CHAPTER I

INTRODUCTION
Trivalent manganese, trivalent cobalt, tetravalent cerium and pentavalent vanadium are a group of metal ion oxidants which apparently react via one electron steps.

\[ M^{n+} \rightarrow M^{(n-1)+} + e^- \]

They have similar redox potentials and the reactive ion in each case in aqueous solution is a cation which is stable in solutions of mineral acids, though unstable in neutral solution. They are all ions of transition metals except cerium(IV).

**Thermodynamic evidence for one-equivalent processes:**

The range of redox processes which can possibly occur is limited by thermodynamic considerations. The simple one-equivalent process is open to all these oxidants:

\[ M^{n+} + S \rightarrow M^{(n-1)+} + R^* \]  \hspace{1cm} (1)

\[ M^{n+} + R^* \rightarrow M^{(n-1)+} + P \]

(S=substrate, R*=radical, P=product)

but the alternative two-equivalent processes may also be available:

\[ 2M^{n+} \rightleftharpoons M^{(n+1)+} + M^{(n-1)+} \]  \hspace{1cm} (2)

\[ M^{(n+1)+} + S \rightarrow M^{(n-1)+} + P \]
It is often observed that two-equivalent oxidations proceed faster than one-equivalent ones, since (a) no high energy free radicals are formed during two-equivalent processes, and (b) there is, over-all, twice the free energy change.

In the case of manganese, the Mn(IV) - Mn(III) potential in 15N sulphuric acid is recorded as 1.64 volt, and the Mn(III) - Mn(II) potential as 1.50 volts.\(^1\) This gives the Mn(IV) - Mn(II) couple a potential 1.57 volts, which is rather higher than 1.24 volts as listed for solid MnO\(_2\).\(^2\) Thus thermodynamically, Mn(IV) (arising by scheme 2) could be a very powerful two-equivalent oxidant and also a vigorous one-equivalent oxidant. Even though there is evidence for the existence of Mn(I) in certain complexes,\(^3\) the Mn(II)\(_{aq}\) - Mn(I)\(_{aq}\) potential is too low for scheme (3) to be possible.

Kinetic and other evidences for one-equivalent processes:

One equivalent process requires the generation of a free radical as in scheme (1) or a radical-cation followed by subsequent decomposition.

\[
\text{RH} + \text{M}^{n+} \quad \overset{\text{RH}^+}{\rightarrow} \quad \text{RH}^+ + \text{M}^{(n-1)+}
\]

\[
\text{RH}^+ \quad \overset{\text{E}^+ + \text{H}^+}{\rightarrow}
\]
This mechanism is first proposed by Dewar et al.\(^4\) in the case of the oxidation of p-methoxytoluene by manganese(III) acetate. In many cases the attack on the substrate is direct, involving the formation of inner sphere or outer sphere complexes. These complexes subsequently dissociate giving radicals and other products. In all cases the initial electron abstraction is indicated to be the rate-determining step.

Although the free radical \(R^*\) formed is normally rapidly oxidised to \(P\), it also has a choice of other reactions,\(^5\) some of which produce effects which cannot be observed if radicals are not present:

1. **Reaction with oxygen**, \(R^* + O_2 \rightarrow RO_2^*\)
2. **Reduction of inorganic ions**, e.g.;
   \[ R^* + Hg(II) \rightarrow R^+ + Hg(1) \]
3. **Reaction with added organic materials inert to oxidant**, e.g.;
   \[ R^* + CH_3CH_2OH \rightarrow RH + CH_3CHOH \]
4. **Polymerisation of an added olefinic monomer**, such as acrylonitrile or methylmethacrylate. The polymer is itself detectable, and the kinetics may be altered if the polymer radical is not itself eventually oxidised.

These reactions of free radical may alter the observed kinetics and sometimes the nature of the oxidation products.

All these phenomena have been observed when manganese(III) acetate\(^6,7,8\) is the oxidant, and some of them have been
observed with all the other manganese(III) species such as manganese(III) pyrophosphate, \( \text{Mn}_2\text{P}_2\text{O}_7 \), sulphate, and manganese(III) in aqueous perchlorate media.

**The chemical nature of Mn(III) species:**

Trivalent manganese exists as the red manganic ion, \( \text{Mn}^{2+} \), in concentrated acid solution. At low acidities it undergoes disproportionation unless it is stabilised by being complexed with such groups as pyrophosphate or sulphate to some extent:

\[
2\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{2+} + \text{Mn}^{4+}
\]

but perchlorate is without effect. However, in the presence of a large excess of manganous ion, a solution of the cation \( \text{Mn(H}_2\text{O})_6^{3+} \) aquomanganese(III) ions in perchloric acid is stable with the molarity of acid being as low as 1.5 M. It is prepared by reduction of permanganate by manganous ions, and the redox potential of the \( \text{Mn(III)}_{\text{aq}} - \text{Mn(II)}_{\text{aq}} \) couple is not higher than 1.568 volts.

The sulphate complex of manganese(III) in sulphuric acid is easy to prepare and is stable, provided that the acidity is not too low, and the observed redox potential is 1.51 volts.

The pyrophosphate complex of manganese(III) is stable at lower acidities than in any other manganese(III) species, and the ion \( \text{Mn(H}_2\text{P}_2\text{O}_7)^3^- \) has found use as an oxidant in quantitative inorganic analysis, and as a glycol clearing reagent.
in organic chemistry and is stable to disproportionation even in neutral solution. In more acidic solution the complex ion exists in the protonated form. Waters et al. have examined the mechanism of the oxidation of various organic compounds with manganic pyrophosphate. The general observation that oxidations by manganese(III) pyrophosphate are retarded by excess of pyrophosphate shows that the formation of the reaction complex involves displacement of a ligand molecule, and direct kinetic evidence (i.e., Michaelis-Menten type kinetics) has often been obtained for complex formation. The complex cannot be in equilibrium with Mn(IV)\textsubscript{aq}, as at low acidities used, precipitation of manganese dioxide would be extremely rapid, but it may, like the sulphate complex, be in equilibrium with a small amount of a manganese(IV) pyrophosphate ion.

Manganese(III) acetate in glacial acetic acid is easy to prepare and it is stable to a considerable extent. In activity the compound is likely to be complex salt with three nuclei of the following structure: \(\text{Mn}_3(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2 - (\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}\). The efficiency of manganese(III) acetate (MTA) as one electron transfer oxidant in the oxidation of organic compounds is well known. It has been mostly used in non-aqueous medium.

**Role of Mn\textsuperscript{3+} cations in acid permanganate oxidations**:

Oxidations of organic compounds by potassium permanganate are usually multi-stage processes, for the degradation of organic molecules proceed by the rupture of discrete two-electron bonds whilst the manganese undergoes an overall 5-electron
transition, $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$, in acid solution. The manganic cation, $\text{Mn}^{3+}$, is certainly involved in many of the rate-determining processes in acid solution. It has been shown that the induction period preceding the oxidation of oxalic acid by acid permanganate can be prolonged almost indefinitely by adding fluoride anions to form complexes with manganic cations, thus proving that it is $\text{Mn}^{3+}$ cations and not $\text{MnO}_4^-$ anions which oxidise oxalic acid.

**Analytical methods:**

The two major analytical methods available for following the reactions of manganese(III) oxidant, are spectrophotometry and iodometry. In the case of spectrophotometry, the method is straightforward and economical. When iodometry is used, the error due to air oxidation should be minimised by the addition of small quantities of sodium bicarbonate.

**Kinetics and mechanism of manganese(III) oxidation of Inorganic Species:**

Manganese(III) perchlorate solutions are found to be reasonably stable in the presence of an excess of manganese(II). The reaction between manganese(III) and atomic mercury ($\text{Hg}^0$) in solution follows the kinetic expression:

$$-d \left[ \text{Mn(III)} \right] / dt = k_1 \left[ \text{Mn(III)} \right] \left[ (\text{Hg}^1)_2 \right] / \left[ \text{Hg(II)} \right] + k_2 \left[ (\text{Hg}^1)_2 \right] x \left[ \text{Mn(III)} \right]^2 / \left[ \text{Mn(II)} \right]$$

The $k_1$ term arising from the reaction of manganese(III) with atomic mercury ($\text{Hg}^0$) in solution, the $k_2$ term from that of Mn(IV)
with dimeric mercury(1). \( k_1 \) and \( k_2 \) are composite and include the equilibrium constants for dismutation of \((\text{Hg}^1)^2\) and disproportionation of Mn(III), respectively. The course of the reaction is consistent with a two-parameter kinetic expression which could be interpreted by assuming two rapid pre-equilibria, (1) and (2), followed by two rate-determining paths (3) and (5):

\[
\begin{align*}
(\text{Hg}^1)^2 & \xrightleftharpoons{} \text{Hg}^0 + \text{Hg(II)} \\
2\text{Mn(III)} & \xrightleftharpoons{} \text{Mn(IV)} + \text{Mn(II)} \\
\text{Mn(III)} + \text{Hg}^0 & \rightarrow \text{Mn(II)} + \text{Hg(I)} \\
\text{Mn(III)} + \text{Hg(I)} & \rightarrow \text{Mn(II)} + \text{Hg(II)} \text{ (rapid)} \\
\text{Mn(IV)} + (\text{Hg}^1)^2 & \rightarrow \text{Mn(II)} + 2\text{Hg(II)}
\end{align*}
\]

An investigation by spectrophotometry of the kinetics of the manganese(III) oxidation of the oxy cation \( \text{VO}^{2+} \) has been reported. The stoichiometry \([\text{manganese(III)} \text{ consumed}] / [\text{vanadium(V)}] \) produced is spectrophotometrically established as being closely unity. The rate law \( \frac{d[\text{VO}]}{dt} = k_{\text{obs}} [\text{Mn(III)}] [\text{V(V)}] \) is found to be valid at various \([\text{H}^+]\) and temperatures. The addition of appreciable amounts of the products at the start of some runs has no effect on \( k_{\text{obs}} \), confirming the simple bimolecularity of the reaction. Thus the simplest mechanistic assumption is:

\[
\begin{align*}
\text{Mn}^{3+} + \text{VO}^{2+} (+\text{H}_2\text{O}) & \rightarrow \text{Mn}^{2+} + \text{VO}_2^+ (+2\text{H}^+) \\
\text{Mn}^{3+} + \text{H}_2\text{O} & \rightarrow \text{MnOH}^{2+} + \text{H}^+ \text{ (rapid)} \\
\text{MnOH}^{2+} + \text{VO}^{2+} & \rightarrow \text{Mn}^{2+} + \text{VO}_2^+ + \text{H}^+
\end{align*}
\]
The rapid reaction of Mn(III) with hydrogen peroxide has been investigated spectrophotometrically in perchlorate media using the stopped-flow technique. A new species of Mn(III) is formed rapidly during mixing which then decomposes by a first-order process. Two Mn(III) ions disappear for each \( \text{H}_2\text{O}_2 \) molecule consumed. A mechanism is suggested involving a \( \text{Mn}^{3+}\text{H}_2\text{O}_2^- \) complex: Comparison is made with Co(III) and Fe(III) with hydrogen peroxide. A possible mechanism for the oxidation involves the following reactions:

\[
\begin{align*}
\text{Mn}^{3+}\text{aq} & \quad \overset{\text{MnOH}^{2+}\text{aq} + \text{H}^{+}\text{aq}}{\rightleftharpoons} \\
\text{Mn}^{3+}\text{aq} + \text{HO}_2^- & \quad \overset{\text{Mn}^{3+}\text{HO}_2^-\text{aq}}{\rightleftharpoons} \\
\text{Mn}^{3+}\text{HO}_2^-\text{aq} & \quad \overset{\text{Mn}^{2+}\text{aq} + \text{HO}_2}{} \quad \downarrow \\
\text{Mn}^{2+}\text{aq} + \text{H}^{+} + \text{O}_2 & \quad \overset{\text{Mn}^{2+}\text{aq} + \text{H}^{+} + \text{O}_2}{\rightleftharpoons}
\end{align*}
\]

The reaction of aquomanganese(III) ions with hydrazoic acid in perchlorate media is of the first order in total \([\text{Mn(III)}]\) and second order in \([\text{HN}_3]\), and one Mn(III) ion is consumed for every \( \text{HN}_3 \) molecule which disappears. The observed third-order rate constant increases with increasing acidity. This is interpreted by the reaction of a hydrazidopentaaquomanganese(III) ion, \( \text{Mn(H}_2\text{O})_5\text{HN}_3^{3+} \) with \( \text{HN}_3 \) to produce an azide radical \( \text{H}_2\text{N}_6^{3+} \), which then reacts rapidly with another Mn(III) ion to produce molecular nitrogen. The energy and entropy of activation are determined. The significance of hydrazido-complexes in the equation of azido-complexes is discussed. The stoichiometry, the initiation of
vinyl polymerisation, the dependence of the rate of dis­
appearance of \([\text{Mn(III)}]^+)\, \text{On} \, [\text{Mn(III)}]^+ \, [\text{HN}_3]^2^+\) and the in­
crease in the observed third-order rate constant \(k_0\) with in­
creasing \([\text{HgI}_6]^-\) suggest the mechanism:

\[
\begin{align*}
\text{Mn}^{3+}_{\text{aq}} & \rightleftharpoons \text{MnOH}^{2+}_{\text{aq}} + \text{H}^+_{\text{aq}} \\
\text{Mn}^{3+}_{\text{aq}} + \text{HN}_3 & \rightleftharpoons \text{MnHN}^3_{\text{aq}} \\
\text{MnHN}^3_{\text{aq}} + \text{HN}_3 & \rightarrow \text{Mn(II)} + \text{H}_2\text{N}^+ \\
\text{Mn(III)} + \text{H}_2\text{N}^+ & \rightarrow \text{Mn(II)} + 3\text{N}_2 + 2\text{H}^+_{\text{aq}}
\end{align*}
\]

**Kinetics and mechanism of manganese(III) oxidation of organic substrates:**

**Oxidation of hydrocarbons:**

Kinetic study of the oxidation of toluene by manga­
nese(III) sulphate has been reported. First order constants
have been determined at four different temperatures. The acti­
vation energy is estimated. No benzoic acid is produced, and
the main products are benzaldehyde and benzyl alcohol.

Oxidation of eight alkanes and four cycloalkanes with
\text{Mn(III)} in \text{H}_2\text{SO}_4 at 90° is first order in [hydrocarbon] and
variable order in \([\text{Mn(III)}]^+\). Addition of \text{Mn(II)} inhibits the
reaction in 85% \text{H}_2\text{SO}_4, but has no effect in 90% \text{H}_2\text{SO}_4. A free
radical mechanism involving \cdot\text{HSO}_4 is proposed.

**Oxidation of alcohols:**

The rate of oxidation of methanol by \text{Mn(III)} ions in
aqueous perchlorate media is first order in both $[\text{Mn(III)}]$ and $[\text{CH}_3\text{OH}]_{\text{Total}}$ and the observed second order rate constant varies with both $[\text{HClO}_4]$ and $[\text{Mn(II)}]$. Mn(III)-methanol complexes have been detected spectrophotometrically. The stoichiometric ratio $\Delta[\text{Mn(III)}] / \Delta[\text{HCHO}]$ is 2 and it is unaffected by bubbling nitrogen through the reaction mixture to remove oxygen. Hence the overall reaction is as in equation:

$$2\text{Mn(III)} + \text{CH}_3\text{OH} \rightarrow 2\text{Mn(II)} + \text{HCHO} + 2\text{H}^+_{\text{aq}}$$

In consistent with all the observed facts, the following mechanism is suggested.

$$\begin{align*}
\text{Mn}^{3+}_{\text{aq}} & \rightleftharpoons \text{MnOH}^{2+}_{\text{aq}} + \text{H}^+_{\text{aq}} \\
\text{CH}_3\text{OH} + \text{H}^+_{\text{aq}} & \rightleftharpoons \text{CH}_3\text{OH}^+_{\text{aq}} \\
\text{Mn}^{3+}_{\text{aq}} + \text{CH}_3\text{OH} & \rightleftharpoons \text{Mn}^{3+}\text{CH}_3\text{OH}_{\text{aq}} \\
\text{Mn}^{3+}\text{CH}_3\text{OH}_{\text{aq}} & \rightleftharpoons \text{Mn}^{3+}\text{CH}_3\text{O}^-_{\text{aq}} + \text{H}^+_{\text{aq}} \\
\text{Mn}^{2+} + \text{CH}_3\text{OH} & \rightleftharpoons \text{Mn}^{2+}\text{CH}_3\text{OH}_{\text{aq}} \\
\text{Mn}^{3+}\text{CH}_3\text{OH}_{\text{aq}} & \rightarrow \text{Mn}^{2+} + \cdot\text{CH}_2\text{OH} + \text{H}^+_{\text{aq}} \\
\text{Mn}^{3+}\text{CH}_3\text{O}^-_{\text{aq}} & \rightarrow \text{Mn}^{2+} + \cdot\text{CH}_2\text{OH} \\
\text{Mn}^{3+} + \cdot\text{CH}_2\text{OH} & \rightarrow \text{Mn}^{2+} + \text{HCHO} + \text{H}^+_{\text{aq}}
\end{align*}$$

Kinetic studies of the oxidation of MeOH, EtOH, and PrOH by Mn(III) in acid media show that the reaction is
initially first order with respect to \([\text{alcohol}]\) and second order with respect to \([\text{Mn(III)}]\). The effects of temperature and \([\text{Mn(II)}]\) on the rate of reaction are studied. A mechanism involving Mn complexes is proposed.

The kinetics and products of the reaction of manganic ions with isopropanol have been investigated in perchlorate media at an ionic strength of 4.0 with \([\text{HClO}_4]\) = 0.5–3.7M. One molecule of acetone is formed for every two manganic ions which disappear. The reaction is first order in \([\text{Mn(III)}]\), first order in \([\text{isopropanol}]\), and insensitive to changes in acid concentration and hence it is suggested that the rate-determining step is the reaction of the hexa-aquomanganic ion with unprotonated isopropanol. The rate is independent of ionic strength and independent of \([\text{Mn(II)}]\), which shows that Mn(IV) is not involved in the reaction. The energy of activation and temperature-independent factor are derived for this reaction. The isotope effect suggests that hydrogen atom abstraction occurs from the \(\alpha\) C–H bond. As \text{Mn(III)} + isopropanol mixtures induce rapid polymerisation of acrylonitrile, a mechanism involving free radical intermediates is proposed.

\[\text{Mn}^{II} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{Mn}^{III} + (\text{CH}_3)_2\text{COH} + \text{H}^+\text{aq}\]

\[\text{Mn}^{II} + (\text{CH}_3)_2\text{COH} \rightarrow \text{Mn}^{III} + (\text{CH}_3)_2\text{CO} + \text{H}^+\text{aq}\]

The reactions of \text{Mn(III)} with sec-butanol and cyclohexanol in aqueous perchlorate media are first order in \([\text{Mn(III)}]\) and first order in \([\text{alcohol}]\). The rate-determining
step is the attack of Mn(III) on the alcohol. The product of this reaction is a hydroxy alkyl radical with a hydrogen atom removed from the carbon atom α to the hydroxyl group of the alcohol. The rapid attack of another Mn(III) on this radical produces a ketone, and the overall stoichiometry conforms to the equation

$$2\text{Mn(III)} + \text{alcohol} \rightarrow 2\text{Mn(II)} + \text{ketone} + 2\text{H}^+_{\text{aq}}$$

At a longer extent of reaction with cyclohexanol, Mn(III) also reacts with the cyclohexanone. The observed bimolecular rate constant is insensitive to changes in acidity and is independent of $[\text{Mn(II)}]$. The energy of activation, the temperature independent factor $A$ and the entropy of activation are compared. No intermediate complex is detected.

The oxidation of cyclohexanol by manganese(III) sulphate is of the first order in manganese(III) for at least 50% of the reaction. The reaction is independent of acid concentration. The variation of the rate with the concentration of cyclohexanol indicates that an alcohol-manganese(III) complex is formed.

$$R_2\text{CH} \cdot \text{OH} + \text{Mn(III)} \rightleftharpoons R_2\text{CH} \cdot \text{O} \cdot \text{Mn(III)}$$

Although acid manganic pyrophosphate does not oxidise either monohydric alcohols or olefines, allyl alcohol and
crotyl alcohol are very slowly oxidised by manganic pyrophosphate. The reaction order with respect to Mn(III) is complex, becoming of first order at high Mn(III) concentrations. Manganese ions retard the oxidation but this retardation reaches a limiting value. The dependence of the rate on acidity may be due to the effect of acidity on the redox potential of complexed manganic pyrophosphate. Addition of vinylcyananide to the oxidising allyl alcohol increases the consumption of Mn(III) showing the formation of free radicals. The spectrographic examination of reacting mixtures give no indication of the formation of transient manganic complex.

\[ C_3H_5^+OH + Mn(III) \rightleftharpoons R^+ + Mn(II) \]

\[ R^+ + Mn(III) \longrightarrow Product \ I \ + \ Mn(II) \]

\[ 2 R^+ \longrightarrow Product \ II \]

The oxidation of 1:2 glycols by manganic pyrophosphate does not always proceed through the initial formation of a cyclic organometallic complex. It is found that trans-1:2-dimethylcyclopentane-1:2-diol is oxidised more easily than cis-cyclohexane-1:2-diol or cis-1:2-dimethylcyclohexane-1:2-diol. Explanatory studies of glycol oxidation by manganic pyrophosphate indicate that more than one reaction mechanism may be concerned in oxidative glycol fissions. Stereochemical significance should not therefore be attached to simple measurements of relative rates of oxidation.
Initial-rate studies of the oxidation of pinacol by aqueous manganic pyrophosphate\textsuperscript{35} have enabled the mechanism of the reaction to be elucidated in detail. The oxidation proceeds in stages: (a) ternary manganic-pinacol-pyrophosphate complexes are rapidly and reversibly formed; (b) these complexes slowly breakdown by a one-electron transition to give manganous pyrophosphate, acetone, and an active organic free radical which (c) is rapidly oxidised by a further equivalent of manganic salt. The oxidation of pinacol by manganic pyrophosphate does give an organic free radical active enough both to catalyse vinyl polymerisation and to reduce mercuric chloride. It can be represented by the following equations:

\begin{align*}
\text{HO-CMe}_2\cdot\text{CMe}_2\cdot\text{OH} + \text{Mn(III)} & \xrightarrow{\text{slo}} \cdot\text{O-CMe}_2\cdot\text{OH} + \text{Mn(II)} + \text{H}^+ \\
\cdot\text{O-CMe}_2\cdot\text{CMe}_2\cdot\text{OH} & \xrightarrow{\text{fast}} 0;\text{CMe}_2 + \cdot\text{CMe}_2\cdot\text{OH} \\
\text{Mn(III)} + \cdot\text{CMe}_2\cdot\text{OH} & \xrightarrow{\text{fast}} \text{Me}_2\text{C}=\text{O} + \text{Mn(II)} + \text{H}^+
\end{align*}

The oxidation of pinacol (2,3-dimethylbutane-2,3-diol) by aquomanganese(III) ions in aqueous perchlorate media\textsuperscript{36} is of the first order in both $[\text{Mn(III)}]$ and $[\text{pinacol}]$ at high $[\text{pinacol}] / [\text{Mn(III)}]$. The variation of the rate of oxidation with acidity shows that the intermediate complexes formed are $\text{Mn}^{3+}\text{Me}_2\text{COH}\cdot\text{Me}_2\text{COH}_{\text{aq}}$ and $\text{Mn}^{3+}\text{Me}_2\text{COH}\cdot\text{Me}_2\text{CO}^-_{\text{aq}}$. Overall energies and entropies of activation are determined.

Investigation of the kinetics of the oxidation of α-glycols by Mn(OAC)\textsubscript{3} in acetic acid\textsuperscript{37} has been carried out. The reaction velocity constants are determined by titration of
unused Mn(OAc)$_3$ with Na$_2$S$_2$O$_3$ for the following α-glycols: (i) pinacol, (ii) sydimethyl diphenyl ethylene glycol, (iii) benzopinacol and (iv) hydrobensoin. The temperature effect and solvent composition variation are studied.

Oxidation of diols by aquomanganic ions in aqueous perchloric acid$^{36}$ has been reported. The kinetics of oxidation of HO(CH$_2$)$_n$OH (n=4,5,6) and MeOH(OMe) CH$_2$OH by Mn(III) are studied at 20-35° and ionic strength 4M (HClO$_4$). The reaction is first order with respect to [Mn(III)] and diol concentration but is independent of [Mn(II)]. As acidity increases the rate increases. No distinction between inner and outer sphere mechanism could be made, but oxidation mechanisms are proposed.

Kinetics of polymerisation of acrylonitrile initiated by the redox systems glycerol-Mn(III) and allyl alcohol-Mn(III) has been investigated$^{39}$ at 25-45° in aq. H$_2$SO$_4$- HOAC and aq. H$_2$SO$_4$ respectively. Oxidation of both glycerol and allyl alcohol proceeds through an intermediate complex. Decomposition of the complex is reversible with glycerol, whereas with allyl alcohol it is not reversible. Addition of Mn(II) retards both oxidation and polymerisation in the former system, while with the latter, oxidation in the absence of monomer, is unaffected, although polymerisation rates are retarded. Rate and equilibrium parameters are evaluated and their significance is discussed.

Kinetics of reactions of manganese(III) pyrophosphate with some hexitols have been studied.$^{40}$ The value of $k_{obs}$, the
pseudo-first order rate constant for the oxidation of D-mannitol, D-glucitol and galactitol with manganese(III) pyrophosphate at different values of \([\text{Mn(III)}]\) and \([\text{hexitol}]\) are given. The rate constant increases proportionately with \([H^+]\) and decreases with \([\text{free pyrophosphate}]\). Added Mn(II) has no effect on the oxidation rate. Thermodynamic parameters are determined. A mechanism is proposed and a rate expression is given.

Adonitol is oxidised to ribose by manganese(III) pyrophosphate under the conditions \([\text{adonitol}] \gg [\text{Mn(III)}]\). The oxidation rate is first order with respect to both oxidant and substrate and decreases inversely with free pyrophosphate concentration. Thermodynamic parameters are reported and suitable mechanism involving free radicals is proposed.

**Oxidation of benzoin:**

The second order reaction velocity for the oxidation of benzoin by Mn(OAC)\(_3\) in acetic acid are determined by titration of unused oxidant with Na\(_2\)S\(_2\)O\(_3\). The rate constants for the reaction in glacial acetic acid and 90% acetic acid are reported at different temperatures.

**Oxidation of 1,2-dihydroxy benzene:**

A stopped flow technique has been used to investigate the mechanism and kinetics of reaction of Mn\(^{3+}\) with 1,2-dihydroxybenzene in aqueous perchlorate solutions. The acidity range investigated is \(0.5 \leq [\text{HClO}_4] \leq 3.00\text{M}\), at ionic strength \(I = 3.0\text{M}\) and at 25, 18, and 12°C. The oxidation product o-benzoquinone is obtained according to the stoichiometry given by:

\[
2\text{Mn(III)} + C_6H_4(\text{OH})_2 \rightarrow 2\text{Mn(II)} + C_6H_4\text{O}_2 + 2\text{H}^+ 
\]
The reaction rate is first order in both reactants and the variation of the rate with acidity points out that the overall reaction takes place through two paths, one independent and one dependent on $[H^+]^{-1}$. These paths are discussed in terms of alternative inner or outer sphere mechanisms due to the lack of evidence of intermediate complex formation.

**Oxidation of quinols:**

The stopped-flow method has been used to investigate the kinetics of the rapid reaction between manganese(III) and hydroquinone in aqueous perchlorate solution at 25°C. The sole oxidation product is p-benzoquinone and the stoichiometry of the reaction corresponds to

$$2\text{Mn(III)} + p-C_6H_4(OH)_2 \rightarrow 2\text{Mn(II)} + p-C_6H_4O_2 + 2H^+$$

The reaction is first-order in each reactant, and is independent of variations in $[\text{Mn(III)}]_0$, $[p$-hydroquinone$]_0$, $[\text{Mn(II)}]$, total ionic strength, $[\text{NaClO}_4]$, $[\text{NaNO}_3]$ and the presence of oxygen at fixed acidity. Variation of acidity in the range $[\text{HClO}_4] = 0.60 - 3.60\text{M}$ is used to determine the rate constants for reaction of $\text{Mn}^{3+}_{\text{aq}}$ and $\text{MnOH}^{2+}_{\text{aq}}$ with the hydroquinone molecule, respectively. The following mechanism is proposed in the absence of oxygen:

$$\text{Mn}^{3+} + Q(\text{OH})_2 \rightarrow \text{Mn}^{2+} + \text{HOQO}^- + H^+$$

$$\text{MnOH}^{2+}_{\text{aq}} + Q(\text{OH})_2 \rightarrow \text{Mn}^{2+} + \text{HOQO}^- + H_2O$$

$$\text{Mn}^{3+} + \text{HOQO}^- \rightarrow \text{Mn}^{2+} + \text{QO}_2^- + H^+$$

$$\text{MnOH}^{2+}_{\text{aq}} + \text{HOQO}^- \rightarrow \text{Mn}^{2+} + \text{QO}_2^- + H_2O$$
The rapid reaction of aquomanganese(III) ions with quinol has been investigated in aqueous perchlorate media using the stopped-flow technique.¹ The oscilloscope traces suggest the presence of an intermediate Mn(III)-quinol complex. The rate of oxidation of the quinol is of the first-order in \([\text{Mn(III)}]_{\text{total}}\) and of first-order in \([\text{QH}_2]\), and the second-order rate constant increases with decreasing acidity. The manner in which this rate constant varies with acidity shows that the rate-determining step in the oxidation is an electron transfer within a complex \(\text{MnOH}^{2+}_{\text{aq}}\). The ratio \(\Delta [\text{Mn(III)}] : \Delta [\text{Q}] = 2\) and the other observations made are in consistent with the following mechanism:

\[
\begin{align*}
\text{Mn}^{3+}_{\text{aq}} & \rightleftharpoons \text{MnOH}^{2+}_{\text{aq}} + \text{H}^+_{\text{aq}} \\
\text{Mn}^{3+}_{\text{aq}} + \text{QH}_2 & \rightarrow \text{MnQH}^{3+}_{\text{aq}} \\
\text{MnOH}^{2+}_{\text{aq}} + \text{QH}_2 & \rightarrow \text{MnQH}^{2+}_{\text{aq}} \\
\text{MnQH}^{3+}_{\text{aq}} & \rightarrow \text{Mn(II)} + \cdot \text{QH} + \text{H}^+_{\text{aq}} \\
\text{MnQH}^{2+}_{\text{aq}} & \rightarrow \text{Mn(II)} + \cdot \text{QH} \\
\text{Mn(II)} + \cdot \text{QH} & \rightarrow \text{Mn(II)} + \text{Q} + \text{H}^+_{\text{aq}}
\end{align*}
\]

**Oxidation of ethers:**

A detailed kinetic study of the oxidation of p-methoxytoluene (PMT) by manganic acetate in acetic acid has been carried out. ² Two series of rate measurements are carried out for the
reaction at 70° and at 100°; oxygen is carefully excluded and the reactions are followed by iodometric titration of Mn(III). Mn(II) retards the rate of reaction. The reaction is first-order with respect to \([\text{PMT}]\) and \([\text{MTA}]\). The kinetics of the reaction are consistent with the following rate law:

\[
\frac{-d [\text{Mn(III)}]}{dt} = k \frac{[\text{Mn(III)}][\text{PMT}]}{[\text{Mn(II)}]}
\]

Since the reaction given p-anisyl acetate (PAA) as almost the sole product, the overall course of the reaction must presumably be

\[
\text{PMT + 2Mn(OAC)}_3 \quad \longrightarrow \quad \text{PAA + 2Mn(OAC)}_2 + \text{ACOH}.
\]

The oxidation involves an initial reversible electron transfer yielding the ion radical \((\text{PMT})^+\); this then loses a proton in a slow rate-determining step to form a radical which undergoes rapid further oxidation to p-methoxybenzyl acetate.

\[
\begin{align*}
\text{ArCH}_3 + \text{Mn(III)} & \quad \rightleftharpoons \quad (\text{ArCH}_3)^+ + \text{Mn(II)} \\
(\text{ArCH}_3)^+ & \quad \longrightarrow \quad \text{ArCH}_2^+ + \text{H}^+ \\
\text{ArCH}_2^+ + \text{Mn(III)} & \quad \overset{\text{fast}}{\longrightarrow} \quad \text{ArCH}_2^+ + \text{Mn(II)} \\
\text{ArCH}_2^+ + \text{ACOH} & \quad \overset{\text{fast}}{\longrightarrow} \quad \text{ArCH}_2\text{OAC} + \text{H}^+
\end{align*}
\]

The dissociation constants of metal acetates in acetic acid are low. If manganic acetate is essentially undissociated in acetic acid, the first step in the oxidation of PMT will be a reaction between neutral PMT and undissociated \(\text{Mn(OAC)}_3\). When the ion
radical PMT$^+$ is formed, acetate ion will be formed simultaneously; these will exist for an appreciable period as an intimate ion pair. If the radical ArCH$_2^+$ is formed by internal proton transfer inside this ion pair, then the above equation should be modified thus

$$
\text{ArCH}_3 + \text{Mn(OAC)}_3 \quad \underset{K}{\overset{k}{\rightleftharpoons}} \quad [(\text{ArCH}_3)^+, \text{ACO}^-] + \text{Mn(OAC)}_2
$$

$$
[(\text{ArCH}_3)^+, \text{ACO}^-] \quad \overset{k'}{\longrightarrow} \quad \text{ArCH}_2^+ + \text{ACOH}.
$$

Kinetic studies of the oxidations of 1- and 2-methoxy naphthalene by manganic acetate in acetic acid are reported. Both reactions follow the kinetic scheme:

$$
\frac{-d [\text{Ar}]}{dt} = k \frac{[\text{Ar}] [\text{Mn(III)}]}{[\text{Mn(II)}]}
$$

where Ar represents the aromatic substrate. The initial rates of oxidation are first-order with respect to Ar and Mn(III) and inverse first-order with respect to Mn(II). The products of oxidation are 4-methoxy-1-naphthyl acetate and 2-methoxy-1,4-naphthoquinone respectively. A mechanism analogous to that of PMT involving the reversible abstraction of an electron from the aromatic substrate by Mn(III) as the first step is proposed:

$$
\text{Ar} + \text{Mn(III)} \quad \overset{\text{slow}}{\underset{\text{fast}}{\rightleftharpoons}} \quad \text{Ar}^+ + \text{Mn(II)} + \text{ACO}^-
$$

$$
\text{Ar}^+ + \text{ACO}^- \quad \overset{\text{slow}}{\longrightarrow} \quad \text{R} \quad \overset{\text{fast}}{\longrightarrow} \quad \text{product}
$$

where Ar$^+$ represents a cation-radical formed from Ar by abstraction of an electron, while R is a neutral radical formed from Ar$^+$ by
reaction with acetic acid or acetate ion.

**Oxidation of aldehydes:**

Aldehydic compounds, with the conspicuous exceptions
of formaldehyde, formic acid, and chloral, are oxidised rapidly
by manganic sulphate, and at a measurable speed by manganic
pyrophosphate solutions. The oxidations of both propaldehyde
and n-butaldehyde with manganic pyrophosphate have been
followed kinetically at 37.3° and proved to be reaction of
zero order with respect to the manganic compound, but of first
order with respect to both aldehyde and hydrogen-ion concentra-
tion (at pH 1-2). When the manganic solution is in excess,
propaldehyde consumes 4-15 equiv. and n-butaldehyde 3.90 equiv.
per mole, so that they are degraded beyond the stage of the
respective carboxylic acid. This evidence points to oxidation
via the enol, the rate-determining stage being the slow acid
catalysis of enolisation

\[
\begin{align*}
RCH_2\cdotCHO + H^+ & \overset{\text{fast}}{\longrightarrow} RCH_2\cdotCH = O^+ H \\
RCH_2\cdotCH = O^+ H & \overset{\text{rate}}{\longrightarrow} RCH_2\cdotOH + H^+ \\
\end{align*}
\]

and it is significant that the aldehydes cited above as being
resistant to oxidation cannot form enols.

The initial, rate-determining stage in the oxidation
of acraldehyde by manganic pyrophosphate is acid-catalysed
and does not involve oxidant. It is suggested that this is the
formation of the enol of β-hydroxypropionaldehyde:

\[
H_2O + CH_2=CHCHO + H^+ \rightarrow HO\cdot CH_2\cdot CH\cdot CH\cdot OH
\]

The faster oxidation of crotonaldehyde and the slower oxidation of α-methylcrotonaldehyde appear to take a similar course, though with crotonaldehyde the oxidation step is rate-determining at low concentrations of the oxidant. The first oxidation product of acraldehyde appears to be glyceraldehyde and later a chelated manganic complex of glyceric acid seems to be formed. Further oxidative degradation occurs by glycol fission, formaldehyde and carbon dioxide being the eventual products, 10 equivalents of Mn(III) in all being consumed.

\[
OCH\cdot CH\cdot CH_2 \xrightarrow{\text{oxidation}} CH\cdot CH\cdot CH_2 \xrightarrow{\text{2 equiv.}} CH\cdot CH\cdot CH_2 \xrightarrow{\text{2 equiv.}} O\cdot OH\cdot OH
\]

The rate of oxidation of formaldehyde by manganese(III) sulphate is of the first order in oxidant for 95% of the reaction. The dependence of the oxidation rate on the concentration of formaldehyde is approximately first order and under conditions of constant ionic strength the rate is independent of acid concentration. A small overall retardation is also produced when the ionic strength is increased simply by adding sodium perchlorate. Added Mn(II) retards the rate of oxidation.
The kinetics of one-electron oxidation of aldehydes by manganese(III) acetate has been studied in acetic acid and in acetonitrile. The rate of oxidation of aldehydes by manganese(III) acetate is measured spectrophotometrically by following the concentration of manganese(III) acetate. The optical density of the solutions is determined in the 580 m\(\mu\) region. The rate constants of the oxidation of aldehydes by manganese(III) acetate decrease in the order \((\text{CH}_3)_3\text{CCHO} > \text{CH}_3\text{CH} = \text{CHCHO} \gg \text{CH}_3\text{CHO} > \text{n-C}_3\text{H}_7\text{CHO} > \text{iso-C}_3\text{H}_7\text{CHO} \gg \text{CCl}_3\text{CHO} > \text{C}_6\text{H}_5\text{CHO} \) benzaldehyde is the least reactive among the aldehydes. The low reactivity of benzaldehyde shows that the formation of acyl radicals is not the result of a direct attack by manganese(III) acetate upon the C–H bond of the aldehydic group.

\[
\text{R-CHO} + \text{Mn(OAC)}_3 \xrightarrow{k_1} \text{R-C} = \text{O}^+ + \text{Mn(OAC)}_2 + \text{ACOH}.
\]

In agreement with the suggested mechanism, benzaldehyde should be oxidised with a rate which should be the same order as for the aliphatic aldehydes because the liberation of a hydrogen atom from benzaldehyde and aliphatic aldehydes is equally easy. The intermediate formation of an enol from enolisable aldehydes in their oxidation by manganese(III) acetate is ruled out by the experimental data that acetaldehyde is more reactive than all the other aliphatic normal and iso-aldehydes because in one-electron oxidation of aldehydes by V(V) and Cu(II) ions in which the enol form is the reacting species, acetaldehyde is considerably less reactive than all the other aliphatic normal and iso-aldehydes. The oxidation of aldehydes by manganese(III) acetate goes through the stage of cation–radical formation:
Mechanism of acyl radical formation during the oxidation of aldehydes by manganese(III) acetate has been investigated. Kinetic data have been tabulated for reaction of variously deuterated forms of ACH with Mn(OAC)$_3$ in ACOH at 50°, along with similar data for deuterated Me$_2$CO. The kinetic isotope effect of 5.5 - 6 is observed only for α-deuterated aldehydes and one of similar magnitude is found in oxidation of the deuterated ketone. Hence the loss of a proton occurs only from the α-C atom and oxidation via •CHRCHO is similar to oxidation of ketones.

The kinetics of the manganese(III) acetate oxidation of benzaldehyde and four substituted benzaldehydes have been studied in 95% (V/V) acetic acid. The reaction velocity is of first order with respect to both [Aldehyde] and [Manganese(III)]. The reaction velocity increases with increase of acid concentration. The reaction rate is unaffected by manganese(II) ions. The rate decreases with increasing the proportion of water in the reaction mixture.

The reaction occurs according to the following equation:

$$
C_6H_5CHO + 2\text{Mn(III)} + H_2O \rightarrow C_6H_5COOH + 2\text{Mn(II)} + 2H^+
$$
It is found that electron withdrawing groups accelerate the rate of oxidation and electron releasing groups retard it. The observed rate conforms to the following order:

\[ p-\text{NO}_2 > m-\text{NO}_2 > \text{H} > p-\text{CH}_3 > p-\text{OCH}_3 \]

The oxidation may be schematically represented as

\[
\text{ArCHO} + \text{Mn(III)} \xrightarrow{\text{slow}} \text{ArCO}^- + \text{Mn(II)} + \text{H}^+
\]

\[
\text{ArCO}^- + \text{Mn(III)} + \text{H}_2\text{O} \quad \text{-----} \quad \text{ArCOOH} + \text{Mn(II)} + \text{H}^+
\]

The oxidation of acetaldehyde by Mn$_2$(SO$_4$)$_3$ is first order with respect to both reactants. The rate is independent of the acidity in 2-5M H$_2$SO$_4$ and of Mn(II) addition. A mechanism with direct attack of Mn(III) on ACH is proposed.

Glycolaldehyde is oxidised by Mn$_2$(SO$_4$)$_3$ with exchange of 2 electrons to give HCHO and HCO$_2$H. The oxidation is first order each in Mn(III), glycolaldehyde, HSO$_4^-$ and H$^+$. The reaction rate is independent of the concentration of Mn(II). The mechanism involves a reversible formation of a complex of the oxidised substance with the oxidant. In the rate-determining step, this complex breaks down to give HOCH$_2$ and C$^+$HO. The former is then oxidised rapidly to HCHO; the latter reacts with water to give HCO$_2$H. A procedure is suggested for an indirect determination of glycolaldehyde based on its oxidation with excess Mn(III) and subsequent retitration of the unreacted reagent with FeSO$_4$.

**Oxidation of ketones:**

Oxidation of aliphatic ketones by manganic sulphate
Oxidation of acetone, \textsuperscript{11} ethyl methyl ketone, \textsuperscript{53} methyl propyl ketone, \textsuperscript{54} and methyl isobutyl ketone \textsuperscript{55} with manganese(III) sulphate in aqueous acetic acid have been reported. The reaction is first order with respect to oxidant and ketone. The rate is independent of acidity and solvent composition. Addition of Mn(II) does not alter the rate. The oxidation induces reduction of mercuric chloride indicating the formation of reducing intermediate—a free radical. The main product of oxidation is the corresponding aldehyde. In the presence of excess of ketone further oxidation of aldehyde is not significant. The thermodynamic parameters for oxidation and enolisation have been evaluated. The rate of enolisation under similar conditions is less than that of oxidation. A mechanism involving a direct attack on the keto form by Mn(III) has been suggested.

\[
\begin{align*}
CH_3COCH_3 + Mn(III) & \xrightleftharpoons{C = O} \xrightarrow{\text{slow}} Mn(III) \xrightarrow{\text{fast}} CH_3COCH_2 \\
CH_3COCH_2 & \xrightarrow{Mn(III)} CH_3COOH + HCHO
\end{align*}
\]

Radical reactions of carbonyl compounds initiated by manganese(III) acetate \textsuperscript{56} have been investigated. The mechanism of \(\alpha\)-oxoalkyl radical formation is studied in detail. Kinetic data indicates that oxidation of \(Me_2CO\) by \(Mn(OAc)_3\) in acetic acid
involved rapid formation of a radical ion complex $\text{Me}_2\text{CO}^+$\[\text{Mn}($\text{OAC}$)$_3\]$^-\) followed by rate-determining proton loss to give $\text{MeCOCH}_2^+$. An isotope effect is observed for $\text{CD}_3\text{COCD}_3$ at $60^\circ$.

The capacity of $\text{Mn}($OAC$)_3$ to easily attack enolisable ketones is used for the selective autoxidation of Me-ketones into carboxylic acids; the attack on the least substituted position involves initial attack by $\text{Mn(III)}$ on the acetyl group to give $\text{RCOCH}_2^-$ (I) and $\text{Mn(II)}$. I and $\text{O}_2$ gives $\text{RC(O)CH}_2\text{COO}^-$ which with $\text{Mn(II)}$ gives $\text{RC(O)CH}_2\text{COO}^-$ (II) $\text{Mn(III)}$ as the last step of the radical chain. II gives $\text{RCO}_2\text{H}$.

$\text{(MeCO)}_2\text{CH}_2$ oxidation with $\text{Mn(III)}$ ions in $\text{H}_2\text{SO}_4$ an inner-sphere reaction which proceeds via intermediate complexes. The reaction is first order in $\text{Mn(III)}$ ions even if the concentrations of both reactants are equal. The experimental rate constant $k_{\text{exp}}/S^{-1}$ increases initially linearly and subsequently nonlinearly with the substrate concentration and then passes through a maximum. A mechanism is proposed in which the rate determining step is an intramolecular redox reaction of the intermediary Mn-enol complex or the less reactive Mn-(enol)$_2$ complex. The temperature dependence of the experimental rate constant is used for evaluating the activation enthalpy and entropy which are also dependent on temperature.

The oxidation kinetics of acetophenones by trivalent Manganese have been reported by a number of workers.
The oxidation of the intermediate acetophenones obtained in the autoxidation of isopropylbenzenes to benzoic acids with $O$ at 150° with Mn salts as catalyst and butyric acid as solvent is first order with respect to the ketone and butyric acid, except at very high acid concentrations; and independent of the Mn concentrations as long as these exceed 0.008M. The most satisfactory mechanism involves enolisation of the ketone as the rate determining step. The enol is then assumed to be oxidised by Mn(III) to form the phenacyl radical which adds $O$ to form the phenacyl peroxy radical. This readily oxidises Mn(II) to Mn(III). The phenacyl peroxy anion rearranges to form formaldehyde and the benzoate anion. Electron withdrawing nuclear substituents have a retarding effect while electron donors have an accelerating effect, probably owing to their influence on enol formation.

The oxidation of acetophenone with Manganese(III) sulphate is first order with respect to each of the oxidant and ketone. The rate is independent of acidity and solvent composition. The thermodynamic parameters have been evaluated. A mechanism consistent with the observed data is proposed.

In the oxidation of mono and disubstituted acetophenones by $\text{Mn}_2(\text{SO}_4)_3$ at 30-50°, the reaction constant varies inversely with the temperature i.e. the reaction series is isoentropic. Electron attracting groups accelerate the reaction.

Oxidation of PhCOCH$_3$ and substituted PhCOCH$_3$ by Manganese(III) acetate in 95% (Vol/Vol) CH$_3$COOH is found to be
The rate decreases with increasing proportion of water. The rate of oxidation is found to be faster than enolisation. The oxidation involves the direct attack on the ketoform by Mn(III) which also supports the view of Littler. In consistent with the above facts and stoichiometry 4:1 (ΔMn(III)/ΔPhCOCH₃) the following mechanism involving the formation of free radical is proposed.

\[
\text{C}_6\text{H}_5\text{COCH}_3 + 4\text{Mn(III)} + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{HCHO} + 4\text{Mn(II)} + 4\text{H}^+ \\
\text{C}_6\text{H}_5\text{COCH}_3 + \text{Mn(III)} \xrightarrow{\text{slow}} \text{C}_6\text{H}_5\text{COCH}_2^+ + \text{Mn(II)} + \text{H}^+ \\
\text{C}_6\text{H}_5\text{COCH}_2^+ + \text{Mn(III)} \xrightarrow{\text{fast}} \text{C}_6\text{H}_5\text{COOH} + \text{HCHO} + \text{Mn(II)}
\]

The oxidation of cyclohexanone has been studied in considerable detail with manganese(III) species, in an attempt to discover whether it attacks the ketonic or the enolic form of cyclohexanone.

Aliphatic ketones are attacked by manganic pyrophosphate only after enolisation. With cyclohexanone, under nitrogen, the enolisation rate equals the limiting oxidation rate, and
since the addition of vinylcyanide, which then polymerises, does not affect the oxidation rate, it is suggested that the initial organic radical rapidly disproportionates. Oxidation commences at the \( \alpha \)-CH groups of ketones and eventually leads to very extensive degradation, though 2-hydroxycyclohexanone is much less rapidly oxidised than cyclohexanone itself. Oxygen can combine with the organic radicals that are generated and affects both the rate and the mechanism of the oxidations. However, pyruvic acid, which is oxidised quantitatively to acetic acid and carbon dioxide, reacts by first forming a chelated manganic complex, enolisation not being involved. The oxidation of diethyl ketone very closely resembles that of cyclohexanone.

Since ketones appear to be oxidised only after enolisation, and monohydric alcohols are not attacked by manganic pyrophosphate, the slowness of oxidation of 2-hydroxycyclohexanone may perhaps be due to the diminution of its ketonic character by hydrogen-bonding as in structure (V)

\[
\begin{align*}
\text{II} & \quad \text{CH} + \text{Mn}^{(III)} \rightarrow \text{Mn}^{(II)} + \text{H}^+ + \left[\begin{array}{c}
\text{CH}_2 \text{O} \text{H} \\
\text{CO}
\end{array}\right] \\
\text{III} & \quad 2 \left[\begin{array}{c}
\text{CH}_2 \\
\text{CO}
\end{array}\right] \rightarrow \left[\begin{array}{c}
\text{CH}_2 \text{O} \text{H} \\
\text{CO}
\end{array}\right] + \left[\begin{array}{c}
\text{CH}_2 \text{O} \text{H} \\
\text{CO}
\end{array}\right]
\end{align*}
\]
The initial rates of the oxidations of cyclohexanone by vanadium(V), cobalt(II), cerium(IV), and manganese(III) have been studied and comparative reaction velocities have been measured for cyclohexanone and 2,2,6-tetradecuterocyclohexanone in water and in deuterium oxide. It is concluded that these one-equivalent oxidants attack the ketone rather than the enol form of the substrate.

The rates of these oxidations are of the first order in oxidant and the enolisation rate of a ketone under the same conditions is independent of oxidant concentration. Oxidation is faster than enolisation.

Manganese(III), in the form of a sulphate complex can also oxidise cyclohexanone at a rate greater than that of enolisation and the primary isotope effect observed in considerably smaller than would be expected if it were due to the enolisation pre-equilibrium. It is therefore clear that oxidation by manganic sulphate involves direct attack on the ketone, and that the α-C-H bond is broken in the rate-determining step. A mechanism analogous to that written for oxidation by vanadium is consistent with these facts and with the observed kinetics.

\[ \text{VO}_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+} \]

\[ V(OH)_3^{2+} + \text{C}=\text{O} \rightleftharpoons V^{2+} \]
The main products are $\alpha$-diketone and adipic acid. Similar kinetics are observed in oxidation of ketones by manganese(III) acetate.

It is apparent therefore that the enol form does not provide the easiest route for one-electron oxidation of a ketone. This is in agreement with the resistance of olefins to attack by one-electron oxidants. Attack on either ketone or enol would give the same mesomeric free radical; even if these reactions proceed at a comparable rate the much lower concentration of enol than of ketone would ensure that attack on the ketone predominates. The oxygen atom of an enol molecule is less nucleophilic than that of a corresponding ketone molecule, and therefore a substrate-oxidant complex could more easily be formed from the ketonic form. Obviously these arguments do not apply to neutral or alkaline solution where attack on the strongly nucleophilic enolate anion provides an easy route for oxidation.
Evidently, manganese(III) pyrophosphate is an exception to the rule of direct attack in acid conditions, one possible explanation might be that the solution could contain a small amount of manganese(IV) pyrophosphate, which would be expected to be a two-equivalent oxidant and attack the enol form rapidly.

The rate of oxidation of cyclohexanone by aquamanganese(III) ions in aqueous perchloric acid, has a first order dependence both on Mn(III) and cyclohexanone. The rate is retarded by increasing H\(^+\) but unaffected by Mn(II). The oxidation is found to be much faster than the rate of enolization. The value of \(\Delta \frac{[\text{Mn(III)}]}{[\text{cyclohexanone}]}\) is 6. Hence the stoichiometric equation is

\[
\text{C}_6\text{H}_{10}\text{O} + 6\text{Mn(III)} + 3\text{H}_2\text{O} \rightarrow \text{HOOC(CH}_2)_4\text{COOH} + 6\text{Mn(II)} + 6\text{H}^+
\]

An outer-sphere mechanism is suggested. The rate constants corresponding to the oxidation effected by Mn(III)(aq) and Mn(OH)\(^2+\)(aq) are separated and the associated thermodynamic parameters discussed.

\[
\text{Ketone} + \text{Mn(III)} \text{aq} \rightarrow \text{radical} + \text{Mn(II)} \text{aq} + \text{H}^+
\]

\[
\text{H}_2\text{O} + \text{Radical} + \text{Mn(III)} \rightarrow \text{2-Hydroxycyclohexanone} + \text{Mn(II)} + \text{H}^+
\]

\[
2\text{H}_2\text{O} + 2\text{-2-Hydroxycyclohexanone} + 4\text{Mn(III)} \rightarrow \text{HOOC(CH}_2)_4\text{COOH} + 4\text{Mn(II)} + 4\text{H}^+
\]
The oxidation of deoxybenzoin by manganese(III) acetate\(^7\) in 95% acetic acid at 30-45° is first order in substrate and in oxidant; perchloric acid catalyses the oxidation and introduction of NO\(_2\) group into the para position of the benzyl moiety also increases the rate. PhCO⋅CHPh⋅CHPh is the main product. The activation energy and activation entropy evaluated are found to support the free radical mechanism suggested.

**Oxidation of amines:**

Oxidation of p-phenylenediamine by manganese(III) acetate\(^8\) in aqueous sulphuric acid medium is first order each in [Amine] and [Mn(III)]. Increase in H\(^+\) decreases the pseudo-first order rate constant and added Mn(II) has no effect on the rate. The reaction shows a positive salt effect. The reaction product has been isolated and characterised as p-benzoquinone. The probable mechanism involves formation of a complex between monoprotonated amine and manganese(III), which decomposes in a slow step to form the product.

**Scheme I**

\[
\text{NH}_2 \quad \text{Mn}^{3+} \quad \text{NH}_2 ^+ \\
\text{NH}_3 \quad \text{slow} \quad \text{NH}_3 ^+ \\
\text{Mn}^{2+}
\]
Scheme II

\[
\begin{align*}
[\text{Amine } H^+]_{di} & \xrightleftharpoons[ka]{kb} \left[\text{Amine } H^+\right]_{m} + H^+ \\
[\text{Amine } H^+]_{m} + \text{Mn(III)} & \xrightarrow{kb} \text{complex} \\
\text{Complex} & \xrightarrow{k_1} I + \text{Mn}^{2+} \\
I + \text{Mn}^{3+} & \xrightarrow{\text{hydrolysis}} II + \text{Mn}^{2+} \\
II & \xrightarrow{\text{hydrolysis}} III \xrightarrow{\text{hydrolysis}} \text{product}
\end{align*}
\]
Scheme II gives the observed rate as

\[ k_{\text{obs}} = \frac{k_1 k_a k_b [\text{amine H}^+] [\text{di}]}{[\text{H}^+] + k_a k_b [\text{amine H}^+] [\text{di}]} \]

Mn(III) ion reacts with small amount of monoprotonated form of p-phenylenediamine present in solution rather than diprotonated as assumed in scheme I.

**Oxidation of oximes:**

In the conversion of benzaldoxime to benzaldehyde with Mn(OAC)₃ in acetic acid,⁶⁵ the orders with respect to [substrate] and [oxidant] are unity each. Added Mn(II) retards the rate of reaction. The reactivities of various substituted benzaldoximes follow the order

\[ p-OCH₃ > H > m-OCH > p-Cl > m-Cl > m-NO₂ > p-NO₂ \]

A free radical mechanism is proposed involving the intermediacy of a iminoxy radical. The rate law is found to be

\[ \frac{-d [\text{Mn(III)}]}{dt} = k [\text{Mn(III)}] [\text{oxime}] \]

In the case of disproportionation of Mn(III) to Mn(II) as

\[ 2\text{Mn(III)} \rightarrow \text{Mn(II)} + \text{Mn(IV)} \]

the order with respect to [Mn(III)] would be greater than one. The rate of oxidation decreases with increase in HOAC supports that the reactants could be neutral Mn(OAC)₃ and benzaldoxime.
molecules forming an activated complex more polar than the reactants.

The iminoxy radicals are known to be the first product of oxime oxidation. Based on the experimental evidence the following mechanism is proposed.

\[
\begin{align*}
\text{Ph} & \\
C = N - OH + Mn^{3+} & \rightarrow \\
\text{H} & \\
\text{Ph} & \\
C = N - OH & + Mn^{2+} \\
\text{H} & \\
\text{Ph} & \\
\text{C} = N - O & \quad \text{slow} \\
\text{H} & \\
\text{Ph} & \\
\text{C} = N - O & \\
\text{H} & \\
\text{Ph} & \\
\text{C} = N - 0 & \quad \text{fast} \\
\text{H} & \\
\text{Ph} & \\
\text{C} - N = 0 & + H^+ \\
\text{H} & \\
\text{Ph} & \\
\text{C} - N = 0 & \\
\text{H} & \\
2 \text{Ph} & \\
\text{C} - N = 0 & \rightarrow \\
\text{H} & \\
2 \text{Ph} & \\
\text{C} - 0 & + H_2N_2O_2
\end{align*}
\]

**Oxidation of acids:**

A kinetic study has been made of the oxidation of formic acid, and deuterio formic acid by manganese(III) sulphate in sulphuric acid. The oxidation is retarded by manganous ions. The retardation is much more pronounced if the initial
manganese(III) concentration is more than 0.005M; the reaction kinetics then include a term involving \( \frac{[\text{Mn(III)}]^3}{[\text{Mn(II)}]} \) and the primary kinetic isotope effect is almost doubled. So the rate of oxidation of formic acid is of combined first and third order with respect to manganese(III).

The kinetics of the slow oxidation of formic acid by aquomanganese(III) ions in aqueous perchlorate have been studied.\(^6\) The formation of aquo complexes of \( \text{Mn}^{3+}\text{HCO}_2^- \), \( \text{Mn}^{3+}\text{HCO}_2\text{H} \) and \( \text{Mn(OH)}^-\text{HCO}_2 \) explains the variation of rate with acidity. The enthalpies and entropies of decomposition of the complexes are calculated and discussed in relation to the structure of the transition states.

The slow oxidation of isobutyric acid by Mn(III) in perchlorate media\(^6\) yields isopropanol, acetone and \( \text{CO}_2 \). No formic acid is detected. The yield of acetone is very small in the absence of oxygen. The rate is the same with and without oxygen present, and is first order in both Mn(III) and [isobutyric acid] and insensitive to changes in acidity in the range 0.5 to 3.7M \( \text{HClO}_4 \). The absence of spectral changes in Mn(III) on adding isobutyric acid confirms that the rate-determining step is an outersphere interaction of the hexaaquomanganese(III) ions with unprotonated and unionised isobutyric acid. Reaction mixtures rapidly initiate the polymerisation of acetonitrile and a mechanism is proposed involving free radicals.
The kinetics of oxidation of isobutyric acid (IBA) and diglycollic acid (DGA) by manganese(III) acetate have been carried out in the temperature range 15-45° in aqueous sulphuric acid medium. The reaction is overall second order-first order with respect to each reactant. The absence of spectral changes of manganese(III) acetate on adding diglycollic acid and isobutyric acid confirms the outer-sphere interaction of the substrate and the oxidant. The energy of activation and other thermodynamic parameters have been evaluated and discussed. A mechanism involving free radical intermediate is proposed.

\[ \text{CH}_3\text{CH}_2\text{COOH} + \text{Mn}^{3+} \xrightarrow{\text{slow}} \text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2 + \text{H}^+ + \text{Mn}^{2+} \]

\[ \text{CH}_3\text{CH}_2\text{COOH} + \text{Mn}^{3+} \xrightarrow{\text{H}_2\text{O}} 2\text{HCHO} + \text{CO}_2 + \text{H}^+ + \text{Mn}^{2+} \]

The similar mechanism for both systems is supported by the same free energy of activation value.

The oxidation of malonic acid by manganic pyrophosphate under nitrogen is completed at the stage \( \text{CH}_2(\text{CO}_2\text{H})_2 + 3\text{O} = 2\text{CO}_2 + \text{H-CO}_2\text{H} \), tartronic acid being an intermediate. An initial complex, probably \([\text{Mn(III), CH}_2(\text{CO}_2\text{H})_2, (\text{H}_2\text{P}_2\text{O}_7)]^-\), is
first formed and this decomposes by a rate-determining reversible reaction to manganous pyrophosphate and an active radical $\cdot \text{CH}(\text{CO}_2\text{H})_2$ capable both of inducing vinyl polymerisation and of oxidising alcohols, ethers, and Mn$^{2+}$ ions. In the presence of oxygen, the complete oxidation $\text{CH}_2(\text{CO}_2\text{H})_2 + 40 = 3\text{CO}_2 + 2\text{H}_2\text{O}$ occurs with consumption of one molecule of oxygen gas per molecule of malonic acid. Oxygen is absorbed by the radical $\cdot \text{CH}(\text{CO}_2\text{H})_2$, carbon dioxide evolution then sets in, and the molecule $\text{HO} \cdot \text{O} \cdot \text{CH}(\text{CO}_2\text{H})_2$ does not seem to be formed. Oxalic acid seems to be an intermediate in this complete oxidation. Both ethyl and benzyl malonic acid give radicals $\cdot \text{CR}(\text{CO}_2\text{H})_2$ which are incapable of oxidising alcohols or Mn$^{2+}$, but these acids do form hydroperoxides, $\text{HO} \cdot \text{O} \cdot \text{CR}(\text{CO}_2\text{H})_2$, of low stability. The investigation has disclosed a novel example of a radical-induced oxidation, since Mn(III) does not attack monohydric alcohols in the absence of malonic acid.

Kinetic studies of the oxidation of malonic acid by manganic sulphate$^{69}$ reveal that the singular features of the oxidation of malonic acid by manganic pyrophosphate are largely reproduced in the case of manganese(III) sulphate. It is possible to account for retardations of manganese(III) oxidations by manganese(II) ions by postulating reversible radical formation

$$\text{(Mn(III), CH}_2(\text{CO}_2\text{H})_2, (\text{H}_2\text{P}_2\text{O}_7)_2)} \rightleftharpoons \text{CH}(\text{CO}_2\text{H})_2 + \text{H}^+$$

$$+ \left(\text{Mn(II)}(\text{H}_2\text{P}_2\text{O}_7)_2\right)^{2-}$$
or by postulating that the active oxidising agent is a compound of manganese(IV), $2\text{Mn(III)} \rightleftharpoons \text{Mn(IV)} + \text{Mn(II)}$.

The reproduction of the main kinetic features of the oxidation of malonic acid by manganese(III) pyrophosphate in the oxidation by manganese(III) sulphate indicates that both oxidations proceed by a common mechanism:

$$\text{Mn(III)}L_3 + \text{CH}_2(\text{CO}_2\text{H})_2 \rightleftharpoons L_2\text{Mn(III)}\text{Ma} + L \text{ rapid equilibrium}$$

$$\text{Mn(III)MaL}_2 + \text{Mn(III)} \rightleftharpoons \text{Mn(IV)MaL}_2 + \text{Mn(II)}$$

$$\text{Mn(IV)MaL}_2 \rightarrow \text{Mn(II)} + \text{Products}$$

$$L_2\text{Mn(IV)Ma} + \text{Mn(III)} \rightarrow \text{Mn(II)} + \text{Mn(III)} + \text{Products}$$

$L = \text{SO}_4^{2-} \text{ or } H_2\text{P}_2\text{O}_7^{2-}$, $\text{Ma} = \text{CH}_2(\text{CO}_2\text{H})_2$

The oxidation of malonic acid by manganese(III) in sulphuric acid\textsuperscript{70} is an inner-sphere redox reaction, the first step of which is the formation of an intermediate complex. It is followed by the slow and rate-determining formation of $\text{CH}_2(\text{CO}_2\text{H})_2$ and $\text{Mn(II)}(\text{SO}_4)_n$ in a reversible reaction. The influence of oxygen on the activation parameters is described.

Kinetic analysis of oxalic and citric acid mixtures with manganese(III) sulphate\textsuperscript{71} are used to verify the applicability of the log extrapolation method for second order reactions to the analysis of pairs of substances reacting with an oxidant in reactions that involve the transfer of different numbers of electrons.
The kinetics of oxidation of cinnamic and crotonic acids by manganese(III) acetate have been studied in 90% aqueous acetic acid in the temperature range 30–60°C. The overall order of reaction is found to be 1.5; 0.5 with respect to the substrate and 1.0 with respect to the oxidant. The stoichiometry is found to be 1:3. The free energy of activation for both the substrates is the same suggesting a similar mechanism for both the substrates.

\[
R - C = C - H + 2 \text{MTA} \rightleftharpoons \begin{array}{c} R - C = C - H \text{MTA} \end{array} \quad \text{slow}
\]

\[
\begin{array}{c}
R - C = C - H \text{MTA} \rightarrow \begin{array}{c} R - C = C - H \text{MTA} \end{array}
\end{array}
\]

\[
\begin{array}{c}
R - C = C - H \text{MTA} \rightarrow \begin{array}{c} R - C = C - H \text{MTA} \\
\text{H}_2\text{O}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
R - C = C - H \text{MTA} \rightarrow \begin{array}{c} R - C = C - H \text{MTA} \\
\text{OH}
\end{array}
\end{array}
\]

Oxidation of amino acids:

The kinetics of oxidation of DL-\(\alpha\)-aminobutyric acid, DL-isovaline, DL-\(\alpha\)-valine and L-leucine by manganese(III) sulphate in sulphuric acid medium keeping excess of amino acids have been investigated spectrophotometrically. All the four amino acids have been found to follow a similar kinetics. The nature of the reaction is very much dependent upon the initial
[Mn(II)] present in the reaction mixture. The reaction shows a first or second order dependent on [Mn(III)], depending upon whether initial [Mn(II)] in the reaction mixture is less than 0.01M or greater than 0.15M. In either case, the reaction shows first order dependence on [aminoacid] and an inverse first order dependence on [H⁺]. A plausible mechanism has been proposed in which Mn(III) has been suggested as the main oxidising species. The reaction sequence is consistent with the experimental data

\[
A + Mn^{3+} \rightleftharpoons MnA^{2+} + H^+ \\
MnA^{2+} \rightleftharpoons A^- + Mn^{2+} \\
A^- + Mn^{3+} \rightleftharpoons \text{Product} + Mn^{2+}
\]

where \(A\) stands for the aminoacid molecule and \(A^-\) for a free radical.

In \(\alpha\)-aminoacids other than glycine, decarboxylation followed by deamination looks more probable and reaction mechanism may be written as shown in scheme I.
The kinetics of the oxidation of leucine by manganic sulphate in acidic medium is first order in leucine and in \( \text{Mn}_2(\text{SO}_4)_3 \) and inverse first order in \( H^+ \). A suitable mechanism is proposed.

The kinetics of the oxidation of glycine with aquomanganese(III) ions in perchlorate has been reported. The reaction proceeds through an outer-sphere mechanism. The reaction is first order in \( [\text{Mn}(\text{III})] \) and in \( [\text{glycine}] \). The rate is proportional to \( [H^+]^{-1} \) at 45° whereas at 55° and 65° it becomes proportional to \( [H^+]^2 \). A mechanism consistent with the rate data is proposed.

**Oxidation of hydroxyacids:**

Kinetic investigations of manganic pyrophosphate oxidations of simple \( \alpha \)-hydroxy acids have been made. Whilst (+) tartaric, mesotartaric and DL-malic acids have been studied more particularly, racemic, lactic and glycollic acids have been examined sufficiently to show that they are oxidised by the same mechanism, and it has been shown that \( \beta \)-hydroxybutyric acid
is hardly attacked. The initial reactions are strictly of first order with respect to \( [\text{Mn(III)}] \). The oxidation is retarded by the addition of vinyl cyanide and also by manganous sulphate. The oxidation involves the reversible formation of a cyclic complex which then breaks down with loss of \( \text{CO}_2 \) and formation of a free radical. Further extensive oxidation follows, tartaric and malic acids being degraded to \( \text{CO}_2 \) and formic acid. The general oxidation scheme is therefore considered to be

\[
\begin{align*}
\text{CO\cdot OH} + [\text{Mn(H}_2\text{P}_2\text{O}_7]_3^- & \rightleftharpoons \text{CO-O} - [\text{Mn(H}_2\text{P}_2\text{O}_7]_2^- + [\text{H}_3\text{P}_2\text{O}_7^-] \\
\text{(Products of aldehyde oxidation)} & \downarrow \\
\text{CHR\cdot OH + CO}_2 + \text{Mn(H}_2\text{P}_2\text{O}_7]_2^- \\
& \text{H\cdot COR + Mn(III)} \\
& \text{fast} \\
& \text{slow}
\end{align*}
\]

A mechanism for the one-electron oxidation of \( \alpha \)-hydroxy-acids by manganic pyrophosphate has been suggested. It does not involve a rate-determining C-H bond cleavage and so can operate with acids, \( \text{HO\cdot CR}_2\cdot \text{CO}_2\text{H} \), that contain no \( \alpha \)-hydrogen atom.
All the measurements have been carried out spectrophotometrically, taking hydroxy-acid in large excess. It is found in each case that the consumption of the oxidant follows first order kinetics. The oxidation rates for acids \( \text{HO-CHR-CO}_2\text{H} \) and \( \text{HO-CR}_2\text{-CO}_2\text{H} \) are much more alike, differing only by factors which can easily be attributed to effects of the substituent group, \( R \), in facilitating the formation of radicals \( \text{HO-CR}_2^* \), i.e. \( \text{Ph} \gg \text{Me} \gg \text{H} \).

The kinetics of oxidation of glycol and glycollic acid by aqueous manganese(III) sulphate in acidic medium is reported. The oxidation appears to proceed through the rapid reversible formation of a manganic complex followed by its decomposition by a slow one-electron transition giving among other products, a free radical which is further rapidly oxidised by the manganic ion. Acidity has no detectable effect on the oxidation rate, which is appreciably retarded by the presence of added Mn(II). The oxidation of lactic and mandelic acids, the derivatives of glycollic acid with manganic sulphate are very much faster than that of glycollic acid.

\[
\begin{align*}
\text{CH}_2\text{OH-CO}_2\text{H} + \text{Mn(III)} & \xrightarrow{\text{K rapid}} \text{Mn(III)} (\text{CH}_2\text{OH-CO}_2\text{H}) \\
\text{Mn(III)} (\text{CH}_2\text{OH-CO}_2\text{H}) & \xrightarrow{\text{k slow}} \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ + \text{Mn(II)} \\
\text{CH}_2\text{OH} + \text{Mn(III)} & \xrightarrow{\text{K rapid}} \text{CH}_2\text{O} + \text{H}^+ + \text{Mn(II)}
\end{align*}
\]
The kinetics and mechanism of oxidation of tartaric acid, malic acid, cyclohexanol and ally alcohol by Mn(III) in H₂SO₄ has been investigated spectrophotometrically. The reaction shows first order dependence, in the presence of low (0.01-0.15M) Mn(II) and second order in the presence of high (0.4-0.6M) Mn(II), on [Mn(III)]. The rate of oxidation is slightly increased by increasing [H⁺]. The energy and entropy of activation are calculated in both the conditions. It is suggested that in the oxidation of hydroxy compounds by Mn(III) deprotonation of oxidation product is the rate determining step at low [Mn(II)]. In the presence of high [Mn(II)], the reaction is zero order for allyl alcohol oxidation of some other organic compounds such as HCOOH, HCHO, maleic and fumaric acids, malonic and pyruvic acids do not show the change of order but there is only retardation by Mn(II).

\[
\text{Mn(III)} + H₂O \xrightleftharpoons{K_A} \text{MnOH}^{2+} + H^+ \\
\text{Mn(III)} + \text{substrate} \xrightleftharpoons{\text{fast}} [\text{complex}]
\]

\[
\begin{align*}
[\text{Complex}]_1 & \xleftarrow{\text{Moderate}} \text{Mn(II)} + [\text{complex}]_2 \\
[\text{Complex}]_2 + H₂O & \xrightarrow{\text{slow}} R + H^+ \\
R + \text{Mn(III)} & \xrightarrow{\text{fast}} \text{product} \\
[\text{Complex}]_1 + \text{Mn(III)} & \rightarrow \text{product}.
\end{align*}
\]

Oxidation of mandelic acid (MA) by manganic pyrophosphate in acetic acid-water binary mixtures of different
compositions with a view to gaining insight into the mechanism of oxidation and role of HOAC as a solvent has been investigated. The effect of other solvents like dioxane has also been studied. With the increase in the proportion of acetic acid or dioxane, the rate of oxidation diminishes. The order with respect to oxidant is one. The rate of oxidation increases with the increase in the concentration of UA and decreases by the addition of free pyrophosphate. The addition of Mn(II) has no appreciable effect, +ve free radical test is obtained in the polymerization of acrylonitrile. Under the kinetic conditions products of oxidation are \( \text{C}_6\text{H}_5\text{CHO} \) and \( \text{CO}_2 \). The enthalpy of activation in both the media (acetic acid-water and aqueous medium) is almost the same indicating that acetic acid is not involved in the transition state of the rate-determining step.

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H}_5\text{C} & \quad \text{COOH} \\
+ \text{Mn(III)} \quad (\text{H}_3\text{P}_2\text{O}_7)_3 & \Leftrightarrow \text{H}_5\text{C} \quad \text{O} \\
\text{H}_5\text{C} & \quad \text{O} \\
\text{C} \quad \text{H} \quad \text{O} \\
\text{Mn(III)} \quad (\text{H}_3\text{P}_2\text{O}_7)_2 & \quad + \text{H}_4\text{P}_2\text{O}_7 \\
\text{rate determining} & \\
\text{Mn(II)} \quad (\text{H}_3\text{P}_2\text{O}_7)_2 & + \text{CO}_2 + \text{C}_6\text{H}_5 - \text{CH(OH)} \\
\text{C}_6\text{H}_5 - \text{CH(OH)} + \text{Mn(III)} & \quad \text{fast} \quad \rightarrow \quad \text{C}_6\text{H}_5\text{CHO} + \text{Mn(II)} + \text{H}^+ \\
\end{align*}
\]

The rate-determining step is breaking of complex with C-C cleavage and free radical formation. The decrease in the rate of oxidation due to increase in acetic acid or dioxane concentration may be due to the effect of dielectric constant of the medium.
The kinetics of the oxidation of glycollic acid by aquomanganese(III) ions in perchlorate solutions has a first order dependence both in \([\text{Mn(III)}]\) and glycollic acid and a zero order dependence in \([\text{Mn(II)}]\) and \([\text{H}^+\]). Two equivalents of Mn(III) are consumed for the oxidation of each molecule of glycollic acid into HCHO. Reaction mixtures initiate the polymerisation of acrylonitrile suggesting the generation of free radicals. The insensitivity of the rate to changes in \([\text{H}^+\]) and \([\text{Mn(II)}]\) is explained by assuming that the reactivity of Mn\(^{3+}\) (aq) ~ MnOH\(^{2+}\) (aq) and that Mn(IV) is not an active oxidant. A suitable mechanism has been proposed for the oxidation.

\[
\begin{align*}
\text{Mn}^{3+}(\text{aq}) & \xrightleftharpoons{K_k} \text{MnOH}^{2+}(\text{aq}) + \text{H}^+ (\text{aq}) \\
\text{CH}_2\text{OH}^+\text{CO}_2\text{H}^+ + \text{H}^+ & \xrightleftharpoons{K_k} \text{CH}_2\text{OH}^+\text{CO}_2\text{H}_2^+ \\
\text{CH}_2\text{OH}^+\text{CO}_2\text{H}^+ + \text{Mn}^{3+}(\text{aq}) & \xrightarrow{\text{fast}} \text{Mn}^{2+}(\text{aq}) + \text{CH}_2\text{OH}^+ + \text{CO}_2 + \text{H}^+ \\
\text{CH}_2\text{OH}^+\text{CO}_2\text{H}^+ + \text{MnOH}^{2+}(\text{aq}) & \xrightarrow{\text{fast}} \text{Mn}^{2+}(\text{aq}) + \text{CH}_2\text{OH}^+ + \text{CO}_2 + \text{H}_2\text{O} \\
\text{Mn}^{3+} + \text{CH}_2\text{OH} & \xrightarrow{\text{fast}} \text{Mn}^{2+} + \text{HCHO} + \text{H}^+
\end{align*}
\]

The kinetics of oxidation of lactic acid by Mn(OAC)\(_3\) in HACOH has been studied at 40°. The total order of the reaction is two, one with respect to each reactant. Mn(II) retards the reaction. A mechanism suggesting the formation of an initial co-ordination complex for which kinetic evidence is obtained is suggested. The disproportionation of this complex is the rate-determining step. The activation energy calculated from an Arrhenius graph is 14k cals/mole and \(\Delta S = -26.88\) e. u.
The oxidation of tartaric acid by manganese(III) pyrophosphate has been investigated. The reaction obeys first order rate law with respect to Mn(III) up to 50% of the reaction, then the rate constants fall off. The work has been undertaken to determine the energy of activation, frequency factor and entropy of activation of the reaction to throw more light on the mechanism of oxidation. The decomposition of a complex formed between Mn(III) and tartaric acid is the rate determining step.

The reaction between malic acid and Mn(III) gave the complex Mn C₄O₅H₄⁺, glycol aldehyde and Mn(II). The rate of reaction at 20-30° is described by the Arrhenius equation with activation energy 14.8 K cal/mole and frequency factor $5.6 \times 10^9$ sec⁻¹mole⁻¹. The reaction is first order.

A kinetic study of the redox system containing citric acid and manganic acetate has been reported. It has been found that one molecule of citric acid requires 9.5 equivalents of manganic acetate in order to be oxidised in the temperature range 20 to 30°C. The rate constants have been determined graphically. It has been noted that if the concentrations of the reactants are approximately equal, the total order of the reaction is two-one with respect to each reactant separately. There is a slight increase in the total value of the rate constant as the concentration of Mn(III) is decreased. It appears, that a complex is formed between Mn(III) and citrate which slowly
decomposes, giving the reaction product. The temperature coefficient for a 10°C raise in temperature is slightly less than two.

The kinetics and mechanism of citric acid(I) oxidation with $\text{Mn}_2(\text{SO}_4)_3$ have been followed. Volumetric determination and optimal conditions for indirect volumetric determination are found. The excess oxidant is determined potentiometrically with FeSO$_4$ solution using a Pt indicating electrode.

$$I + 14\text{Mn}^{3+} + 5\text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + 4\text{CO}_2 + 14\text{Mn}^{2+} + 14\text{H}^+$$

The presence of air causes a non-stoichiometric reaction. The dependence of the reaction rates on $\text{Mn}^{3+}$, $\text{Mn}^{2+}$, $I$, $\text{HSO}_4^-$ and $\text{H}^+$ concentrations is established.

Oxidation of citric acid by hexaaquo Mn(III) ions in a noncomplex perchloric acid medium has been reported. The dependence of the reaction rate on $\text{Mn}^{3+}$, citric acid, $\text{Mn}^{2+}$ and $\text{H}^+$ concentrations is established and a procedure for indirect microdetermination of citric acid is developed. The concentration of the oxidant is determined potentiometrically. Oxidation of citric acid with $\text{Mn(H}_2\text{O})_6^{3+}$ in HClO$_4$ and with $\text{Mn}_2(\text{SO}_4)_3$ shows the same course of reaction.

**Oxidation of ketonic acid:**

Pyruvic acid is so easily oxidised by manganic pyrophosphate that accurate kinetic measurements could be obtained
only by lowering the reaction temperature to 10°. The reaction has the peculiar feature of being specifically retarded to a limited extent by manganous salt. Pyruvic acid which is oxidised quantitatively to acetic acid and carbon dioxide, reacts by first forming a chelated manganic complex, enolisation not being involved. Free radicals are undoubtedly formed for if vinylcyanide is added to the oxidising mixture, insoluble polymer containing carbonyl groups separates. A satisfactory mechanism is proposed.

\[
\begin{align*}
\text{Mn} & \left( \text{H}_2\text{P}_2\text{O}_7 \right)_3^{3-} + \text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{H} & \rightleftharpoons \text{Mn} \left( \text{H}_2\text{P}_2\text{O}_7 \right)_2 \cdot \text{Me} \cdot \text{CO} \cdot \text{CO}_2^{2-} \\
& + \left( \text{H}_2\text{P}_2\text{O}_7 \right)^{2-} + \text{H}^+ \\
\text{Me} \cdot \text{CO} \cdot \left( \text{H}_2\text{P}_2\text{O}_7 \right)_2 & \text{Me} \cdot \text{CO} \cdot \text{CO}_2^{2-} \longrightarrow \text{Me} \cdot \text{CO} \cdot \left( \text{H}_2\text{P}_2\text{O}_7 \right)_2^{2-} + \text{Me} \cdot \text{CO} \cdot + \text{CO}_2 \\
\text{Me} \cdot \text{CO} \cdot + \text{Mn} \text{(III)} & \longrightarrow \text{(Me} \cdot \text{CO} \cdot)^{+} + \text{Mn} \text{(II)} \quad \text{(Fast)} \\
\text{(Me} \cdot \text{CO}^{+}) & + \text{H}_2\text{O} \longrightarrow \text{Me} \cdot \text{CO}_2\text{H} + \text{H}^+ \quad \text{(Fast)}
\end{align*}
\]

**Oxidation of phosphonous acid:**

Kinetics of oxidation of phenylphosphonous acid by manganese(III) in sulphuric acid has been studied. The reaction is found to be of first order with respect to both reactants. Hydrogen ions retard the rate of reaction. The addition of \( \text{MnSO}_4 \) and increase in dielectric constant enhance the rate of reaction. The addition of acrylamide to the reaction mixture during the oxidation by \( \text{Mn}(\text{III}) \) increased the viscosity of the same enormously indicating the formation of free radical
in solution. Stoichiometry is found to be 2.

\[ P(III) + 2Mn(III) \rightarrow P(V) + 2Mn(II) \]

The dependence of acid on reaction rate suggests that \( MnHSO_4^{2+} \) is the reacting species in solution, since with the increase in acid concentration, the concentration of \( MnHSO_4^{2+} \) would decrease according to the following equilibrium

\[ Mn^{3+} + H_2SO_4 \rightleftharpoons MnHSO_4^{2+} + H^+ \]

The steps of the reaction are,

\[ \text{PhPO}_2H_2 + MnHSO_4^{2+} \xrightarrow{\text{slow}} \text{PhPO}_2H + MnHSO_4^{+} + H^+ \]
\[ \text{PhPO}_2H + MnHSO_4^{2+} \xrightarrow{\text{fast}} \text{PhPO}_2H + MnHSO_4^{+} \]
\[ \text{PhPO}_2H + H_2O \xrightarrow{\text{fast}} \text{PhPO}_3H_2 + H^+ \]
\[ \text{PhPO}_2H_2 + Mn^{3+} \xrightarrow{\text{fast}} [\text{MnPhPO}_2H]^{2+} + H^+ \]
\[ [\text{MnPhPO}_2H]^{2+} + H_2O \xrightarrow{\text{slow}} \text{PhPO}_3H_2 + Mn^{1+} + H^+ \]
\[ Mn^{3+} + Mn^{1+} \xrightarrow{\text{fast}} 2 Mn^{2+} \]

**Oxidation of esters:**

Mechanism of oxidation of isopropyl mandelate by manganese(III) pyrophosphate has been investigated kinetically. The reaction is first order in both ester and Mn(III). The rate is proportional to \( [H^+]^2 \), but inversely proportional to the concentration of free pyrophosphate in the solution. Addition of
Mn(II) has no effect on the rate of reaction. The rate decreases with increase in the proportion of HOAC in the HOAC-H₂O solvent mixture. Activation parameters are calculated. The proposed mechanism involves a rate-determining reaction of the ester with \( \left[ \text{Mn(H}_2\text{P}_2\text{O}_7 \right]^- \).

Kinetics of the oxidation of the methylmandelate by manganese(III) pyrophosphate \(^{87}\) has been studied. The reaction is first order in each reactant. The rate is proportional to \( [\text{H}^+]^2 \) and inversely proportional to the concentration of free pyrophosphate in solution. Addition of Mn(II) ion has no effect on the rate, but it decreases with increase in the proportion of HOAC in the solvent mixture HOAC-H₂O. The kinetic isotope effect shows that C-H is not involved in the rate-determining step. The activation parameters are evaluated. A mechanism which is consistent with the observed rate laws and other experimental facts has been proposed. The overall reaction is represented by the equation:

\[
\text{CHOH}-\text{COOCH}_3 + 2\text{Mn(III)} + \text{H}_2\text{O} \rightarrow \text{CHO} + \text{CO}_2 + \text{CH}_3\text{OH} + 2\text{Mn(II)} + 2\text{H}^+
\]

Oxidation of dimethyl malonate by manganic pyrophosphate \(^{86}\) has been investigated. Significant differences have been observed in the mechanisms of oxidations of dimethyl malonate and
malonic acid by manganic pyrophosphate. It is found that the order with respect to $[\text{Mn(III)}]$ is one. An increase in the concentration of the substrate increases the rate of oxidation. This shows that the fast reversible formation of complex of manganese(III) pyrophosphate with substrate precedes the rate-determining step. Added Mn(II) ions have no effect. The rate of oxidation is proportional to $[H^+]$. The activation parameters are evaluated. The mechanism is shown in scheme 1.

\[
\begin{align*}
[\text{Mn(H}_2\text{P}_2\text{O}_7)_3]^{3-} + \text{H}_2\text{C(COOCH}_3)_2 & \xrightarrow{K} [\text{Mn(H}_2\text{P}_2\text{O}_7)_2\cdot\text{H}_2\text{C(COOCH}_3)_2]^{-1} \\
+ (\text{H}_2\text{P}_2\text{O}_7)^{-2} & \\
[\text{Mn(H}_2\text{P}_2\text{O}_7)_2\cdot\text{H}_2\text{C(COOCH}_3)_2]^{-1} & \xrightarrow{k} \text{rate-determining} \text{Mn(H}_2\text{P}_2\text{O}_7)^{2-} \\
+ \text{CH(COOCH}_3)_2 & \\
\text{CH(COOCH}_3)_2 + \text{Mn(III)} + \text{H}_2\text{O} & \xrightarrow{\text{fast}} \text{HO}\cdot\text{CH(COOCH}_3)_2 + \text{Mn(II)} \\
+ \text{H}^+ & \\
\text{HO}\cdot\text{CH(COOCH}_3)_2 + \text{Mn(III)} & \xrightarrow{\text{fast}} \text{HCOOH} + \text{CO}_2 + \text{Mn(II)}
\end{align*}
\]

The kinetics of oxidation of C$_1$-C$_4$ alkyl-acetate by Mn(OAc)$_3$ have been determined in 90% vol% ACOH. The products are identified as HCHO, CO$_2$ and the aldehyde or ketone derived from alkyl-moiety. A mechanism involving alkyl-O bond rupture is suggested.
Manganic pyrophosphate oxidation of diethyl malonate in HOAC-\textit{H}_2\textit{O} medium\textsuperscript{90} is first order in Mn(III) and dependence of the rate on [substrate] obeys Michaelis-Menten type kinetics. The rate of oxidation increases with increase in [H\textsuperscript{+}] and HOAC or dioxane content of the solvent medium. The rate is retarded by excess pyrophosphate and remains unaffected by added Mn\textsuperscript{2+} ions. The activation parameters are determined. The products of oxidation in stoichiometric runs are found to be CO\textsubscript{2}(\textit{gas}) and HCOOH. Based on these results a reaction mechanism similar to that of oxidation of dimethyl malonate by manganic pyrophosphate is proposed.

The rates of manganic pyrophosphate oxidation of dipropyl and dibutyl malonates in aqueous HOAC\textsuperscript{91} increase with increase in [H\textsuperscript{+}]. The reaction is first order in Mn(III). The dependence of rate on [substrate] is as expected. Increase in HOAC content of the solvent medium increases the rate of oxidation. Addition of Mn(II) ions has no effect. Based on kinetic data a probable mechanism involving the fast formation of complex and its slow decomposition, is proposed.

\textbf{Oxidation of thioureas:}

Stoichiometry and kinetics of the Mn(III) oxidation of thiocyanates, thiourea and some alkyl thioureas in acid perchlorate solution\textsuperscript{92} have been investigated. The kinetics of the rapid Mn(III) oxidation of excess thiourea, N,N'-dimethylthiourea, and N,N'-ethylenethiourea, N,N'-diethylthiourea have been studied in a stopped-flow apparatus over a range of acidities and
temperatures at ionic strength 4.0M. Although the reaction with $\text{SCN}^-$ is too fast to be followed by this method at 25°, the stoichiometry of reaction with excess $\text{SCN}^-$ is the same as that measured with the thioureas in the presence of excess Mn(III), viz; $\Delta [\text{Mn(III)}]/\Delta [\text{reductant}] = 1$, corresponding to the formation of S-S bonded products in each case. The activation parameter and the rate constants determined suggest an inner sphere mechanism, with substitution at the Mn(III) centre as the rate-determining process.

**Oxidation of carbohydrates:**

The oxidation of D-xylose by manganese(III) pyrophosphate in $\text{H}_2\text{SO}_4$ is first order with respect to $[\text{Mn(III)}]$. Variation of rate with $[\text{D-xylose}]$ suggests the rapid reversible formation of cyclic complex between Mn(III) and D-xylose which further disproportionates in a slow rate-determining step. The oxidation rate increases with increasing $[\text{H}^+]$. Retardation of rate due to $[\text{pyrophosphate}]$ and increase due to $[\text{Mn(II)}]$ are also observed. The values of thermodynamic parameters are evaluated. A mechanism involving a free radical is proposed for the reaction.

**Kinetics of oxidation galactose by manganese(III) sulphate** has been reported. A procedure is worked out for indirect titrimetric determination of galactose based on its oxidation with excess manganese(III) sulphate and potentiometric retitration of the unreacted reagent with Fe(II)$\text{SO}_4$. A suitable mechanism has been suggested.
Kinetics and mechanism of oxidation of 4-piperidones:

Piperidones are the heterocyclic ketones, prepared by Mannich reaction. The usual procedure for the reaction is to reflux an aqueous or alcoholic solution of the ketone, aldehyde and amine or amine hydrochloride. As the quality and the yield of the products were discouraging, improvement has been brought later on, by carrying out the condensation in acetic acid medium, to get 2,6-diaryl-4-piperidones.

Stereochemistry of the 4-piperidones:

The principles of conformational analysis, as applied to cyclohexane derivatives are also applicable to six membered heterocyclic compounds having nitrogen, oxygen or sulphur in the ring. Since 4-piperidones, on reduction afforded two epimeric 4-piperidinols, it shows that 2,6-diphenyl-4-piperidones have the cis orientation of the phenyl groups. In the chair conformation of the piperidone the two phenyl groups should occupy the equatorial positions to overcome 1,3-diaxial interactions. Further studies on cyclohexane derivatives show that the phenyl group has a large preference for the equatorial position. Consequently cis 2,6-diphenyl-4-piperidone and its N-Methyl derivative can be assumed to be anchored in a single chair conformation.

4-piperidones are expected to behave as cyclohexanone towards oxidation, as they are nothing but 1-hetero-4-cyclohexanone. With this view, kinetics of oxidation of some substituted
4-piperidones (3-alkyl and 3,5-dimethyl substituted 1-methyl-2,6-diphenyl-4-piperidones) by vanadium(V) (ammonium meta vanadate in sulphuric acid) in the presence of sulphuric acid in aqueous acetic acid medium have been investigated. The rate of the reaction is followed titrimetrically by finding the unused V(V). The stoichiometry is found to be 1:2, by treating the substrate with excess oxidant. The reactions are first order each in oxidant and substrate at constant acid concentration. It has been found that the order with respect to sulphuric acid is a fractional one in the acid range 0.2M to 0.6M. The plot $1/k_{obs}$ Vs $1/[S]$ passes through the origin, suggests that there may not be any complex formation between the reacting species. The appearance of turbidity in the reaction mixture on adding acrylamide solution indicates that the reaction proceeds through a free radical mechanism. It is found that the addition of $\text{Na}_2\text{SO}_4$ does not affect the rate, whereas $\text{NaHSO}_4$ increases the rate at constant acid concentration. Hence the active species of vanadium may be taken as $\text{V(OH)}_3\text{HSO}_4^+$. The tentative mechanism is proposed as

$$\text{VO}_2^+ + \text{H}_2\text{O} + \text{H}_2\text{SO}_4 \xrightleftharpoons{K} \text{V(OH)}_3\text{HSO}_4^+$$

$$\text{V(OH)}_3\text{HSO}_4^+ \xrightarrow{ks} \text{V(OH)}_3\text{HSO}_4^+ + \text{H}^+ + \text{V(IV)}$$

$$X^o + \text{V(V)} \xrightarrow{k_f} \text{product} + \text{V(IV)} + \text{H}^+$$
In accordance with the above mechanism the rate equation is

\[-\frac{d[V(T)]]}{dt} = k_8 \left[V(OH)_3HSO_4^+\right][S] = k_8 K\left[VO_2^+\right][H_2SO_4][S] = \frac{k_8 K\left[V(V)\right]T[H_2SO_4][S]}{1 + K[H_2SO_4]}\]

where S is the substrate.

The order of reactivity of the four piperidones studied is found to be 3-ethyl > 3-methyl > 3-isopropyl > 3,5-dimethyl.

The kinetics of oxidation of 2,6-diphenylpiperidin-4-one, 3-methyl-2,6-diphenylpiperidin-4-one and 3-isopropyl-2,6-diphenylpiperidin-4-one by acid potassium permanganate have been studied in aqueous medium, at an ionic strength of 2.25M Na₂SO₄, under pseudo-first order condition, with piperidone:permanganate ratio of 10:1. Sodium sulphate is added as a complexing agent to prevent the autocatalytic activity of manganese ions of intermediate valency. The rate of the reaction is followed titrimetrically. The oxidation reaction is found to be first order each with respect to the oxidant, substrate and hydrogen ion. The kinetics
has also been studied in aqueous acetic acid medium. Increase of acetic acid concentration increases the rate of the reaction. The influence of varying $[\text{Na}_2\text{SO}_4]$ is not significant although there is slight positive salt effect. Activation parameters have been evaluated from Arrhenius plots. The stoichiometry between piperidone and potassium permanganate is found to be 1:4. The only product which could be isolated is identified by m.m.p and Co-I-R as benzoic acid.

The results are discussed in terms of a mechanism involving a rate-determining formation of a manganate ester between permanganate and substrate followed by the rapid decomposition of the intermediate. From the results of the kinetic study, the rate expression should be of the form

$$\text{Rate} = k_t \left[\text{substrate}\right] \left[\text{oxidant}\right] \left[\text{H}_2\text{SO}_4\right].$$

**Mechanism:** $\text{MnO}_4^- + \text{H}_3\text{O}^+ \overset{\text{slow}}{\underset{\text{fast}}{\leftrightarrow}} \text{HMnO}_4 + \text{H}_2\text{O}$

$$\text{H}_2\text{O} + \text{NH}_3 + \text{CO}_2 + \text{C}_6\text{H}_5\text{COOH} \overset{\text{K}_\text{MnO}_4}{\longrightarrow} \text{H}_2\text{O} + \text{NH}_3 + \text{CO}_2 + \text{C}_6\text{H}_5\text{COOH}$$

The effect of 3-alkyl substituent has been analysed.

The steric interactions of the 3-alkyl function is responsible
for the rate retarding effect as evidenced by the greater
decrease in the rate for the 3-isopropyl substituted compound.

Kinetic behaviour of 2,6-diphenyl-N-methyl-4-piperidone, 2,6-diphenyl-3,3-dimethyl-N-methyl-4-piperidone and
2,2-dimethyl-6-phenyl-N-methyl-4-piperidone towards oxidation
by vanadium(V) in presence of perchloric acid in acetic acid
medium at 50° is studied. The oxidation reaction follows
pseudo-first order rate law when the piperidone concentration is
in large excess over V(V). The oxidation is therefore first
order each in substrate and oxidant. The second order rate con­
stants are found to be directly proportional to the first power
of the concentration of perchloric acid employed in the reaction,
indicating a first order dependence on H\textsubscript{3}O\textsuperscript{+} concentration. These
results and the fact that the reaction mixture induces polymeri­
sation of acrylonitrile lead to propose a radical mechanism.

\[ \text{VO}_2^+ + \text{H}_3\text{O}^+ \rightleftharpoons K \quad \text{V(OH)}_2^{2+} \]

\[ \begin{array}{c}
\text{O} \\
\phi \\
\phi \\
\text{N} \\
\text{CH}_3
\end{array} + \text{V(OH)}_3^{2+} \xrightarrow{\text{ks}}
\begin{array}{c}
\text{O} \\
\phi \\
\phi \\
\text{N} \\
\text{CH}_3
\end{array} \xrightarrow{\text{fast}}
\begin{array}{c}
\phi \\
\text{N} \\
\text{CH}_3
\end{array} + \text{H} + \text{V(iv)}
\]

Radical intermediate + V(V) \xrightarrow{\text{fast}}
\begin{array}{c}
\phi \\
\text{N} \\
\text{OH} \\
\text{CH}_3
\end{array} + \text{V(iv)}
The mechanism leads to the rate law

\[
\text{Rate} = \frac{k_S K \left[ H_3O^+ \right] \left[ S \right] \left[ V(V) \right]_T}{1 + K \left[ H_3O^+ \right]}
\]

If \( K \) is negligible

\[
\text{Rate} = k_S K \left[ H_3O^+ \right] \left[ S \right] \left[ V(V) \right]_T
\]

The reactivity of the three compounds studied has been found to be: 2,2 dimethyl-6-phenyl > 2,6 diphenyl > 2,6 di-phenyl — 3,3 dimethyl.

**Solvent effects:**

When a chemical reaction takes place in solution, the solvent is usually in such great excess that its concentration cannot change appreciably as the reaction proceeds and the rate expression accordingly need not involve it. In some cases, moreover, the stoichiometric equation for the reaction does not involve the solvent, which may then merely provide a smooth and continuous physical environment for the reaction in solution. In other instances the solvent enters into the chemical change and may or may not be regenerated at the end of the process. In these cases the solvent would be said to exert a chemical effect on the reaction, this being superimposed on its physical effect. Hence it can markedly influence both the rate and mechanism. Sometimes it alters the rate without changing the forces between the reacting species as illustrated by the effect of dielectric constant
on electrostatic forces between the reacting species. The solvent may change the rate of diffusion by virtue of its viscosity and hence the frequency of collisions between the reactants; thus the rates of diffusion controlled reactions may be altered. Solvation or selective solvation of reactant or reactants will change both the rate and mechanism of a reaction. Many other characteristics of the solvents such as electrophilicity, nucleophilicity, cohesion, hydrogen bonding and solvolysing action will also have a bearing on rates and mechanism. Reaction in solutions are usually classified as (i) reactions between neutral molecules (ii) reactions between dipoles (iii) reactions between ions and dipoles and (iv) reactions between ions.

Electrostatic forces have very little influence compared to van der waals forces so far as reaction between neutral molecules are concerned. But in the case of the other three types, electrostatic forces are so large and predominant that van der waals forces become insignificant.

Solvation is essentially an electrostatic phenomenon in which polar molecules or ions are surrounded by a solvent sheath. This process involves electrostatic work. The energy of solvation of an ion can be very large often approximating to that of a covalent bond. A change from a less polar to a more polar solvent may increase or decrease the rate of a reaction depending on the relative polarity of reactants and products.

The corresponding theory of solvent effects developed by Hughes and Ingold,\textsuperscript{108,109} is that a change to a more polar
solvent will decrease or increase the heat of activation (which is generally equated to the Arrhenius energy of activation) according as the transition state is more or less polar than the initial states. There may be counteracting changes in the entropy of activation (approximately represented by the Arrhenius frequency factor) but qualitative theory assumes that the energy change will accelerate or retard the reaction according as the transition state is more or less polar than the initial state. The following assumptions regarding the extent of solvation have been made.

(i) Solvation will increase with magnitude of electrical charge. 

(ii) Solvation will decrease with increasing dispersal of a given charge. 

(iii) The decrease of solvation due to dispersal of charge will be less than due to its destruction.

The polarity of solvents will (a) increase with the molecular dipole moment of the solvent and (b) decrease with increased thickness of shielding of charge. These predictions have been confirmed by various workers.

A few examples of solvation involving the solvent water have been reported. Hammett and Deyrup have correlated the rates of reactions in solvation with a factor $H_0$ called the Hammett acidity function.

$$H_0 = -\log \left( a_{H^+} \times \frac{f_B}{f_{BH^+}} \right)$$
Zucker and Hammett \(^{113}\) have suggested that the rates of acid catalysed reactions involving a water molecule in the transition state would depend on the concentration of hydrogen ion; but when the transformation of the protonated substrate to the transition state did not involve a reaction with water, the rates would depend on the \(H_0\) acidity function. Although the Zucker–Hammett hypothesis has been widely applied with success \(^{114}\) has been criticised in recent times.

Bunnett \(^{115}\) has classified the acid catalysed reactions on the basis of a parameter called 'w'. This factor is the slope of the plot of \((\log k + H_0)\) versus \(\log a_{H_2O}\). Most of the 'w' values fall between -2 and +7. On an analysis of the results of a very large number of acid catalysed reactions, Bunnett concludes that a large 'w' than 3.3 indicates that water is acting as the proton transfer agent in the slow step.

Many attempts have been made to correlate the dielectric constant of a solvent (as a measure of its polarity) with reaction rates.