# CHAPTER II : INTRODUCTION AND RESEARCH PLAN

Potassium permanganate has been regularly used as oxidising agent for well over a century both in volumetric analysis and in degradative organic chemistry, yet even today, knowledge of the mechanism of its reactions is only fragmentary. In organic chemistry few of their reactions are specific or even quantitative.

## Properties of Permanganate

Nearly all oxidising agents are inorganic compounds, among common oxidising agents, the reactions of oxidation by permanganate are interesting because of the several oxidation states to which it can be reduced. Hence kinetic studies of permanganate oxidations have contribute greatly to our knowledge of the mechanistic path ways by which this reagent reacts with many organic and inorganic substrates.

The overall valency chances which the respective anions undergo when they are reduced to stable products (equs. 1-2) can not occure except by a series of consecutive changes.

$$(MnO_4)^- \xrightarrow[\text{acid}]{\text{strong}} Mn^{2+} \quad \text{(5-electron change)} \qquad \text{equ}^n\ 1$$

$$(MnO_4)^- \xrightarrow[\text{Alkaline}]{\text{Neutral(or)}} MnO_2 \quad \text{(3-electron change)} \qquad \text{equ}^n\ 2$$

Ions derived from every valence state of manganese from VII to III as well as hydroxyl radical and other oxygenated species (e.g. $O^-$ and $H_2O$) have proposed as the active entities for oxidation by permanganate. It is not expected that single mechanism will satisfy every reaction; the nature of the substrate and of the medium profoundly affect course of reaction. However, some advance will be made if it is possible to recognise certain more important intermediates and the conditions under which they are produced.

## 1) Oxidation states of Manganese :

Manganese species having oxidation numbers between +1 and +7 all known, but of these the +2, +4 and +7 states are the only [redacted] which are stable over wide range of acidity. Whereas manganese (VI) and manganese (V) species undergo decomposition to manganese (IV) only in strongly basic solution. Manganese (III) on the other hand disproportionates to manganese (II) and manganese(IV) in all but strongly acid solution. There is evidence for the existence of manganese(I) in certain complexes.

### (a) Manganese(VI) (Manganate) :

Manganese(VI) exists in basic solution as the green. Manganate ion, $MnO_4^{2-}$. The stability and oxidising action of manganate has been investigated by Water,[2] Symons[3], Duke[4] and others. In basic solutions which are less than 1 M in hydroxide ion, manganate ion slowly disproportionates to permanganate and manganese dioxide.[5]

$$3\ MnO_4^{2-} + 2\ H_2O \longrightarrow 2\ MnO_4^{-} + MnO_2 + 4\ OH^{-}$$

In neutral and acid solution the disproportion is instantaneous. An equilibrium value for the above reaction has been measured.[6]

$$K = \frac{[MnO_4^-]^2\,[OH]^4}{[MnO_4^{2-}]^3} = 16 \pm 7$$

but this quantity is not actually constant because of the varying activity of manganese dioxide.

Oxidations by manganate are almost always much slower than those of permanganate. A rare exception to this generalization is the oxidation of aromatic aldehydes; the rates of manganate and permanganate oxidation are virtually the same for these compounds at the same pH[7]; cyanide ion is oxidised by manganate at about one-eightieth the permanganate rate.[8]

(b) Manganese(V) (Hypomanganate) :

The blue salt, potassium hypomanganate, $K_3MnO_4$[9] was first prepared by Lux in 1946.[10] Hypomanganate solutions are fairly stable in the cold for a few days ion concentrated alkali but slowly deposit manganese dioxide. In 4 N alkali disproportion occurs within few minutes.

$$2\ MnO_4^{3-} + 2\ H_2O \longrightarrow MnO_4^{2-} + MnO_2 + 4\ OH^-$$

The reactivity towards reductants thus varies inversely with the charge on the oxidant.

$$MnO_4^{\text{[illegible]}} > MnO_4^{2-} > MnO_4^{3-}$$

Pode and Waters showed that hypomanganate oxidises primary and secondary alcohols but little effect on alkenes, tertiary alcohols and phenols.[11]

(c) Manganese(IV) :

Manganese dioxide, the brown insoluble material whose degree of hydration, is the normal form of manganese(IV). However, under certain circumstance soluble form can exist.

Manganese dioxide when used in solvents such as chloroform, acetone and ether has become a favoured oxidant for unsaturated alcohols.[12] Oxidation of aryl alcohols to ketones[13] can be brought about by manganese dioxide dispersed in aromatic hydrocarbon solvents.

(d) Manganese(III) (Manganic Ion) :

Trivalent manganese exists as the red manganic ion, Mn(III), in concentrated acid solution. At low acidities it undergoes disproportionation.[14]

$$2\ \mathrm{Mn^{III}} \rightleftharpoons \mathrm{Mn^{II}} + \mathrm{Mn^{IV}}$$

Aldehydes and ketones which can enolize are degraded by this reagent and the rate determining step in the oxidation proved to be enolization itself.[15]

(e) Manganese(II) (Manganous Ion) :

Manganous ion is the end product of permanganate oxidation only in acid solution and only when fairly good reducing agents like iodide or ferrous ions are used. Most organic compounds reduce permanganate to manganese dioxide even in acid solution.

The oxidation usually known as the Guyard reaction and has been used for the volumetric determination of Manganese.[17]

The extensive work by Tompkins,[18] Polissar[19] and Adamsen[20] on the mechanism of the Guyard reaction has been reviewed in detail by Ladbury and Cullis.[21]

2) <u>Oxidation Potentials</u> :

Oxidation potentials can be measured precisely, depend on whether the reaction is conducted in acidic or basic solution. Thus, $Mn^{VII}$ - $Mn^{IV}$ couple has the values:[22,23]

$$3\,\bar{e} + MnO_4^- + 4.H^+ \longrightarrow MnO_2 + 2\,H_2O \quad E^o = 1.70 \text{ (volts)}$$

The higher potential for the reaction in acid solution is, of course, a consequence of the free energy change corresponding to the reaction.

$$4\,H^+ + 4\,OH^- \longrightarrow 2\,H_2O$$

The corresponding couple, measurable only in basic solution, involving manganate and manganese dioxide have the values[22,23]:

$$2\,\bar{e} + MnO_4^{2-} + 2\,H_2O \longrightarrow MnO_2 + 4\,\overline{OH}$$

$$E^o = +0.60 \text{ volt}$$

Manganese dioxide, as an oxidant has fairly large potential for reaction to manganous ion :

$$2\,\bar{e} + MnO_2 + 4\,H^+ \longrightarrow Mn^{2+} + 2\,H_2O$$

$$E^o = 1.23 \text{ volt}$$

The potential of the $Mn^{VII}$ - $Mn^{II}$ couple is larger 1.51 volts.

The vigour with which oxidation of various substrates is brought about by the oxidants whose potentials are given above is related to the magnitude of these potential in most cases. With organic substrates, mechanistic factors are of major importance. Thus, despite the lower potential of permanganate in basic solution than in acid solution, the oxidation rate of alcohols and hydrogen cyanide are greater at pH 12 than at pH 2.

### 3) Ultraviolet and Visible Spectra of Permanganate :

The three manganese oxy-anions $MnO_4^-$, $MnO_4^{2-}$ and $MnO_4^{3-}$ all absorb strongly in the visible;[24-26] the colours produced are purple, green and blue respectively. The absorption maxima data for permanganate, manganate and hypomanganate salts are given in the following Table 1.

Table 1.

| $MnO_4^-$ | | $MnO_4^{2-}$ | | $MnO_4^{3-}$ | |
|---|---|---|---|---|---|
| Max (mμ) | e x $10^{-3}$ | Max (mμ) | e x $10^{-3}$ | Max (mμ) | e x $10^{-3}$ |
| 546 | 2.38 | 606 | 1.71 | 667 | 0.90 |
| 526 | 2.40 | 439 | 1.38 | 313 | 3.90 |
| 311 | 1.80 | 347 | 1.83 | - | - |
| - | - | 299 | 1.66 | - | - |

The visible spectrum of permanganate is unaltered by changes in solvent and temperature.[27]

4) Infrared Spectra :

The infrared spectra of several permanganate salts have been obtained by Miller et al. a wide frequency range.[28,29] A very strong bond occurs near 900 $cm^{-1}$ in all the salts that were examined. At lower frequency, in the cesium bromide region a doublet at 380 and 400 $cm^{-1}$ occurs in most cases.

The principal bands of the permanganate salt is given in Table 2.

Table 2

| Salt | Frequency $cm^{-1}$ | Intensity | Characteristic |
|---|---|---|---|
| $KMnO_4$ | 387 | Medium | Sharp |
| | 402 | Strong | Sharp |
| | 845 | Weak | |
| | 900 | Very strong | |
| | 1725 | Weak | |

5) Decomposition of Permanganate :

(a) Neutral Solution :

The decomposition of aqueous permanganate is autocatalytic since manganese dioxide is an effective catalyst for the process.[30]

$$2\ MnO_4^- + H_2O \xrightarrow{MnO_2} 2\ MnO_2 + 2\ OH^- + \frac{3}{2}\ O_2$$

It follows that even traces of dust or of other reducing materials will reduce decomposition of permanganate solutions.

(b) Acid Solution :

Dilute aqueous acid solutions of permanganate are less stable than neutral solutions, but the decomposition is relatively slow at low temperature. The decomposition rate is roughly proportional to the acidity and manganese dioxide were also found to promote the decomposition in acid solution.[31]

(c) Alkaline Solution : Concentrated alkaline solution of permanganate slowly decomposes to give oxygen and manganate. The mechanism proposed by Symons and Jezowska-Trezebiatowska et al. involves an initial electron abstraction from hydroxyl ion by permanganate.[32-35]

$$MnO_4^- + OH^- \longrightarrow MnO_4^{2-} + OH.$$

$$4\ MnO_4^- + 4\ OH^- \longrightarrow 4\ MnO_4^{2-} + 2\ H_2O + O_2$$

It is known that manganate retards the reaction and that the liberated oxygen comes from the solvent, not from the permanganate.[32-35] Potassium permanganate is utilised within thirty minutes.

In the Symons mechanism, subsequent one electron attraction by permanganate involves conversion of $OH^{\bullet}$ to $O^-$ to $HO_2^-$ to $O_2$, and manganate inhibition is believed to be the result of the reversibility of some of these steps.[36]

Permanganate Oxidation of Organic Substrates :

Permanganate is a vigorous and drastic oxidant which has long been used in the laboratory. The reactivity of this reagent is mainly dependent to a great extent on whether the reaction conditions are neutral, acidic or basic. In alkaline medium the permanganate oxidations of organic substrates are often faster than in neutral solution. This is usually due to a change in the organic substrates than occurs when the solution is made basic.

Alkanes :

The information regarding the oxidation of saturated hydrocarbons is, so far very little known. Reaction can be studied, however, with saturated chains containing an inert functional group such as carboxyl. The oxidation by both manganate and permanganate of branched chain carboxylic acids to the tertiary hydroxyl acids was studied by Kenyon and Symons.[37] A more detailed study of the permanganate oxidation of 4-methyl hexanoic acid has been made by Wiberg and Fox.[38]

Alcohols :

Oxidation of primary and secondary alcohols by alkaline permanganate solution is easy, whereas tertiary alcohols are difficult to oxidise unless extreme conditions are used to degrade the molecule. Primary alcohols give aldehydes whereas secondary alcohols give ketone on oxidation. Alcohols are oxidised very slowly in neutral solution and rapidly in base with the rate in most cases being proportional to the hydroxyl ion concentration.[39,40]

Permanganate oxidation of aromatic alcohols in acid solution has been studied by Ross Stewart.

## Aldehydes and Ketone :

Permanganate oxidation of aliphatic aldehydes in acid, neutral and basic solution is easy, whereas ketones react rapidly only in alkali or concentrated acid. Phenyl alkyl ketones, such as acetophenone, are degraded to benzoic acid and carbondioxide.[42] Aliphatic ketones in fact, may suffer stepwise degradation via successive enol intermediates.[43,44] The course of the permanganate oxidation of aromatic aldehydes has been studied by Tronov,[45] Tompkins,[46] and Wiberg and Stewart.[47]

## Phenols :

Phenols are readily oxidised by permanganate and with a sufficient oxidant, are degraded to carbondioxide and water. Electron withdrawing groups, such as nitro, helps to stabilize the phenol to attack by permanganate, but this simply means that the oxidation of di and tri-nitrophenols is slow enough to be measured.[48-50]

## Amines :

Most aromatic amines are oxidised by neutral or basic permanganate to give ring cleavage product and carbondioxide and ammonia. For example, diethylamine is oxidised a mixture of acetic acid and ammonia, ethanol and acetohydroxamic acid.[51] Acid and base catalysis in the oxidation of 6,7,8-trimethyllumazine has been studied by Stewart.[52]

## Sugars :

Kuhn and Wagner-Jaursg[58] have studied rate of oxidation of various sugars, e.g. Fructose, arabinose, galactose, maltose and mannose, etc. by permanganate in phosphate buffered media. With fructose the rate varies with pH, a minimum occuring at pH 4; the mechanism of oxidation is not discussed.

## Aliphatic Acids :

The mechanism of oxidation of formic acid suggested by Mann and Tompkins[59] has been discussed. The oxidation of formic acid has been studied also by Wiberg and Stewart.[60] The oxidation of citric acid by acid permanganate has been studied by Bhale, Mahammad, Bagawat and Bafna.[61] A kinetic study of the reaction between acid permanganate and tartaric acid has been made by Sanz-Garcia.[62,63] A two stage reaction in which complex formation occurs is suggested by this author.

## Amino Acids :

The kinetics of oxidation of glycine, alanine, phenylalanine, serine, threonine, aspartic and glutamic acid by acid permanganate well investigated by V.Surender Rao, B.Sethuram and T.Navaneeth Rao[64] to elucidate the mechanism of the reactions. The rate law was found to be :

$$-\frac{d\left[\mathrm{Mn(VII)}\right]}{dt} = k_o \left[\text{amino acid}\right]\left[\mathrm{Mn(VII)}\right]$$

The reactions were found to be acid catalysed, and the kinetic data indicate the participation of the water molecules in the rate determining step as a proton-abstracting agent from the substrate, as per Bunnett's hypothesis. As $Ag^+$ was found to catalyse these reactions, the oxidation of glycine and glutamic acid was studied, and the rate law was found to be :

$$\frac{d \ln [Mn(VII)]}{dt} = \frac{K \times k_c \; [\text{amino acid}][Ag^+]}{1 + K \; [\text{amino acid}] + K[Ag^+]}$$

Further kinetics study of oxidative decarboxylation of L-β-phenylalanine[65] and L serine[66] by acid permanganate were made by Ameta, Pande, Gupta and Chowdhary. They have shown $H_2O$ molecule acts as proton abstracting agent in rate determining step. Bromide ion catalysed oxidation of glycine by permanganate in an acid medium were determined and a complex rate law was obtained.[67]

Unsaturated Compounds :

Kinetics and mechanism of the permanganate oxidation of unsaturated compounds (Maleic and fumaric acid[68-69], substituted butynes,[70] cis-2-butane-1,4-diol,[71] diethyl maleate and diethyl fumarate,[72] methyl fumaric acid and methyl maleic acid,[73] trans cinnamic acid[74]) were studied by stopped-flow technique. The oxidation intermediates and mechanism of reaction was discussed. The course of the permanganate oxidation of olefins has been studied by Ogino,[75] Srinivasan,[76] Soul.[77,78] A soluble manganese-(IV) intermediate in the permanganate oxidation of uracils is shown by Simandi and co-workers.[79]

Amides :

Kinetics of the oxidation of acetamide with alkaline potassium permanganate observed colorimetrically and the rate determining step shown to be the formation of $ACNH^-$ which rapidly attacks $MnO_4^-$ to give $A\dot{C}NH$ and $MnO_4^{--}$.[80]

**Esters :**

Kinetics of oxidation of esters by potassium permanganate were investigated by T.Navneeth Rao and co-workers.[81] The mechanism is proposed involving rate determining ~~hydraizde~~ hydride ion transfer from the alcoholic moiety of the ester to the oxidant.

**Hydrazines :**

Hydrazide is oxidised quantitatively in acid solutions containing $F^-$ with $KMnO_4$, in presence of $Cu^{+2}$ as catalyst to yield N and $H_2O$ by the uptake of 4 electrons.[82]

**α,β unsaturated ethers :**

Structure and reactivity of α-β unsaturated ethers were investigated by Toyoshima[83] by permanganate oxidation and results were compared with oxidation by $OsO_4$.

**Some examples of recent permanganate oxidations :**

Gopalan, R. and co-workers[84] have studied the kinetics of oxidation of ethoxy ethanol by acid permanganate in presence of sodium pyrophosphate. A mechanism involving the formation of a free radical initially and permanganate ester subsequently is proposed for the oxidation.

Kinetics of the oxidation of acetic acid by potassium permanganate was studied in 4 M sulphuric acid and shown that water is a proton abstracting agent,[85] in the rate determining step. Oxidation of formic acid by $MnO_4^-$ shows a positive salt effect in both alkaline and highly acidic (40 vol % $H_2SO_4$) media. In highly acidic media the effect is more sensitive to changes in the anion than in the cation.[86] A kinetic study of oxidative decarboxylation of DL-aspartic acid by acid permanganate has been made by chaudhary & co-workers[87] and application of Bunnetts hypothesis indicated that a water molecule acts as a proton transfer agent in the rate determining step.

The oxidation of benzaldehydes by permanganate in sulfuric acid-acetic acid mixture were investigated by Rao & co-workers[88] and they found the rate was enhanced by electron releasing groups and retarded by electron withdrawing group. However kinetics & mechanism of aliphatic aldehydes in acid permanganate were investigated by Freeman and co-workers.[89]

The Zucker-Hammett & Bunnett Hypothesis were tested for acid catalysed permanganate oxidation of xylose-[90] and a free radical mechanism is proposed. However, mechanism of oxidation of D-glucose by permanganate in aqueous $H_3PO_4$ solution proposed by Sharma and co-workers.[91]

A mechanism involving phenoxyl radicals (a free radical chain mechanism) was suggested for the oxidation of phenol & chlorophenols by alkaline permanganate.[92,93]

The information regarding the oxidation of hydrocarbons is so far very little known. More detailed study of the permanganate oxidation has been made by Lee, Donald and co-workers,[94] Gopalan, R & co-workers.[95]

The acid catalysed oxidation of tartaric acid with $MnO_4^-$ in $H_2SO_4$ was investigated, the Bunnett-Olsen linear free energy graph indicated the proton abstraction by water molecule to be the rate determining step.[96] The oxidation mechanism of Et-COOH with alkaline permanganate was re-examined, the preferential reptures of C ($\alpha$)-C ($\beta$) bond in Et $COO^-$ in highly concentrated aqueous NaOH & KOH was confirmed.[97]

The oxidation of oleic acid by permanganate was investigated by Garti, Missim & co-workers.[98]

## Research Plan :

The decomposition of acetamide and substituted amides with peroxydisulphate has been studied by number of workers.[53-57] It is observed that the decomposition rate is quite slow with peroxydisulphate.

The literature survey upto this date reveals that the previous workers did not use potassium permanganate for the study of oxidation of heterocyclic amides with alkaline permanganate.

The present work deals with the kinetic study of oxidation of heterocyclic amides with alkaline permanganate. Further, the rate of hydrolysis found to be very slow as compared to the rate of oxidation. It is observed that the oxidation rate is neither too slow nor too fast. It is also observed that the reaction is too slow in neutral and acidic potassium permanganate.

The following two amides have been chosen for kinetic study of oxidation of heterocyclic amides with alkaline permanganate.

1) Nicotinamide,

2) iso-Nicotinamide.

The thermodynamic constant such as $\Delta E$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ and A have been calculated.

A major goal is the exploration of possible extension of such type of work to many other substituted aliphatic and aromatic amides. In addition to above, observations are made on the kinetics, equilibria and mechanism of these reactions which are of considerable chemical interest.

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