CHAPTER I

OXIDATION STUDIES OF VARIOUS ORGANIC SUBSTRATES WITH CHROMIC ACID-A SURVEY
INTRODUCTION

The subject of reaction kinetics is concerned with the detailed study of rates of chemical reactions. The study of chemical systems from the standpoint of kinetics is of practical importance since it determines the feasibility of various chemical reactions. It is also of great theoretical value since interpretation of experimental results leads to a better understanding of the mechanism of reactions, that is to determine the intermediate steps on the way to the end product.

Living organisms are all chemically reacting systems depending on the continuance of oxidations and reductions, for plants proliferate by using radiant energy to reduce carbon dioxide whilst animals obtain their vital energy by the oxidation of carbon compounds. Thus the comprehension of mechanisms of oxidation and reduction processes is essential to the understanding of the nature of life.

Organic compounds are essentially covalent and covalent bond fission is a special feature of organic reactions. It can be effected by two different pathways. In homolytic oxidations, electrons are removed singly from organic molecules by active atoms such as chlorine or by active free radicals.

\[ R_3C-H + Cl_2 \rightarrow R_3C^+ + H-Cl \] (1)

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents which can gain a further electron pair. These heterolytic
oxidants therefore attack the exposed electron pairs of atoms such as oxygen, nitrogen or sulphur or the loosely held $\pi$-electrons of olefins.

Reactions in which electrons are transferred from one to another are known as redox reactions. While redox reactions in general involve a clear transfer of electrons from one atom to another, most organic redox reactions involve no obvious transfer of electrons.

In equation (2), each atom has the same number of electrons before and after the change is in the relative electronegativities of the attached atoms. Thus oxidation in covalent molecules consists of a movement of shared electrons closer to the reduced atom.

Two general types of mechanisms are available for oxidation: (i) exchange of more electronegative atom for less electronegative atom.

and (ii) coordination of oxygen atoms
The coordination involves the acceptance of unshared electron pairs by the added oxygen atoms, which contribute none of their own to the bond. The resulting coordinate covalent bond places formal ionic charges on the attached atoms.

1.1 Role of Cr(VI) as Oxidant

Oxidation and reduction of organic molecules play an important part in organic synthesis. Chromic acid, a derivative of hexavalent chromium, is one of the most versatile of the available oxidising agents, reacting with almost all types of oxidisable groups. The reactions often may be controlled to yield largely one product, and this makes chromic acid oxidation an useful synthetic tool. During the course of the reaction, chromium is reduced from the hexavalent to the trivalent state, the most stable oxidation state of chromium with a net transfer of three electrons. Chromium(VI) oxide or chromium trioxide and sodium or potassium dichromate are the most commonly employed reagents. Chromium oxide dissolves in water to form chromic acid. This reagent is used as potassium dichromate and sulphuric acid mixture. The presence of sulphuric acid prevents chromium(VI) from complexing with its reduced form chromium(III) to form a salt having a considerably lower oxidation potential. Therefore, its presence is necessary to ensure that all the hexavalent chromium is available for oxidation and that the process of oxidation is rapid and complete. Solution of hexavalent chromium in aqueous sulphuric acid contains an equilibrating mixture of the acid chromate(VI) ion and the dichromate(VI) ion.

\[ 2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \] (5)
This reaction has an equilibrium, the position of which is independent of pH. This position varies with the total concentration of hexavalent chromium referred to as gross concentration of chromic acid. In water, at concentrations greater than about 0.05 M, the dichromate ion (and its protonated forms) is the predominant species; at lower concentrations, the monomer predominates. The monomer-dimer equilibrium constant may be determined by using the difference in absorption spectrum between the acid chromate and dichromate ions.

Organic compounds are often not soluble in water, and therefore a mixed solvent is commonly used in effecting chromic acid oxidations. The majority of work has employed acetic acid as the cosolvent. The monomer-dimer equilibrium constant in 91% acetic acid has been determined, although it is not clear whether monomeric chromium(VI) exists in this medium as the acid chromate ion or as the acetochromate ion (CH$_3$CO CrO$_2$O$_7$).

The conversion of chromic acid to a compound of trivalent chromium is a three-electron change. The oxidation of organic compounds usually occurs in steps. The organic molecule is oxidised in one-electron steps or oxidised directly in two-electron steps. Either of these alternatives for the first step in the reaction leads to an intermediate in which chromium atom occurs in an unusual and unstable valence state. If the organic molecule is oxidised in one-electron steps, free radicals are the intermediates and the hexavalent chromium is temporarily pentavalent. A two-electron transfer makes hexavalent chromium temporarily tetravalent. Those reducing agents, which preferentially lose two electrons, reduce chromic acid in the following steps.
\[ \text{Cr}^6 + \text{H}_2\text{A} \rightarrow \text{Cr}^4 + \text{A} \] \hspace{1cm} (6)

\[ \text{Cr}^6 + \text{Cr}^4 \rightarrow 2 \text{Cr}^5 \] \hspace{1cm} (7)

\[ \text{Cr}^5 + \text{H}_2\text{A} \rightarrow \text{Cr}^3 + \text{A} \] \hspace{1cm} (8)

\( \text{H}_2\text{A} \) and \( \text{A} \) are the reduced and oxidised forms of the reducing agent. The first is converted to the second by a two-electron change. Equation (7) is only stoichiometrically significant. The intermediates \( \text{Cr}(\text{V}) \) and \( \text{Cr}(\text{IV}) \) are themselves powerful oxidants. Hence they may effect further oxidations and may lead to products different from those formed in the initial \( \text{Cr}(\text{VI}) \) oxidation. The intermediates \( \text{Cr}(\text{V}) \) and \( \text{Cr}(\text{IV}) \) are unstable under ordinary experimental conditions and they rapidly disproportionate to \( \text{Cr}(\text{III}) \) and \( \text{Cr}(\text{VI}) \) compounds.

1.2 Oxidation Studies of Various Organic Substrates with Chromic Acid.

1.2.1 Oxidation of Hydrocarbons

The oxidation of toluene, chlorotoluenes and xylenes to their corresponding carboxylic acid have been effected in good yield using aqueous sodium dichromate at elevated temperatures. With aqueous sodium dichromate the oxidation of methyl side chains in substituted polycyclic aromatic hydrocarbons has been examined in considerable detail by Friedman and co-workers. Side chain oxidation occurs in preference to ring oxidation with aqueous sodium dichromate. The oxidation of aryl alkanes such as diphenyl methane and triphenyl methane with chromic acid using glacial acetic acid as the solvent has been reported by Slack and Waters.
In saturated hydrocarbons, oxidations require vigorous conditions and preferentially occurs at tertiary C-H groups or at \( \alpha \)-CH\(_2\) groups of aromatic side chains. This is the site of homolytic oxidation and one-electron transfer occurs. Oxidations of hydrocarbons are retarded by bases and catalysed by acids, indicating attack by a cation \( HCrO_3^+ \). A concerted electrophilic substitution followed by cleavage of an O-Cr link, as in hydrolysis of chromate esters has been indicated.

\[
\begin{align*}
(HO-Cr=O)^+ + \text{C}-\text{H} + \text{B} & \rightarrow HO-Cr-O-O-Cr^- + (HB) \\
(\text{9})
\end{align*}
\]

1.2.2 Oxidation of Alcohols

Westheimer and Novick\(^{12}\) have studied the oxidation of isopropyl alcohol by chromic acid. The reaction is shown to be first order with respect to the acid chromate ion \( HCrO_4^- \), first order with respect to the alcohol and second order with respect to hydrogen ion. The dependence of the rate constant on the concentration of chromic acid has been correlated with the equilibrium between the dichromate ion and the acid chromate ion.

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} & \rightleftharpoons 2 \text{HCrO}_4^- \\
(\text{5})
\end{align*}
\]
From this equation, it is clear that the proportion of the chromic acid present in the form of acid chromate ion increases as the solution is diluted. The fact that the rate constant is greatest in the dilute solutions where the $\text{HCrO}_4^-$ ion predominates suggests that the acid chromate ion is the principal oxidising agent in this oxidation. The reaction involves a two-electron change in which case the products are acetone and a compound of tetravalent chromium. As the rate of oxidation of isopropyl alcohol is reduced to 50% by the presence of manganous ion, it implies the formation of an intermediate such as an unstable compound of pentavalent or tetravalent Cr during the oxidation. The hydrogen ions involved in the reaction get attached to the oxygen atoms of the acid chromate ion, and an activated complex(I) is formed which then decomposes to yield the oxonium ion of acetone and a compound of tetravalent chromium.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{-CH}_3 \\
\text{H} & \quad \text{O} \quad \text{-Cr} \quad \text{-OH} \\
\text{OH} & \quad \text{OH} \\
\text{I}^+ 
\end{align*}
\]

The kinetic study of oxidation of isopropyl alcohol by chromic acid has been carried out by Watanabe and Westheimer.\textsuperscript{13} The chromic acid oxidation of isopropyl alcohol induces the oxidation of manganous salts to manganese dioxide. Chromic acid in dilute acid solution, or in acid solution containing acetone and a chromic salt does not oxidise Mn$^{2+}$ to MnO$_2$. The active reagent in the reaction induced by isopropyl alcohol must therefore be one of the transitory compounds of tetravalent or pentavalent chromium. In the presence of manganous ion, the rate at which isopropyl alcohol is oxidised by chromic acid decreases by about 50%. This
50% diminution in rate cited is consistent with the reaction scheme in which the tetravalent chromium reacts with manganous ion, instead of with hexavalent chromium and the rate at which hexavalent chromium is consumed is cut in half. Hence the only possible mechanism in the presence of manganous salts is

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3 \quad (10)$$

$$Cr^4 + Mn^{2+} \rightarrow Cr^{3+} + Mn^{3+} \quad (11)$$

$$2 Mn^{3+} + 2 H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \quad (12)$$

The stoichiometry of equations (10) – (12) is consistent with a limiting value of 0.5 for the induction factor. In the absence of manganous ion, the oxidation may occur by way of equations (13) – (16).

$$HCrO_4^- + H_2A \rightarrow Cr^4 + A \quad (13)$$

$$Cr^4 + H_2A \rightarrow Cr^2 + A \quad (14)$$

$$Cr^6 + Cr^2 \rightarrow Cr^3 + Cr^5 \quad (15)$$

$$Cr^5 + H_2A \rightarrow Cr^3 + A \quad (16)$$

The chromic acid oxidation of isopropyl alcohol has been examined in 97% acetic acid solution at 385 nm using a stopped-flow reactor by Wiberg and Schafer\(^4\). The reaction has a first order dependence on the chromic acid concentration. The ionisation constant of acetochromic acid has been determined. The monomer-dimer equilibrium constant for Cr(VI) has been estimated to be \(\sim 85\)
in 97% acetic acid. At the concentration of chromic acid used in the kinetic studies (1.03 x 10^{-3} M), only 7% of the chromium will be in the dimer form.

$$2 \text{HOCrO}_2\text{Ac} \rightleftharpoons \text{AcOCrO}_2\text{OCrO}_2\text{OH} + \text{HOAc} \quad (17)$$

The mechanism of acid dichromate oxidation of a series of secondary alcohols such as pentan-2-ol, cyclopentanol, cyclohexanol and cycloheptanol has been investigated extensively by Timothy J. Mason. Westheimer has proposed a mechanism for the oxidation of propan-2-ol which involves the rapid initial formation of a chromate ester. This is followed by the slower, rate determining decomposition of the ester by removal of the $\alpha$-proton by a base, which is water in aqueous systems.

$$\text{HCrO}_4^- + \text{R}_2\text{CHOH} + \text{H}^+ \rightleftharpoons \text{R}_2\text{CHOCrO}_2\text{H} + \text{H}_2\text{O} \quad (18)$$

As a strong support for this two-stage mechanism, the chromate ester formation step has become rate determining in the oxidation of secondary alcohols with sterically crowded $-\text{OH}$ group because there is relief of non-bonded interactions. Comparing the rates of acid dichromate oxidation of cyclopentanol, cyclohexanol and cycloheptanol, the observed enhanced rate of oxidation of cyclopentanol and cycloheptanol over that of cyclohexanol is due to strain relief involved in the conversion of the alcohols to their respective ketones. The spectrophotometric method used by the same author to compare the reactivities of
alcohols with bicyclic skeletons such as exonorborneol, endonorborneol, borneol and isononorborneol\textsuperscript{16} reveals that the relief of non-bonded interactions results in an eightfold faster rate of oxidation of endonorborneol than that of cyclopentanol. This again proves chromate ester formation to be the rate-determining step.

The oxidation kinetics of methanol and mono-deutero methanol by chromium(VI) have been studied by K.K. Sengupta et al\textsuperscript{17}, over a wide range of temperatures in perchloric acid medium at constant ionic strength ($\mu = 1.0\text{M}$) maintained with sodium perchlorate wherever necessary. The reactions are found to be first order with respect to the oxidant and first order with respect to mono-ols, but the order with respect to acid is between 2 and 3. Since the rate of oxidation is found to increase with increase in [$\text{Cr}_2\text{O}_7^{2-}$] and the values of $\frac{k_{\text{obs}} [\text{Cr}^{\text{VI}}]}{[\text{Cr}_2\text{O}_7^{2-}]}$ are practically the same at various gross [Cr (VI)], $\text{Cr}_2\text{O}_7^{2-}$ is considered as the reactive oxidant. The rate increases with increase in NaClO\textsubscript{4} concentrations possibly due to the reaction between an ion and dipole. The pseudo-first-order rate constants in the presence of manganous ions decrease to nearly 50% of that in the absence of manganous ions suggesting the formation of intermediate valence states of chromium. The rate is unaffected by the addition of acrylamide. Unlike reaction at lower activities (pH=4.6) where molecular forms of mono-ols reacted with the oxidants, oxidation of protonated mono-ols with alkoxonium ion in higher acid medium (1.0M) is more likely. A mechanism is indicated in which the diprotonated $\text{Cr}_2\text{O}_7^{2-}$ species reacts with the protonated mono-ols to give an intermediate ester which then undergoes slow disproportionation to yield formaldehyde, $\text{H}_2\text{Cr}^{\text{IV}}\text{O}_3$ and $\text{H}_2\text{Cr}^{\text{VI}}\text{O}_4$. Thus Cr(VI) behaves as a two-electron oxidant.
Ethanol, isopropanol and benzyl alcohol\textsuperscript{18} have been oxidised by Cr(VI) oxidant in perchloric acid medium. The results indicate that the rate decreases with an increase in initial gross Cr(VI) concentration suggesting that HCrO\textsubscript{4}\textsuperscript{-} is the reactive species. The constancy of $\frac{k_{\text{obs}}[\text{Cr(VI)}]}{[\text{HCrO}_4^-]}$ has been checked at various Cr(VI) concentrations. The reactions are first order each with respect to [substrate] and [HCrO\textsubscript{4}^-]. The order with respect to [H\textsuperscript{+}] is found to vary form 1.3-1.9 indicating that alkanols have been protonated. Thus the reactive oxidant and reductant species are H\textsubscript{2}CrO\textsubscript{4} and ROH\textsubscript{2}\textsuperscript{+} respectively. The formation of the product proceeds via the
fast generation of an intermediate chromate ester stabilised by intramolecular
H–bonding and subsequent slow disproportionation of the ester to yield carbonyl
compounds and H₂Cr⁴O₃. The formation of transitory compound of tetravalent Cr
is proved by the decrease in pseudo – first order rate constant when the reactions
were carried out in the presence of manganous ions. The rates of the reactions
decrease in the order benzyl alcohol > ethanol > isopropanol. This reactivity order
is attributed to the increased inhibition among these alcohols to the formation of
intramolecularly

\[
\begin{align*}
R_2 - C - O - H & \quad + \quad H_2Cr^VI O_4 \quad \text{fast} \\
 & \quad \Leftrightarrow \\
R_2 - C - O - H & \quad + \quad H_2O^+
\end{align*}
\]

\[R_1 = H, \ R_2 = CH_3 \quad \text{for ethanol}\]
\[R_1 = CH_3, \ R_2 = CH_3 \quad \text{for isopropanol}\]
\[R_1 = H, \ R_2 = Ph \quad \text{for benzyl alcohol}\]
H-bonded ester.

A new mechanism¹⁹ for the chromic acid oxidation of secondary alcohols
based on an analogy to SN₂ reactions has been suggested. An activated complex
consisting of one molecule of alcohol, one of the chromacidium ion HCrO₃ and a
molecule of water is proposed in which there is dispersal of the initial charges.
This means that the transition state is made up of one of the protonated forms of
chromic acid H₃CrO₄. This explains the decrease in the rate of oxidation on the
addition of the more polar component, water. The increased rates in the case of
α-phenylethyl alcohol and benzhydrol over isopropyl alcohol are traced to the
negative inductive effect of the phenyl group which facilitates the nucleophilic attack in the transition state. The point stressed in the above mechanism is that the hydride anion is pulled off by the strongly electrophilic $\text{HCrO}_3^+$ and in this it is aided by a nucleophilic push by a molecule of water.

\[
\begin{align*}
\text{CHOH} + \text{HCrO}_3^+ + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O} \quad \text{Transition State} \\
\text{CHOH} + \text{HCrO}_3^+ + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O} \quad \text{Transition State} \\
\end{align*}
\]

1.2.3 Oxidation of Polyhydric Alcohols

Chromic acid oxidation of pinacol\textsuperscript{20} in aqueous solution has been studied at constant ionic strength in different acids under pseudo-unimolecular conditions. The data show that the reaction is first order each in pinacol, hydrogen ion and acid chromate ion. The observed solvent isotope effect $\frac{k_{\text{D}_2\text{O}}}{k_{\text{H}_2\text{O}}}$ and the lower rate of oxidation of pinacol monomethyl ether compared to that of pinacol precludes the possibility of cleavage of the O-H bond in pinacol in the rate-controlling process. The oxidation of pinacol by chromic acid induces the oxidation of Mn\textsuperscript{2+} to MnO\textsubscript{2} with a low induction factor of 0.3 suggesting the reaction to proceed via formation of tetravalent chromium. These facts are correlated with a mechanism that involves a chromic ester of pinacol as intermediate.

\[
\begin{align*}
(H_3\text{C})_2\text{C} - \text{C}(\text{CH}_3)_2 & \quad \text{H-O} \quad \text{OCrO}_3\text{H}
\end{align*}
\]
The kinetics of chromic acid oxidation of ethylene glycol, 2,3-butane diol and pinacol in perchloric acid medium has been examined by K. K. Sengupta et al.\textsuperscript{1} The reactions exhibit first order dependence with respect to $[\text{HCrO}_4^-]$ as well as $[\text{diol}]_0$ but the orders with respect to $\text{HClO}_4$ are different (1.25-2.0). Since all these oxidations are carried out under the same conditions of acidity, the difference in order with respect to $[\text{acid}]$ is due to the difference in the protonation of organic substrate.

pinacol $< \text{ethylene glycol} < 2,3$-butanediol

This is in conformity with the order of basicity of diols.

\begin{equation}
\begin{align*}
\text{H}_2\text{Cr}^{IV}\text{O}_3 + \text{C} & \xrightarrow{\text{slow}} \text{C} \\
\text{R}_1 = \text{R}_2 = \text{H} & \text{ for ethylene glycol} \\
\text{R}_1 = \text{H}, \text{ R}_2 = \text{CH}_3 & \text{ for 2,3 - butane diol} \\
\text{R}_1 = \text{R}_2 = \text{CH}_3 & \text{ for pinacol}
\end{align*}
\end{equation}
The reactions occur between protonated diols and the effective oxidant, protonated $\text{HCrO}_4^-$, via the rapid formation of intermediate chromate ester. Subsequently, slow disproportionation of the ester occurs and the products are obtained by C-C bond ruptures. There is no direct evidence of such an ester. Hence the equilibrium for the esterification step is considered to be very low.

The rates of the reactions follow the order:

$$\text{pinacol} > 2,3\text{-butane diol} > \text{ethylene glycol}$$

This difference is accounted for, by the greater stability of the carbonium ion by inductive (+I) and hyperconjugative effects in the cases of pinacol and 2,3-butane diol, these effects being absent in ethylene glycol.

The decrease in the pseudo-first order rate constants in the presence of manganous ions indicate that $\text{Mn}^{2+}$ ion catalyses the disproportionation of intermediate valence states of chromium. Cr(V) being a stronger oxidant reacts rapidly with the reactive reductant as

$$2\text{Cr(IV)} \rightarrow \text{Cr(V)} + \text{Cr(III)} \quad \text{(25)}$$

$$\begin{array}{c}
\text{R}_1\text{R}_2\text{C} \quad \text{Cr}_2\text{R}_1 + \text{Cr(V)} \quad \rightarrow \\
+ \text{OH}_2 \quad \text{2R}_1\text{R}_2\text{C}= \text{O} + \text{Cr(III)} + \text{3H}^+ \\
\end{array} \quad \text{(26)}$$

Oxidation of glycerol$^{22}$ by chromic acid in sulphuric acid medium results in the formation of formaldehyde and glyoxal. The title reaction is overall second order, first order in each reactant. The reaction is acid – catalysed and the rates are independent of added salts but dependent upon solvent polarity. A plot of $\log k$ vs $1/D$ is linear with a positive slope indicating the reaction to be of an
ion–dipole type. The active oxidant species is assumed to be $\text{HCrO}_3^-$. Plausible free radical mechanism involving a three-electron transfer is formulated to explain the kinetic data.

### 1.2.4 Oxidation of Aldehydes

The oxidation kinetics of some aromatic aldehydes by chromium(VI) have been followed in perchloric acid medium. The pseudo-first order rate constants are not independent of chromium (VI) concentrations. The constancy of

$$k_{\text{cor}} = \frac{k_{\text{obs}} [\text{Cr}(VI)]}{[\text{HCrO}_4^-]}$$

indicate that the reactions are effected by $\text{HCrO}_4^-$. The reactions are investigated by performing each experiment at constant ionic strength maintained by the addition of sodium perchlorate. The rate is directly proportional to the square of hydrogen ion concentrations. The plot of $\frac{1}{k_{\text{obs}}} \cdot \frac{1}{[\text{aldehyde}]}$ is linear making intercept on y-axis indicating an intermediate complex formation between the reactants. The kinetic and spectrophotometric results substantiate the formation of a 1:1 intermediate ester between the protonated benzaldehyde and the reactive Cr(VI) species, $\text{HCrO}_4^-$. The intermediate ester on further protonation gives the protonated ester which is capable of an internal two-electron transfer oxidation–reduction reaction to give the products in a slow reaction.

\[
\begin{align*}
\text{Ph} & \text{C}^+ + \text{XCrO}_4^- \rightleftharpoons \text{Ph} & \text{C} \text{O} & \text{Cr} \text{OX} & \rightleftharpoons \text{PhCOOH} + \text{Cr}^{IV} \\
\end{align*}
\]

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(27)
The activation parameters associated with the rate-determining step have been computed. The thermodynamic equilibrium constant of 1:1 complex has been determined spectrophotometrically. The analysis of rates of oxidation of different p-substituted benzaldehydes reveals that electron-withdrawing substituents facilitate the reaction and electron-donating substituents have a retardation effect. This is because the positive charge on the benzylic carbon in protonated aldehyde is not neutralised by electromeric shift when an electron-withdrawing para substituent is present. This facilitates attack of HCrO₄⁻ to form the chromate ester.

\[
\begin{align*}
\text{I} & : \text{C}^+ \text{OH} \leftrightarrow \text{etc} & \text{II} & : \text{O}^- \text{N}^+ \text{C}^+ \text{OH} \leftrightarrow \text{etc} \\
\text{III} & : \text{MeO}^- \text{C}^+ \text{OH} \leftrightarrow \text{MeO}^+ \text{C}^+ \text{OH} \leftrightarrow \text{etc} & \text{IV} & : \text{C}^+ \text{OH} \leftrightarrow \text{etc}
\end{align*}
\]

1.2.5 Oxidation studies on ketones

Cr (VI) has been employed to oxidise aliphatic ketones such as acetone, ethyl methyl ketone, methyl n-propyl ketone and methyl isopropyl ketone to the respective 1,2-diketones. The rate constants decrease with increase in [Cr(VI)].
The results indicate that the reaction is first order with respect to acid chromate ion as well as to ketone. Under the conditions of constant ionic strength, the rate is proportional to $[H^+]^2$. Analysis of solvent effect indicates that the reaction involving protonation is favoured by lowering the dielectric constant of the medium. In acetic acid medium, chromic acid exists as acetochromic acid $\text{CH}_3\text{COO CrO}_3\text{H}$ or its conjugate acid $(\text{CH}_3\text{COOCrO}_3\text{H}_2)^+$ which are assumed to be strong acids and much powerful oxidising agents. Addition of Mn(II) does not affect the rate of oxidation appreciably indicating the absence of intermediate valence states of Cr. As enolisation catalysed by acetic acid is faster than oxidation in all the ketones, it is observed that there exists a correlation between the relative rates of oxidation and enolisation at the $\alpha$-CH$_2$ or $\alpha$-CH group. A concerted mechanism has been proposed to explain the kinetic data.

\[
\text{RCH}_2\text{COCH}_3 \xrightleftharpoons{\text{H}^+} \text{RCH}=\text{C} \cdots \text{CH}_3
\]  

\[
\text{H} \quad \begin{array}{c}
\text{C} \\
\text{O}=\text{Cr}^+\text{OH} \quad \text{slow} \\
\text{C} \quad \text{OH} \\
\text{CH}_3
\end{array} \xrightarrow{\text{slo}} \text{R} \quad \begin{array}{c}
\text{C} \\
\text{O} \quad \text{CrO}_2\text{H}_2 + \text{H}_2\text{O} \\
\text{C} = \text{O} \\
\text{CH}_3 \\
\text{H}_3\text{CrO}_3 + \text{RCHOH COCH}_3
\end{array}
\]  

\[
\text{RCHOH COCH}_3 + \text{Cr}^{VI} \xrightarrow{\text{fast}} \text{RCO CO CH}_3
\]
It involves attack of chromic acid (H$_2$CrO$_4$) or its conjugate acid (H$_3$CrO$_4$) on the enol to form the chromate ester. The stabilisation of enols through hyperconjugation from the β-hydrogen atoms explains the higher reactivity of the ketones other than acetone.

Oxidation of meta and para substituted acetophenones by chromic acid in 95% v/v AcOH to yield phenacyl alcohols is first order each with respect to ketone as well as to the oxidant. The reaction is acid catalysed and the pseudo-first order rate constant is proportional to [H$^+$]. The rate constant increases with decrease in dielectric constant of the medium which favours reactions involving protonation. In AcOH medium, H$_2$CrO$_4$ exists as acetochromic acid and its protonated forms which are more powerful oxidising agents than chromic acid. The plot of log $k_1$ vs 1/D is linear as expected for ion-dipole reactions. Further, the extent of enolisation is enhanced by increasing the proportion of acetic acid. Hence the rate of oxidation increases as in aliphatic ketones. The retardation of the rate of oxidation in the presence of added Mn$^{2+}$ ions indicates that intermediate valence states of chromium such as Cr(IV) are involved in the oxidation.

\[ \begin{align*}
R-\overset{\cdot}{\mathrm{CH}_3} & \overset{\text{H}^+}{\rightleftharpoons} R-\overset{\cdot}{\mathrm{CH}_2} \\
\overset{\cdot}{\mathrm{C}}\overset{\cdot}{\mathrm{CH}_2} + \text{HO} & \overset{\cdot}{\mathrm{Cr}=\mathrm{O}} \rightarrow R-\overset{\cdot}{\mathrm{CH}_2}\overset{\cdot}{\mathrm{O}} \equiv \text{Cr} - \text{OH} + \text{H}_2\text{O} \\
\overset{\cdot}{\mathrm{C}}\overset{\cdot}{\mathrm{CH}_2}\overset{\cdot}{\mathrm{O}} & \equiv \text{Cr} - \text{OH} + \text{H}_2\text{O} \rightarrow R-\overset{\cdot}{\mathrm{CO}}\overset{\cdot}{\mathrm{CH}_2}, \text{OH} + \text{H}_2\text{CrO}_3
\end{align*} \]
The reaction rate is reduced in the presence of complexing agents suggesting that the lifetime of Cr(IV) intermediate is decreased by the ligand. The negative $\rho^+$ values computed show that the electron-donating substituents accelerate the rate while electron-withdrawing groups retard it. As the rate of oxidation is slower than the rate of enolisation, a mode of oxidation proceeding through enol intermediate has been conceived for aromatic ketones also as in their aliphatic counterparts. The attack of the $\text{H}_2\text{CrO}_4$ or its conjugate acid $\text{H}_3\text{CrO}_4^+$ on the enol molecule results in the formation of a chromate ester which decomposes on hydrolysis to give the product. A 3:2 stoichiometry between substrate and oxidant has been indicated.

In oxidation of organic compounds by Cr(VI) under acid conditions, the main oxidant is either $\text{HCrO}_4^-$ or any of its protonated species. Participation of both $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$ has been demonstrated for the first time in the oxidation of p-methoxyacetophenone by Cr(VI)\textsuperscript{26} under acid conditions. The results provide kinetic evidence for the participation of both $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$. Under pseudo-first order conditions, the rate of disappearance of Cr(VI) follows first order rate law at least up to 70% conversion. The observed rate of oxidation changes with the changing $[\text{Cr(VI)}]$, in accordance with the following expression.

$$\frac{-d[\text{Cr(VI)}]}{dt} = a[H\text{CrO}_4^-] + b[H\text{CrO}_4^-]^2$$  \hspace{1cm} (36)

where $a$ and $b$ can be evaluated from the linear plot of $\frac{-d[\text{Cr(VI)}]}{dt} \times \frac{1}{[H\text{CrO}_4^-]}$ against $[H\text{CrO}_4^-]$. This indicates that both $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$ are the active oxidising species. The contribution of the path involving $\text{HCrO}_4^-$ to the observed
rate is small and significant only at lower [Cr(VI)]. At higher initial [Cr(VI)], the oxidation is practically due to \( \text{Cr}_2\text{O}_7^{2-} \). This observation is radically different from chromic acid oxidation of acetophenone and nuclear substituted acetophenones under acid conditions where there is a strict first order dependence on \([\text{HCrO}_4^-]\)^{27}. Order with respect to hydrogen ions is two. Since ketone variation has been carried out at relatively higher concentration of Cr(VI), where \( \text{HCrO}_4^- \) contribution to the observed rate is insignificant, a tentative mechanism has been suggested.

\[
\text{k} + \text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{Complex}} \text{products} \quad \quad \quad (37)
\]

\[\text{ketone} + \text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{[Complex]}} \xrightarrow{\text{slow}} 2\text{H}^+ \]

1.2.6 Oxidation Studies on Cyclic Ketones

A series of cycloalkanones have been employed as substrates for chromic acid oxidation. The relative rates of oxidation of cycloalkanones have been determined^{28}. The order of reactivity is cyclohexanone > cyclononanone > cyclooctanone > cyclopentanone > cycloheptanone > cyclobutanone. The kinetics of oxidation of cyclohexanone has been reported^{28,29}. The observed rate law is

\[
\text{Rate} = k[\text{ketone}][\text{HCrO}_4^-][\text{H}^+]
\]

\[\text{(38)}\]

It has been suggested that the enol is an intermediate in the reaction^{29,30-32}. The formation of enol cannot be rate-determining since the rate of oxidation has a first order dependence on Cr(VI) concentration and a measurement of the rate of enolisation showed it to be more rapid than oxidation. The experimental data show that the reaction rate increases with increasing chromic acid concentration. The observed solvent isotope effect \( \frac{k_{D,0}}{k_{H,0}} = 4 - 5 \) indicates that the oxidation involves two acid – base equilibria, one of which must be due to the dissociation,
whilst the other can be assigned to the fast equilibrium involved in acid-catalysed enolisation.

\[ \text{H}_2\text{CrO}_4 \rightleftharpoons \text{HCrO}_4^- + \text{H}^+ \] (39)

\[ -\text{CH} - \text{C} = \text{O} + \text{HA} \rightleftharpoons -\text{CH} - \text{C} - \text{OH} + \text{A}^- \] (40)

The rate-determining stage in the ketone oxidation can, therefore, be written as a concerted addition to an enol, which at once gives a hypothetical Cr(IV) ester of an \( \alpha \)-hydroxy ketone that could be expected to hydrolyse rapidly. The oxidation of cyclohexanone leads to a mixture of products among which adipic acid and glutaric acid predominate.

\[
\begin{align*}
\text{H} - \text{O} & \quad \text{OH} \\
\text{O} = \text{Cr} & \quad \text{OH} \\
\text{C} & \quad \text{C} \quad \text{OH} \\
\text{H}_2\text{CrO}_3 & \quad + \\
\end{align*}
\]

The reaction between camphor and chromic acid in aqueous acetic acid medium has a first order dependence on each reactant. The reaction is acid-catalysed and the order with respect to [H\(^+\)] is unity. The reaction rate is decreased by the addition of Mn(II) and Co(II) ions. The first order rate constant is found to decrease with increase in [Cr(VI)]. The formation of enol cannot be rate-determining since the rate of reaction depends on the chromic acid concentration and the rate of enolisation is faster than that of oxidation.
It could be possible that at higher concentration of chromic acid, the rate of reaction might show zero order dependence on [Cr(VI)] and hence be equal to the rate of enolisation.

Kinetic behaviour of some substituted 4- piperidones towards oxidation by aqueous acidic chromium trioxide has been examined. The oxidation reaction is of first order with respect to both oxidant and substrate. The rate of oxidation increases with increase in solvent composition in the reaction mixture suggesting ion-dipole interaction. The scavenger methyl methacrylate does not induce polymerisation indicating the absence of free radicals during the course of oxidation. A 1:3 stoichiometry between substrate and oxidant leading to dicarboxylic acid as the main product has been indicated. A mechanism involving
nucleophilic attack of $\text{CrO}_3$ on the enol form of piperidone in the rate-determining step has been proposed.

\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^- \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array}
\xrightleftharpoons{\text{H}^+}^{\text{fast}}
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{OH}^{-} \xrightarrow{\text{slow}}
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} \quad \text{H}_2\text{CrO}_4^- \quad \text{OH} + \text{H}_2\text{O} \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} \quad \text{H}_2\text{CrO}_3
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 + \text{H}_2\text{O} \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{N} \quad \phi \\
\text{CH}_3
\end{array} + \text{H}_2\text{CrO}_3 \\
\]
1.2.7 Oxidation of Acetals

Chromic acid has also been used to effect the oxidation of aliphatic and aromatic acetals in aqueous acetic acid medium. A first order dependence each in [oxidant] and [Cr(VI)] is observed. In both the aliphatic and aromatic series, the oxidation is accelerated by decreasing the solvent polarity of the medium. The possibility of free radical mechanism has been ruled out since the reactants fail to induce polymerisation of allyl acetate. The rates of oxidation of acetaldehyde-diisobutyl acetal and benzaldehyde di-n-butyl acetal with Cr(VI) decrease with increasing concentration of sodium acetate. The rates of oxidation of both aliphatic acetals and aromatic acetals are accelerated progressively with the increasing concentration of oxalic acid and disodium salt of EDTA. Oxalic acid forms an ester with HCrO$_4^-$ and H$^+$ and this ester having a positively charged chromium can attack the acetal more easily to form a ternary complex which decomposes to give the products in the rate-determining process.

\[
\begin{align*}
\text{OR} & \quad \text{OR} \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{R} \\
+ \quad + \\
\text{HCrO}_3^+ & \quad \text{H}_2\text{CrO}_3 \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{Cr} & \quad \text{Cr} \\
\text{O} & \quad \text{O} \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]
The effect of substituents in the phenyl ring on the oxidation of acetal have also been examined by Basheer, Nambi and Arulraj. The electron-withdrawing substituents at the meta- and para-positions increase the rate while the electron-releasing substituents retard the reaction considerably. Hammett's correlations on the oxidation show a small positive ρ value (ρ=0.4) for the reaction which is attributed to the cyclic nature of the transition state involving the acetal and HCrO₅ species.

1.2.8 Oxidation of Carboxylic acids

Kinetics of Os(VIII) catalysed chromic acid oxidation of maleic, fumaric, acrylic and cinnamic acids have been followed in aqueous and aqueous acetic acid media in the presence of HClO₄. Maleic and cinnamic acids exhibit zero order dependence in oxidant at lower concentrations of the oxidant and first order dependence at higher concentrations of the oxidant. Acrylic acid shows zero order dependence in oxidant in the total range of [oxidant] studied while a fractional order dependence in oxidant is observed in the case of fumaric acid. The dependence on substrate is unity for all the compounds studied. Analysis of response to solvent polarity reveals the reactions to be dipole-dipole type as reaction rate decreases in all the cases with increase in the percentage of acetic acid. The effect of acidity is marginal. Kinetic features observed in the present investigation are not routed through identical mechanisms in all the substrates studied. The rate-determining step is dependent on the concentration of the oxidant. The zero order dependence is traced to the formation of a complex between unsaturated compound and the catalyst and the first order dependence due that formed between substrate and the oxidant.
Glyoxalic and pyruvic acids\textsuperscript{38} have been oxidised to formic and acetic acids respectively by chromic acid in perchloric acid medium. All the oxidation reactions are first order each with respect to [Cr(VI)], \(\alpha\)-keto acid and hydrogen ion concentration. Under pseudo-first order conditions, the rate is decreased with the increase in initial concentration of Cr(VI). This is possibly because, a progressively smaller portion of the total amount remains in the form of HCrO\textsubscript{4} as the initial [Cr(VI)] is increased. The rate is increased with decrease in dielectric constant of the medium suggesting more protonation of HCrO\textsubscript{4}\textsuperscript{−} or production of stronger oxidants like CH\textsubscript{3}COOCrO\textsubscript{2}OH or CH\textsubscript{3}COOCrO\textsubscript{2}OH\textsubscript{2}. It is apparent from the results that glyoxalic acid reacts faster than pyruvic acid. A tentative mechanism is discussed in which the acid chromate ion, hydrated \(\alpha\)-keto acids and H\textsuperscript{+} react to form R–C(OH)\textsubscript{2} and HCrO\textsubscript{4}\textsuperscript{3−} by the rupture of C–C bond of \(\alpha\)-keto acid. The carbonium ion gets converted eventually to a fatty acid, which is a stable product.

The oxidation of malonic acid to formic acid by acid dichromate in aqueous acetic acid medium has been reported by Saran, Dash and Acharya\textsuperscript{39}. The reaction is observed to be first order with respect to both [oxidant] and [substrate]. Although, the rate at which Cr (VI) disappears, follows a first order rate law, the rate constants show a decreasing trend with increase in initial [Cr(VI)]. This may be due to the hydrolytic equilibrium between Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−} and HCrO\textsubscript{4}\textsuperscript{−}. The ratios between the observed rate and [HCrO\textsubscript{4}\textsuperscript{−}] do not show constancy indicating that HCrO\textsubscript{4}\textsuperscript{−} is not the only oxidising species responsible for this oxidation. The observed rate data fit into the expression

\[
\frac{-d[Cr(VI)]}{dt} = a[HCrO_4^-] + b[HCrO_4^+] \tag{49}
\]
The plot of rate / [HCrO$_4^-$] Vs [HCrO$_4^-$] is linear from which the constants a and b have been computed to be $3.2 \times 10^{-5}$ and $7.5 \times 10^{-3}$ respectively. This is indicative of the participation of both HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ in the oxidation process. The plots of $\frac{1}{k_{\text{obs}}}$ vs $\frac{1}{[\text{substrate}]}$ are linear showing definite intercepts at $\frac{1}{k_{\text{obs}}}$ axis. This provides kinetic evidence for complex formation between the oxidant and the substrate. The anions like ClO$_4^-$ and HSO$_4^-$ increase the tendency of the Cr(VI) species to accept electrons from a reducing agent. Since ClO$_4^-$ is more electron-withdrawing than HSO$_4^-$, the rate of oxidation of malonic acid in HClO$_4$ medium is found to be faster than in sulphuric acid medium. The rate of oxidation increases with increase in [H$_2$SO$_4$]. This linear function proposes the protonation of malonic acid. First order dependence on [H$_2$SO$_4$] does not show the involvement of a positively charged Cr(VI) species. Dependence of rate on the dielectric constant of the medium suggests the possibility of ion-ion or ion-dipole interaction.

\[ \text{HOOCCH}_2\text{COOH} \xrightarrow{\text{fast}} \text{HOOC} \text{C} \text{COOH} \xrightarrow{\text{slow}} \left[ \begin{array}{c} \text{HOOC} \\
\text{H} \\
\text{O} \\
\text{C} \\
\text{Cr}^{\text{IV}} \\
\text{O} \\
\text{O} \\
\text{HO} \\
\text{H} \\
\text{O} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{OH} \\
\text{H} \\
\text{OH} \\
\text{H} \end{array} \right] \xrightarrow{\text{HCrO}_4^-} \text{HCCOOH} + \text{CO}_2 + \text{Cr}^{(V)} + \text{Cr}^{(III)} \]
Hence the reactants must be protonated malonic acid and HCrO$_4^-$. Increase in ionic strength will favour the formation of the dichromate ion and hence will decrease the rate of the reaction as the acid chromate - dichromate equilibrium constant is a function of ionic strength. This suggests the reaction to be between two oppositely charged reactants. The observed rate constant increases linearly with increasing[Mn(II)]. It is not easy to decide the exact Cr(VI) species present in the solution since it is involved in a series of protolytic and hydrolytic equilibria such as

\[ \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HCrO}_4^- \]  
\[ \text{HCrO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CrO}_4 \]  
\[ \text{HCrO}_4^- + 2\text{H}^+ \rightleftharpoons \text{HCrO}_3^+ + \text{H}_2\text{O} \]

Since the reaction has been carried out in 2M H$_2$SO$_4$, Cr(VI) species involved in the reaction seem to be HCrO$_4^-$ and Cr$_2$O$_7^{2-}$. Cr(VI) dissolved in high percentage of acetic acid may also exist in the form of acetyl chromate ion AcOCrO$_3^-$. Solvent dependence on rate indicates a superior oxidising species beyond 60% acetic acid in the mixture. It may be acetyl chromate ion as acetyl group would increase the electron accepting power of Cr(VI). Absence of polymerisation of acrylonitrile indicates that free radical is not formed in the rate - determining step and Cr(VI) appears to behave as a two electron oxidant. Thus the mechanism shown in the scheme below is suggested for the oxidation of malonic acid by acid dichromate.
Chromic acid oxidation of malonic acid in perchloric acid medium has been investigated in detail by M. Senapathi, G. P. Panigrahy and S. N. Mahapatro. Pseudo-first order rate constants which have been calculated from the plots of $\log A_{350}$ vs time are essentially constant indicating that the oxidation reaction is first order in total $[\text{Cr(VI)}]$. At lower acidities, the first order dependence on malonic acid is clearly evident whereas at higher acidities, there is unusual departure from first order dependence at low malonic acid concentrations. A first order dependence on $[\text{H}^+]$ is observed at low acidities and a less than first order dependence at higher acidities. Oxidation rates for deuterio malonic acid have been measured. Hydroxy malonic acid and glyoxalic acid are the two products that could be quantitatively measured by standard methods. The $k_{14}/k_D$ value of 2.5 in $\text{D}_2\text{SO}_4 - \text{D}_2\text{O}$ is a secondary isotope effect. The absence of a primary deuterium kinetic isotope effect rules out rate-determining C-H cleavage. The reaction sequence involves an initial rate-limiting step of two-electron oxidation to hydroxy malonic acid. Cr(IV) intermediate bound to hydroxy malonic acid is oxidised by another molecule of chromic acid to glyoxalic acid, CO$_2$, Cr(V) and Cr(III).

1.2.9 Oxidation of $\alpha$-hydroxy acids

Samal, Patnaik, DharmaRao and Mahapatro have examined the conversion of lactic to pyruvic acid effected by chromic acid. The constancy of pseudo-first order rate constant for various initial concentrations of [Cr(IV)] shows first order dependence on total [Cr(VI)]. The reaction is first order in lactic acid at low substrate concentration and high [H$^+$], and it changes to second order in lactic acid at high substrate concentration and low [H$^+$]. The acidity dependence has been determined which shows that the oxidation is first order in H$^+$ ion at high [H$^+$] and...
low [LA] and approaches a zero order dependence at high [LA] and low acidities. A mechanism is proposed which encounters that in the presence of a bifunctional molecule like lactic acid, the Cr(IV) may well be oxidised to Cr(V).

\[
\text{CH}_3\text{CHOH COOH} + \text{HCrO}_4^- \rightleftharpoons \text{CH}_3\text{COCOOH} + \text{Cr}(\text{IV}) + \text{Cr(III)} + \text{H}_2\text{O} \tag{53}
\]

As iodometric estimations show that Cr (V) is formed in 10% of the theoretical amounts, it is clear that Cr (V) – lactic acid reaction is extremely fast. The only carbonyl product which has been isolated in significant amounts is the two-electron oxidation product identified as pyruvic acid. Acetaldehyde is found in negligibly small amounts. This points to the fact that Cr (V) is reacting by C–H cleavage which is the dominant reaction in the Cr (VI) oxidation of lactic acid.
The oxidation of lactic acid by Cr (VI) has been found to proceed in two measurable steps, both of which give pyruvic acid as the primary product. Build up and decay of Cr (V) intermediates accompany the decay of Cr(VI).

\[
2\text{Cr(VI)} + 2\text{CH}_3\text{CHOHCOOH} \rightarrow 2\text{CH}_3\text{COCOOH} + \text{Cr(V)} + \text{Cr(III)} \quad (54)
\]

\[
\text{Cr(V)} + \text{CH}_3\text{CHOHCOOH} \rightarrow \text{Cr(III)} + \text{CH}_3\text{COCOOH} \quad (55)
\]

Several hydroxy acids such as salicylic, gallic and tartaric acids have been oxidised by acid dichromate in HClO₄ medium. The rate of consumption of Cr(VI) has been followed spectrophotometrically in some cases or iodometrically in other cases. Some experiments under identical conditions have been conducted both iodometrically and spectrophotometrically and the results agree within ±1% accuracy. The first order rate constant decreases with increasing initial [Cr(VI)] suggesting HCrO₄⁻ as the reacting species of Cr (VI). The experiments carried out at different [HClO₄] show a proportional dependence on first power of [H⁺] at constant ionic strength. The oxidation rates are found to be susceptible to changes in ionic strength indicating the reactions to be of ion–dipole type. Decrease in the reaction rate in the presence of Mn(II) substantiate the intermediacy of lower valence states of Cr(VI).

Kinetics of acid dichromate oxidation of α–hydroxy acids such as mandelic, lactic, benzilic, benzylphenyl glycollic acids have been followed in glacial acetic acid medium. The order with respect to [oxidant] and [substrate] is observed to be one each. The reaction is acid catalysed and the order with respect to [H⁺] is unity. The rate constant show a decreasing trend with increasing initial concentration of Cr(VI) due to the hydrolytic equilibrium between Cr₂O₇²⁻ and HCrO₄⁻.
This type of behaviour is however not uncommon with Cr(VI) oxidations. The ratios between the observed rate and [HCrO₄⁻] do not show constancy indicating that HCrO₄⁻ is not the only oxidising species responsible for this oxidation. The observed data fit into the expression.

$$- \frac{d[Cr(VI)]}{dt} = a[HCrO_4^-] + b[HCrO_4^-]^2 \quad \text{(49)}$$

This is indicative of the participation of both HCrO₄⁻ and Cr₂O₇²⁻ in the oxidation process. The absence of mineral acid considerably retards the reaction rate. First order dependence on [H₂SO₄] shows the absence of involvement of a positively charged Cr(VI) species. An increase in ionic strength decreases the rate suggesting qualitatively the interaction between two oppositely charged reacting species. The interaction probably takes place between H⁺ and a negative ion. The rate decreases by increasing the concentration of Mn(II). This indicates the formation of some lower valent Cr species because Mn(II) catalyses the disproportionation of intermediate valency state of chromium suggesting Cr(IV) as the probable intermediate. A common mechanism is envisaged for all the substrates as the energy of activation values are of same order of magnitude. The negative values of entropy of activation suggest a rigid transition state. Hence the oxidation proceeds through the rapid formation of cyclic chromate ester by the interaction α-hydroxy acid with hydrogen ion and acid chromate ion. The ester then breaks down in a rate – limiting step by oxidative decarboxylation to give the products.
The reactivity sequence of the substituted α-hydroxy acids conforms to the order

Benzyl phenyl glycollic acid > benzilic acid > mandelic acid > lactic acid.

(a) (b) (c) (d)

This is rationalised by the fact that the transition state leading to the decomposition of the cyclic chromate ester is stabilised by phenyl or benzyl groups in (a) and (b) as compared to hydrogen atom present in (c) and CH₃ group in (d).

1.2.10 Oxidation of Esters

The kinetics of chromic acid oxidation of some aliphatic esters has been studied in acetic acid – water mixtures in presence and absence of oxalic acid. In the absence of oxalic acid the reaction is overall second order, first order in each
reactant. The oxidation of ester is acid-catalysed and the reaction rate is independent of the added salts. The rate increases with increase in acetic acid content indicating the reaction to be a positive ion-dipole type. Hence in the present reaction, the attacking species is considered to be HCrO₃. The rate data for the oxidation of methyl acetate by Cr(VI) in different mineral acids shows the order of reactivity in different acid media as HClO₄ > H₂SO₄ > HCl. This is in agreement with the oxidation potential of Cr(VI) in these mineral acids. As the hydrolysis rate constant of methyl acetate is much lower than the rate of its oxidation by Cr(VI), a direct oxidation of the ester has been envisaged.

\[
\begin{align*}
\text{O} \\
\text{CH}_3 - \text{C} - \text{O} - \text{CH}_2\text{R} + \text{HCrO}_3 & \rightleftharpoons \text{Complex} \quad \cdots (59) \\
\text{Complex} & \xrightarrow{\text{slow}} \text{CH}_3\text{COOH} + \text{RCHO} + \text{Cr(IV)} \quad \cdots (60) \\
\text{Cr(IV)} + \text{Cr(VI)} & \longrightarrow 2\text{Cr(V)} \\
\text{O} \\
\text{CH}_3 - \text{C} - \text{O} - \text{CH}_3\text{R} + \text{Cr(V)} & \xrightarrow{\text{fast}} \text{H}_2\text{O} \quad \text{CH}_3\text{COOH} + \text{RCHO} + 2\text{H}^+ + \text{Cr(III)} \quad \cdots (61)
\end{align*}
\]
The reactivity sequence n-butyl > isobutyl ~ n-propyl > ethyl > methyl ~ isopropyl is explained in terms of increasing polar effect of the alkyl group resulting in a facile attack by Cr(VI). The deviation observed with isopropyl group is due to steric effect outweighing the polar effects. Absence of induced polymerisation of acrylonitrile, a free radical trap, rules out a free - radical mechanism.

The chromic acid oxidation of dimethyl malonate in presence and in absence of manganous ions has been reported. An increase in the [Cr(VI)] increases the rates of oxidation and the ratio of rate of oxidation to [Cr(VI)] is constant, indicating the order with respect to total Cr(VI) is one. The reaction rate also increases with the increase in the concentration of the ester. A plot of $\frac{1}{rate}$ vs $\frac{1}{ester}$ is linear indicating the formation of intermediate complex between ester and Cr(VI) during the oxidation. Polymerisation of acrylonitrile, when added to the reaction mixture, indicates the formation of free radicals during the course of the reaction. The reaction investigated reports that the order with respect to ester is less than one which rules out direct single step three - electron oxidation. Also there is Michaelis – Menten type dependence of rates on ester concentration. The addition of manganous ions to the reaction mixture catalyses the oxidation reaction. The induction period depends upon the [Mn(II)] and diminishes as [Mn(II)] is increased. The predominant species of Cr(VI) in 10^{-4} to 10^{-2} mol dm^{-3} solutions under the experimental conditions are HCrO_4^- and Cr_2O_7^{2-} while H_2CrO_4 and CrO_4^{2-} are present in negligible amounts. A plot of log(rate) Vs log[HCrO_4^-] is a straight line and the order with respect to [HCrO_4^-] is less than unity. Increase in the concentration of H_2SO_4 increases the rate of oxidation and the rate is proportional to [H^+]^2. The increase in the rate with the increase in the proportion of
acetic acid may be attributed to the increased protonation before reaction in a solvent of low dielectric constant or it may be due to the formation of acetyl chromic acid \( \text{CH}_3\text{COO CrO}_2\text{OH} \) or its conjugate acid \( \text{CH}_3\text{COOCrO}_2\text{OH}_2^+ \) which are more powerful oxidants than chromic acid. There is formation of 1:1 chelated complex of Mn(II) and enol form of the ester which is then oxidised by HCrO\(_4^-\) to produce the corresponding complex of Mn(III). This Mn(III) complex then decomposes to give the product.

### 1.2.11 Oxidation Studies On Organic Sulphides

Effect of substituents on the oxidation of substituted aryl methyl sulphides and diphenyl sulphides by Cr(VI) has been examined by C. Srinivasan, A. Chellamani and S. Rajagopal\(^47\). The kinetic and thermodynamic characteristics of the reaction have been determined by titrimetric procedure. The reactions are first order with respect to Cr(VI). The rate of oxidation is unaffected by change in ionic strength. This may presumably be due to the attack of an ion on a neutral molecule in the rate-controlling step. The enhanced rate of oxidation in solutions containing higher percentage of AcOH is due to the formation of acetyl chromate ion, the acetyl group increasing the electron accepting power of Cr(VI). This solvent effect excludes the formation of a charge-separated complex in the rate-determining step. There is first order dependence on \([\text{H}^+]\). Electron-releasing substituents in the benzene ring are found to accelerate the rate of oxidation whereas a retardation in the rate is observed with electron-attracting substituents. A mechanism involving a one-electron transfer process is proposed for the oxidation of methylphenyl sulphide by Cr(VI).
The rate is almost unaffected by the addition of Mn(II) ruling out the possibility of formation of Cr(IV). Detailed studies with diphenyl sulphides indicate that the order with respect to each of [Cr(VI)] and [DPS] is unity. Rate studies with 4-substituted diphenyl sulphides show that electron-releasing substituents accelerate the rate of oxidation.

The reaction between methylphenyl sulphide(MPS) and Cr(VI) in the presence of oxalic acid has a first order dependence each on [Cr(VI)], [MPS] and [oxalic acid]. The oxidation of the mixed substrate system by Cr(VI) is not sensitive to the variation in ionic strength indicating that the rate determining step involves ion-dipole or dipole-dipole interaction. The rate increases with increase in acetic acid content in the reaction medium. It is presumed that chromic acid – oxalic acid complex is an intermediate in the co-oxidation reaction. This complex reacts with MPS to produce another complex which on solvolysis yields the product sulphoxide.

\[
(COOH)_2 + HC\text{rO}_4^- + H^+ \overset{k}{\rightarrow} \text{(C}_1\text{)}
\]

\[
(C_1) + \text{S}^\circ + H_2C-C_6H_5 \rightarrow \text{(C}_2\text{)}
\]

\[
(C_2) \xrightarrow{\text{solvolysis}} \text{S}=\text{O} + \text{CO}_2 + \text{CO}_2^- + \text{Cr}^{3+}
\]

Scheme 1
1.1.12 Oxidation of Sulphoxides

The kinetic studies involving the oxidation of some monosubstituted methylphenyl sulphoxides by Cr(VI) in 75% (v/v) aqueous acetic acid to yield the corresponding sulphones have been reported. The reaction follows second order kinetics – first order each in sulphoxide and Cr(VI). The rate of the reaction increases with increase in the concentration of HClO₄ at constant ionic strength. The increase in oxidising power of Cr(VI) with increase in acidity proves that Cr(VI) exists as HCrO₄⁺ at high mineral acid concentration because such positive ions are formed with ease in the presence of a proton donor. An increase in the percentage of water in the solvent system shows a decrease in the rate due to a greater solvation of the sulphoxide group and its consequent decrease in nucleophilicity. A plot of logarithms of rate constants for meta substituted phenyl methyl sulphones against Hammett constants gives a negative ρ value indicating a transition state bearing a positive charge on sulphur. A separate plot for the para-substituted compounds using σ⁺ values of Brown and Okamoto gave good correlation. The equation due to Yukawa and Tsuno has been employed to measure the magnitude of positive charge to be stabilised in the transition state. An electron transfer as in eq.(69) from sulfoxide to HCrO₄⁺ occurs in the rate determining step forming a radical cation. A small negative ρ⁺ value obtained for the reaction is consistent with the view that electron depletion occurs at the reaction centre in the transition state which is stabilised by electron-releasing para substituents.
\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} & + 4\text{H}^+ \rightleftharpoons 2\text{HCrO}_3^+ + \text{H}_2\text{O} \\
\text{Ph} & \\
\text{Ph} - \text{SO} - \text{Me} + \text{Cr(VI)} & \rightarrow \text{+S = O} + \text{Cr(V)} \\
\text{Me} &
\end{align*}
\]

Kinetic measurements have been made on the oxidation of dipentyl and diphenyl sulfoxides with Cr(VI) in sulphuric acid medium by Bhatta, Behera and Mohanty.\textsuperscript{50} The reactions are first order each in oxidant and substrate. At constant ionic strength the rate increases with increase in [sulphuric acid]. Thus the mineral acid accelerates the process and the order with respect to [H\textsuperscript{+}] is 2. Increase in the percentage of acetic acid in the reaction medium increases the rate of oxidation of dipentyl sulfoxide while the reaction rate decreases in the case of diphenyl sulfoxide. Plots of log \( k_1 \) Vs 1/D are linear in both the cases with positive and negative slopes for the dipentyl and diphenyl sulfoxides respectively. Retardation by the added Mn\textsuperscript{2+} is quite significant at higher concentration indicating participation of lower valent chromium species. Added acrylamide undergoes induced polymerisation. Hence a free radical mechanism has been postulated. As the S atom is considerably nucleophilic, the cation radical of the substrate attacks the Cr – O bond in HCrO\textsubscript{3} or H\textsubscript{2}CrO\textsubscript{4} which are the probable oxidant species resulting in the formation of a complex. The complex hydrolyses to give the product. The activation parameters have been calculated.

The oxidation of DMSO\textsuperscript{51} by chromic acid in aqueous acid medium affords dimethyl sulphone as the sole product. The reaction is acid catalysed and exhibits fourth order dependence in [H\textsuperscript{+}]. This is in accord with the overall hydrolytic and
protolytic equilibrium which Cr(VI) undergoes in the acid medium. Solvent polarity studies indicate the reaction to be a positive ion-dipole type. The reaction exhibits 1 order dependence each on [oxidant] and [substrate]. Added Mn(II) retards the rate whereas rate enhancement is observed in the presence of 1,10-phenanthroline which is capable of forming a complex with chromic acid.

\[
\begin{align*}
\text{H}_3\text{C}-\text{S}^-\text{O} + \text{HCrO}_3^+ & \rightleftharpoons \text{H}_3\text{C}-\text{S}^-\text{Cr}^+\text{OH} \quad \quad \text{(66)} \\
\text{H}_3\text{C}-\text{O}^- + \text{Cr}^{(IV)} & \xrightarrow{k_{slow}} \text{H}_3\text{C}-\text{SO}_2^- + \text{HCr}^{(IV)}\text{O}_2^- \quad \quad \text{(67)} \\
\text{Cr}^{(IV)} + \text{Cr}^{(IV)} & \xrightarrow{\text{fast}} 2\text{Cr}^{(VI)} \\
\text{Cr}^{(V)} + \text{DMSO} & \xrightarrow{2e_{-}/\text{H}_2\text{O}} \text{DMSO} + \text{Cr}^{(III)} \quad \quad \text{(68)}
\end{align*}
\]

The complex is more effective as an oxidant than chromic acid alone. The complex also diminishes the disproportionation of Cr(VI) leading to enhancement of rate.

Oxidation of DMSO^{32} by Cr(VI) in aqueous acetic acid in the presence of HClO\textsubscript{4} has been reported and it is shown to be first order each in [Cr(VI)] and [DMSO] and second order in [H\textsuperscript{+}]. The pseudo-first order rate constant slightly
decrease with increase in [Cr(VI)], presumably because of the monomer-dimer equilibrium of the latter. The monomer concentrations are calculated testing the reported dimerisation constant of 98 in water because of non-availability of reliable data in 50% aqueous acetic acid medium in which the extent of dimerisation may be expected to be higher. The calculated monomer concentrations are used to calculate the rate constant $k_{corr} = \frac{k[Cr(VI)]}{[HCrO_4^-]}$ which remain constant for different initial concentration of Cr(VI). Protonation of the substrate takes place through H-bonding, as DMSO is a strong hydrogen acceptor. The intervention of Cr(IV) is evidenced by the progressive decrease in rate constant in the presence of increasing amounts of added Mn(II). When the reaction mixture containing acrylamide is kept over 24 hours and diluted with methanol, a precipitate is formed indicating polymerisation. The two prior equilibria have very low equilibrium constant so that an almost integral order of two in acidity results. In the presence of Cl$^-$ ions the reaction is retarded probably due to formation of ClCrO$_5^-$ which is a less potent oxidant than the acid chromate ion. The mechanistic scheme proposed accounts for the data obtained.

$$\text{(H}_3\text{C)}_2\text{SO} + \text{H}^+ \rightleftharpoons \text{(H}_3\text{C)}_2\text{S} \quad \text{OH} \quad \text{(69)}$$

$$\text{(H}_3\text{C)}_2\text{S}^+ + \text{OCrO}_3\text{H} \rightleftharpoons \text{(H}_3\text{C)}_2\text{S} - \text{OCrO}_3\text{H} \quad \text{OH} \quad \text{(70)}$$
\[
\begin{align*}
\text{(H}_3\text{C)}_2\text{S}^\text{2-} & + \text{CrO}_3\text{H} \quad \leftrightarrow \quad \text{(H}_3\text{C)}_2\text{S}^\text{2-} + \text{H}_2\text{CrO}_3 \\
\text{OH} & \quad \text{OH} & (\text{Cr}^{\text{IV}}) \\
\text{Fast} & \quad \text{H}_2\text{O} & . \\
\text{(H}_3\text{C)}_2\text{SO}_2 & + \text{H}_3\text{O}^+ & \text{--------(71)}
\end{align*}
\]

\[
\begin{align*}
\text{Cr}^{\text{IV}} & + \text{(CH}_3\text{)}_2\text{SO} \quad \rightarrow \quad \text{(H}_3\text{C)}_2\text{SO}_2 & + \text{Cr}^{\text{III}} & \text{--------(72)}
\end{align*}
\]