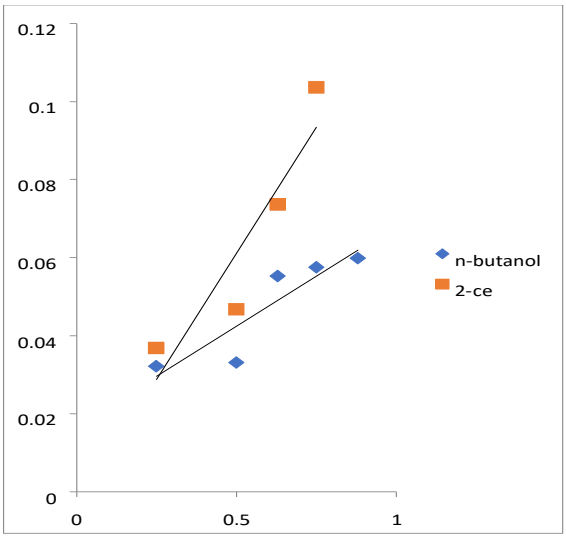
while it decreases with an increasing concentration of the oxidant.

It was observed that the series of alcohol oxidation rate follows the sequence-

1. Cyclic Alcohol: cyclohexanol > Cinnamyl alcohol
2. Aliphatic Alcohol: 2-chloroethanol > n-butanol.



Aliphatic Alcohol



Cyclic Alcohol

4.2.2 Effect of ionic strength on oxidation rate of alcohols:

The effect of ionic strength on the rate of reaction between ions has been studied in detail by Scatchard. The several deviations observed due to high concentration and multiple charged ions were explained by taking into account the Debye Huckel theory of activity coefficient and the following equation was proposed

$$\text{Log } k = \log k_0 + 1.02 Z_A Z_B \sqrt{(\mu)} \quad \ldots\ldots\ldots (4.1)$$

Where k0 is the rate constant at infinite dilution in a given, ZA and ZB are the valencies of the ions and √(μ)is the ionic strength. This equation was tested by Davies for its linear relationship when logk is plotted against √(μ). For reaction involving neutral molecules, the effect of ionic strength on rate constant is negligible.

In the presence study the reaction is between a neutral molecule (alcohol) and another neutral molecule (Potassium metavanadate). Hence the rate constant should be independent of ionic strength since ZA and ZB is zero in sufficiently diluted solution for Debye Huckel limiting law to be applicable. In the present studied in dilute solution in the range μ = 5 to 25 x 10-2 mol.dm3 using Na2SO4.

The effect of ionic strength on the activity coefficient is called the primary salt effect. Since in the present study, the solutions are dilute, no primary salt effect can be expected.

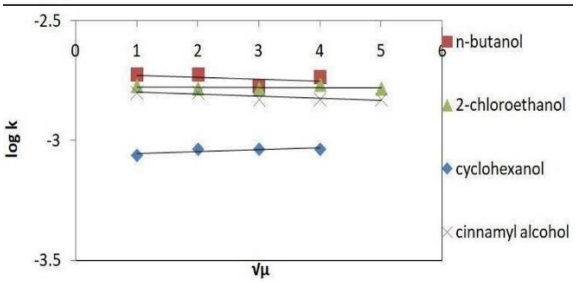
Table below illustrates the effect of ionic strength on the oxidation rates of alcohols by Potassium metavanadate in H2SO4

Data indicates that the rate of oxidation of alcohols is practically constant and independent of ionic strength. The graph of log k v/s √(μ)which are parallel for the √(μ)axis indicating that the rate of oxidation is independent of ionic strength.

Table: Effect of ionic strength on the oxidation rates on alcohols by Potassium metavanadate in H2SO4. [Alc.] = 0.1M, [H2SO4] = 2.5 x 10-2 M, [Potassium metavanadate] = 2.5 x 10-3 , Temperature = 313 K.

$\mu \times 10^2$ mol dm^{-3}	$k \times 10^4 s^{-1}$			
	n-butanol	2-chloroethanol	cyclohexanol	Cinnamyl alcohol
00.00	6.25	5.77	5.29	4.70
05.00	6.36	5.96	5.45	4.70
10.00	6.25	5.51	5.28	4.66
15.00	6.18	5.95	5.39	4.71
20.00	6.36	5.69	5.26	4.81
25.00	6.25	5.72	5.49	4.75

Plot of √μ v/s log k is shown below for effect of ionic strength –



4.2.3 Effect of temperature on oxidation rate of alcohols.

The rate of oxidation was studied in the temperature range 300-315 K. For all the alcohols under study, the oxidation rate increases with temperature. The energy of activation Ea of the oxidation reaction was calculated from the slopes of the linear plots of log k v/s 1/T. The thermodynamic parameters K*, ΔH*, ΔG* and ΔS* were evaluated from the formula.

Effect of temperature on rate constant of alcohols,

Alcohols	ΔE kJmol^{-1}	ΔH kJmol^{-1}	ΔG kJmol^{-1}	ΔS K^{-1} kJmol^{-1}
2-chloroethanol	6.15	8.080	-93.96	-0.2565
n-butanol	11.01	16.56	-80.0376	-0.2028
cyclohexanol	45.88	31.36	-88.1729	-0.0925
cinnamyl alcohol	57.61	49.24	-83.1816	-0.0160

The important findings from the data are:

1. The rate of oxidation of alcohol increases with temperature as expected.
2. The equilibrium constant K* increases with temperature. Since the rate constant is directly proportional to K*, K* is also a function of temperature.
3. For each alcohol under study, there is a slight increase in ΔG* with temperature and slight decrease in ΔH* with temperature.
4. For each alcohol under study, the entropy of activation ΔS* is almost constant at all temperatures indicating that the site of oxidation is the same at all temperatures.

V. CONCLUSION

From the given research work on kinetic study and effect of transition metal ion and some thermodynamic parameter of studied alcohol shows effect on the rate constant of alcohol, we conclude that:

1. The rate constant of alcohol on oxidation when ammonium metavanadate & Potassium metavanadate is used as oxidizing agent increases. Hence, the oxidation rates of studied alcohols follow the sequence:
2-Chloroethanol > n-butanol > Cyclohexanol > Cinnamyl

2. Ionic strength has no effect on the oxidation rates of studied alcohols.

The effect of temperature on oxidation rate of alcohols shows the following conclusion:

1. The rate of oxidation of alcohol increases with temperature as expected.
2. The equilibrium constant K* increases with temperature. Since the rate constant is directly proportional to K*, K* is also a function of temperature.
3. For each alcohol under study, there is a slight increase in ΔG* with temperature and slight decrease in ΔH* with temperature.
4. For each alcohol under study, the entropy of activation ΔS* is almost constant at all temperatures indicating that the site of oxidation is the same at all temperatures.

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