INTRODUCTION
CHAPTER - I
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1.1 Chemical kinetics

Chemical kinetics is a branch of chemistry concerned with the velocity of chemical reactions and the mechanism by which chemical reactions occur. It deals with the rates of chemical reactions and how rates depend on factors, such as concentration and temperature. Ideally, a complete reaction mechanism would require the knowledge of all the molecular details of the reaction.

In most of the reactions, it is only the disappearance of starting materials and the appearance of final products that can be detected. In general, however, the net reaction is not the whole story, but simply represents a summation of all the changes that occur. The net change may actually consist of several consecutive reactions each of which constitutes a step in the formation of final products.

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently to separate products, and to eliminate environmentally harmful by-products.
1.2 Oxidation and reduction reactions

Living organisms are all chemically reacting systems 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 are essential to the understanding of the nature of life and it is a task for the organic chemist to provide a clear picture of ways in which these chemical changes may take place with simple molecules, so that biologists can have a sure basis for their understanding of the behavior of complex organisms.

The redox reactions are very common in nature. It is commonly met within everyday life from living organisms to industries\(^2\). The perishing of rubber, browning of apples, rusting of iron and hardening of paints are some examples which involve direct oxidation by atmospheric oxygen. Inorganic chemists define oxidation as the loss of electrons. This definition cannot be directly applied to organic reactions since in most reactions direct electron transfer does not take place. According to organic chemists, oxidation is defined as the conversion of a functional group in a molecule from a low oxidation state category to a higher one\(^3\).

Among oxidation and reduction reactions, oxidation is the most commonly studied reaction. A large amount of kinetic study is concentrated on oxidation reactions. An interesting fact is that many oxidations are accompanied by the release of energy. Such released energy is the source of work in biological systems including the human system and also in man-made machines. Hence the knowledge of oxidative pathways
may be very useful in understanding processes in nature and synthetic situations. Oxidation is normally brought about in one of the following ways:\(^4,5\)

i. By the removal of an electron.

ii. By the removal of a hydrogen atom

iii. By the removal of hydride ion

iv. By the insertion of oxygen

v. By the catalytic dehydrogenation

The study of mechanisms of oxidation reactions has been a subject of major importance to many chemists and the elucidation of reaction mechanism is undoubtedly one of the most fascinating and challenging problems in chemistry. The study of reaction kinetics of chemical reactions is most important in deciding the reaction mechanisms. The kinetics deals with the study of change of concentrations of the components of a reaction system with the passage of time and the results are summarized in the form of rate expression. Many reactions studied kinetically can be explained by a particular set of simple process which are so reasonable and in accord with all chemical experience. The mechanism can successfully predict reaction products or the optimum conditions for running a chemical reaction.

### 1.3 Chromium(VI) reagents

The most common reagents are \(\text{H}_2\text{CrO}_4\), \(\text{K}_2\text{Cr}_2\text{O}_7\) and \(\text{CrO}_3\) approximately equivalent. Cr (VI) reagents are so powerful that they can oxidize alkenes and alkynes, breaking the carbon-carbon bond as ozone.
In non-aqueous solutions, oxidation by Cr(VI) does not go to completion (the intermediate partially oxidized material containing Cr must be hydrolyzed for oxidation to continue) thus, under these conditions, primary alcohols may be oxidized to aldehydes without forming carboxylic acid. The most common reagents for this partial oxidation are: PCC, or pyridinium chlorochromate (formed by dissolving CrO₃ and HCl in pyridine), collins reagent (CrO₃ in CH₂Cl₂) and chromyl chloride (CrO₂Cl₂).

1.3.1 Chromium trioxide (CrO₃)

Chromium trioxide is a strong oxidizing agent that is not soluble in most organic solvents and tends to explode in the presence of organic compounds and solvents.

\[
\begin{align*}
2 \text{CrO}_3 & \quad \overset{2\text{H}_2\text{O}}\longleftrightarrow \quad \text{2OH-Cr-OH} \quad \overset{\text{H}_2\text{O}}\leftrightarrow \quad \text{OH-Cr-O-Cr-OH} \\
& \quad \text{Chromic acid} \quad \text{Dichromic acid}
\end{align*}
\]

A solution of chromium trioxide in aqueous sulfuric acid can be safely mixed with acetone (Jones Reagent). If this mixture is slowly added to an alcohol in acetone, oxidation products such as carbonyl compounds and carboxylic acids can be isolated in good yields (Jones Oxidation).

\[
\begin{align*}
\text{R'OH} \quad \overset{\text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}}\longrightarrow \quad \text{R'CO}_\text{R} \\
\text{R-OH} \quad \overset{\text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}}\longrightarrow \quad \text{R'-CO}_\text{H}
\end{align*}
\]
The Jones Oxidation allows a relatively inexpensive conversion of secondary alcohols to ketones and of most primary alcohols to carboxylic acids. The oxidation of primary allylic and benzylic alcohols gives aldehydes. The alcohol and chromic acid form a chromate ester that either reacts intramolecularly or intermolecularly in the presence of a base (water) to yield the corresponding carbonyl compound:

\[
\text{HO-Cr-OH} + \text{OH}^- \rightarrow \text{HO-Cr(IV)} + \text{RCHO}
\]

Aldehydes that can form hydrates in the presence of water are further oxidized to carboxylic acids.
Some alcohols such as benzylic and allylic alcohols give aldehydes that do not form hydrates in significant amounts, these can therefore be selectively oxidized with unmodified Jones reagent to yield aldehydes.

1.3.2 Sarett reagent

The highly exothermic reaction of chromium trioxide when added to an excess of pyridine leads to the formation of \( \text{CrO}_3 \cdot 2 \text{pyridine} \) complex (Sarett reagent). Sarett reagent allows the oxidation of various primary alcohols to aldehydes due to the non-aqueous conditions. Unfortunately, the complex is highly hygroscopic and the preparation of the reagent is not without risk because the solvent occasionally catches fire during preparation. In addition, the use of pyridine as solvent does not permit the oxidation of base-sensitive substrates.

1.3.3 Collins reagent

A solution of \( \text{CrO}_3 \cdot 2 \text{pyridine} \) (Sarett Reagent) in methylene chloride is called the "Collins Reagent". The advantage over the sarett reagent is that the addition of one equivalent \( \text{CrO}_3 \) to a solution of two equivalents of pyridine in methylene chloride allows the convenient and safe preparation of the oxidant. Thus, most acid and base-sensitive
substrates can be oxidized with collins reagent, unlike both the sarett and jones reagent. The oxidant is especially useful for the oxidation of primary alcohols to aldehydes.\(^8\)

### 1.3.4 Etard reaction

The Etard reaction is a chemical reaction that involves the direct oxidation of an aromatic methyl group to an aldehyde using chromyl chloride. For example, toluene can be oxidized to benzaldehyde.\(^9\)

![Etard reaction diagram](image)

### 1.4 Toxicity of Cr(VI) reagents

Cr(VI) reagents have been shown to be carcinogenic, upon ingestion either through the stomach or the lungs. Not many years ago chromic acid solutions were the way to clean glassware (they remove organic compounds very well and leave the glass sparkling). They have been shown to leave traces of Cr(VI) on the glass, which can be death to a Grignard reagent. The chromate (CrO\(_4^{2-}\)) looks like sulfate to cells, and is readily incorporated. In the cell, it oxidizes something and is converted to Cr(III). It is the Cr(III) that actually causes the damage that leads to cancer but the Cr(III) itself cannot get into the cells, it has to enter as Cr(VI). Hexavalent chromium is used for the
production of stainless steel, textile dyes, wood preservation, leather tanning, and as anti-
corrosion and conversion coatings as well as a variety of niche uses\textsuperscript{10}.

Cr(VI) is highly toxic and hazardous in nature whereas the reduced chromium(III) is biologically active. Cr(VI) act as irritants of the skin and mucous membranes. Cr(VI) originating from tanneries and industrial wastes contaminates soil, thus presenting a serious environmental hazard due to its toxicity.

Water insoluble Cr(III) compounds and chromium metal are not considered as a health hazard, while the toxicity and carcinogenic properties of chromium(VI) have been known for a long time\textsuperscript{11}.

The acute oral toxicity for Cr(VI) ranges between 50 and 150 $\mu$g/kg. In the body, Cr(VI) is reduced by several mechanisms to chromium(III) already in the blood before it enters the cells. The Cr(III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism. The acute toxicity of Cr(VI) is due to its strong oxidation properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions. Hemolysis, renal and liver failure are the results of these damages.

1.5 Cr(VI) compounds

In an aqueous solution, chromate and dichromate anions are in a chemical equilibrium.

\[ 2\text{CrO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O} \]
In nature, chromium mostly exists in the Cr(VI) and Cr(III) forms, which differ widely in their physicochemical properties and biological activities. Cr(VI) as chromate or dichromate is highly soluble in water, while Cr(III) as hydroxide is insoluble, and Cr(VI) is reported to be highly toxic, while Cr(III) is an essential nutrient and is used as a dietary supplement. The reduction of Cr(VI) in the presence of suitable biomolecules, leading to the formation of Cr(V), is believed to be responsible for the mutagenicity and carcinogenicity of Cr(VI).

Cr(VI) compounds are widely used and very powerful oxidation agents for several functional groups. Their most common application is the selective oxidation of primary and secondary alcohols to aldehydes, ketones or carboxylic acids. The mechanism of this reaction is known to proceed via chromyl ester which are cleaved to their products through base-catalysis. During reaction Cr species of lower oxidation state (IV and V) are also involved. Aldehydes derived from primary alcohols can only be isolated under certain reaction conditions or by using specialized oxidation reagents.

1.6 Cr(VI) as an oxidant

Chromium compounds have been widely used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents capable of oxidizing almost all the oxidizable organic functional groups. The development of newer Cr(VI) reagents for the oxidation of organic substrates continues to be of interest.

Generally Cr(VI) oxidation reactions have been performed in aqueous acidic conditions, the source of Cr(VI) being chromium trioxide and sodium or potassium.
dichromate, chromyl chloride, t-butyl chromate and coordination complexes of chromium trioxide. Aqueous sulfuric acid and acetic acid are the most frequently employed acids. Since the oxidation is strongly acid catalyzed, the reaction rate is generally high. Acetone, benzene, methylene chloride, ether are often used as co-solvents in the case of water insoluble organic compounds.

However, a variety of new Cr(VI) oxidants together with special reaction conditions have been introduced for the chemospecific, regiospecific and stereospecific oxidative degeneration of functional groups in highly sensitive systems. The oxidation rate is generally high under acid catalyzed conditions, the low pH of the reaction medium and the presence of water favoring hydrolytic conditions exclude the use of this class of reagents for the oxidation of molecules containing acid sensitive groups.

Polymer supported Cr(VI) reagents have also been developed. These reagents offer the advantage of reducing the work procedure. Recently some neutral or almost neutral Cr(VI) reagents have been developed to effect oxidation under mild conditions.

In recent years, kinetics and mechanism of oxidation reactions of Cr(VI) for a number of substrates have been fairly well studied. The interesting point in the Cr(VI) oxidation is, the mechanism of oxidation varies with the nature of the Cr(VI) species and the solvent used.

1.6.1 Oxidation with chromic acid

Chromic acid oxidation of saturated hydrocarbons has no selectivity and requires vigorous conditions. But the oxidative degradation has been extensively studied as an
effective method for structure determination. It has been utilized for the determination of the number of methyl groups present in the aliphatic chain. It is known as Kuhn-Roth oxidation and depends on the preferential attack of chromic acid on secondary and tertiary C-H bonds while preserving the methyl group intact^37,38.

Oxidative fission reactions occur when olefinic double bonds are reacted with chromic acid in presence of aqueous sulphuric acid. A symmetric disubstituted olefins lead to the formation of an acid with the same number of carbon atoms as the original olefins39.

Many important Cr(VI) oxidations of alcohols are carried out under acidic conditions. Chromic acid in aqueous sulphuric acid is used to convert alcohols to carbonyl compounds40. The selective oxidation of a primary alcohol in the presence of a secondary one has been carried out with a solution of chromic acid in 90 percent acetic acid41. Less hindered primary alcohols are converted to the corresponding carboxylic acids under milder conditions42.

The rate law for the oxidation of isopropyl alcohol43 has been given as:

\[
\text{Rate} = k_\text{a} [\text{HCrO}_4^-] [\text{R}_2\text{CHOH}] [\text{H}^+] + k_\text{b} [\text{HCrO}_3^-] [\text{R}_2\text{CHOH}] [\text{H}^+]^2
\]

For all other primary and secondary alcohols, the rate depends on the concentration of the acid chromate rather than on total chromium concentration. By comparing the rates of oxidation of \text{Me}_2\text{CHOH} and \text{Me}_2\text{CDOH}, a kinetic isotopic effect
It suggested that secondary hydrogen atom is removed in the rate controlling step of oxidation. Thus the oxidation occurs rapidly with the formation of a reversible chromate ester which decomposes to the product by the cleavage of $\alpha$ – carbon-hydrogen bond.\(^4^5\)

\[
R_2\text{CHOH} + H\text{CrO}_4^- + 2H^+ \rightleftharpoons R_2\text{CHO}\text{CrO}_2\text{OH} + H_2O
\]

\[
R_2\text{CHO}\text{CrO}_2\text{OH} \xrightarrow{\text{slow}} R_2\text{C}=\text{O} + H_2\text{CrO}_3
\]

**1.6.2 Oxidation with chromyl chloride**

In aprotic solvents like carbon tetrachloride or carbon disulphide chromyl chloride adds to alkyl arenes and to certain saturated hydrocarbons to give brown insoluble 2:1 adducts called Etard complexes. On hydrolysis, these complexes are decomposed to mixtures of alcohols, carbonyl and chlorinated compounds.\(^4^6-4^8\) The reaction of toluene with chromyl chloride is given as,

\[
\text{CH}_3\text{C}_{(p)} + 2\text{CrO}_2\text{Cl}_2 \rightarrow \text{CH}_3\text{C}_{(p)}\text{CrO}_2\text{Cl}_2
\]

\[
\text{CH}_3\text{C}_{(p)}\text{CHO} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{C}_{(p)}\text{C} = \text{Cl} + \text{Cl}
\]

When alkenes are reacted with chromyl chloride in 1:1 molar ratio, carbonyl compounds are obtained due to the migration of a hydride or alkyl group.\(^4^9\) In a similar
molar ratio halogen or alkyl substituted phenols react to form brown amorphous solids which on hydrolysis give quinines, diphenoquinones and polymeric compounds^50.

1.6.3 Oxidation with jones' reagent

A chilled solution of 2.67 mol of chromium trioxide in 230 ml concentrated sulphuric acid and 400 ml water made up to one litre with cosolvent acetone is called Jones' reagent. This solution corresponds to 8N oxygen. It oxidizes most of the alcohols to the carbonyl compounds or carboxylic acids. Normally there is little or no epimerization of adjacent chiral centres^51 and the double and triple bonds are inert under the reaction conditions. The reactions are given as,

Benzyl ethers are oxidized with Jones' reagent at 0°C to form the corresponding carbonyl compounds and the carboxylic acids^52.

1.6.4 Oxidation with sodium dichromate

Aromatic hydrocarbons can be oxidized without destruction of the ring or formation of quinine through control of the pH with aqueous sodium dichromate.
Oxidation of the aromatic nucleus increases with increasing acid concentration. Naphthalene, biphenyl and phenanthrene are completely resistant for oxidation. But the corresponding mono- and polyalkyl-substituted arenes are easily oxidized in high yields to polynuclear carboxylic acids. For instance, the oxidation of methyl substituted naphthalene is given as,

\[
\text{Oxidation of naphthalene:} \quad \text{H}_2\text{O} \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7} \text{HOOC}\text{COOH}
\]

\(\alpha\)-allyl phenols are oxidized with tetra alkyl ammonium dichromate in boiling benzene. The reagent is obtained by treating potassium dichromate with adogen 464 (a commercial mixture of methyltrialkyl ammonium chloride) in benzene in a 1:2 ratio.

1.6.5 Oxidation with silver chromate and iodine

Alkenes react with silver chromate and iodine in dichloromethane at 0°C in the presence pyridine to give high yield of the corresponding \(\alpha\)-iodocarbonyl derivatives. Electron rich olefins give better results and the oxidation appears to be regioselective since terminal olefins are converted exclusively to the corresponding \(\alpha\)-iodoketones.

\[
\text{R-CH=CH}_2 \xrightarrow{\text{Ag}_2\text{CrO}_4/\text{I}_2} \text{CH}_3\text{Cl} \quad \text{R-C-CH}_2\text{-I}
\]
1.6.6 Oxidation with compounds of Cr(VI) and heterocyclic bases

The fairly stable chromium trioxide-(pyridine)$_2$ complex has been employed by Sarett$^{56}$ for the oxidation of steroidal alcohols. The oxidant is taken in 3:1 molar ratio with the substrate at room temperature. The yield of ketones is about 90 percent. Acid sensitive functional groups like acetal groups as well as double bonds and thioethers are not affected by the reagent. Pyridinium dichromate has been used for the oxidation of alcohols to the corresponding ketones with a yield of about 88 percent$^{57,58}$. The reagent is used in the form of a dimethyl formamide solution or a methylene chloride suspension. There is no E to Z isomerization in the reaction product. The univalent electrophilic reagent pyridinium fluorochromate is used to convert primary and secondary alcohols in high yields to the corresponding aldehydes and ketones when the reaction is conducted in methylene chloride at room temperature$^{59}$. It is superior to pyridinium dichromate in the sense that it does not react with acetonitrile and hence acetonitrile may be used as the solvent. Chromium trioxide-3,5-dimethylpyrazole complex is employed for the effective oxidation of alcohols to the corresponding carbonyl compound in methylene chloride at room temperature$^{60}$. Two equivalents of the alcohols react with five equivalents of the complex. The 2, 2'-bipyridine salt of chlorochromic acid is an useful oxidizing agent for the conversion of primary and secondary alcohols to carbonyl compounds$^{61}$. The complex is easily prepared by adding 2, 2'-dipyridine to an equimolar mixture of chromic anhydride and dilute hydrochloric acid. It is non hygroscopic and air stable. This reagent is useful for the oxidation of compound with acid sensitive producing group due to internal buffering by the 2, 2'-bipyridyl system.
1.7 Linear free-energy relationships

Empirical correlations of the reactivities of organic compounds are usually linear relationships involving logarithm of rate \(k\) or equilibrium \(K\) constants. Many such relationships involve side chain reaction of mata- or para-substituted benzene derivatives and may be summarized by a very simple equation devised by Hammett\(^{62,63}\). The simple behaviour is due to the influence of these substituents on side-chain, the reactivity being almost entirely polar in nature.

The Hammett equation takes the forms

\[
\log k = \log k_o + \sigma \rho \\
\log K = \log K_o + \sigma \rho
\]

(1)  
(2)

Where \(k\) and \(K\) is the rate or equilibrium constant, respectively for a side chain reaction of a \emph{meta}- and \emph{para}- substituted benzene derivatives. The symbol \(k_o\) or \(K_o\) denotes the statistical quantity approximating to \(k\) or \(K\) for the unsubstituted or parent compound. The substituent constant ‘\(\sigma\)’ measures the polar effect of the substituent and is, in principle independent of the nature of the reaction. The reaction constant \(\rho\), depends on the nature of the reaction and measures the susceptibility of the reaction to the polar effect. The Hammett equation is a more sophisticated extension of the Hixon-Jones approach\(^{64}\). Hammett chose the dissociation constants of substituted benzoic acids in water at 298 K as the standard for determining ‘\(\sigma\)’ values for which \(\rho\) is defined as, 1.0. Thus ‘\(\sigma\)’ becomes \(\log K / K_o\) where \(K\) is the ionization constant of substituted benzoic acid and \(K_o\) is that of benzoic acid itself.
The parent of all the relationships of this kind is the discovery by Bronsted and Pederson\textsuperscript{65} of the general acid base catalysis and of the catalyzed reactions that are linearly related to those of acidity constants of the catalyzing acid (or) base. Pederson\textsuperscript{66} clearly recognized that this is a relationship between the rates and the equilibrium of the same series of reactions, i.e., the proton transfer process. Hammett and Pflunger\textsuperscript{67} have extended the idea of finding out a quantitative relation between the logarithms of rate constants of reactions,

\[ \text{RCOOCH}_3 + \text{N(CH}_3)_3 \rightarrow \text{RCOO}^+ + \text{N(CH}_3)_4 \]  \hspace{1cm} (3)

and those of equilibrium constants of the reactions,

\[ \text{RCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{RCOO}^- + \text{H}_3\text{O}^+ \]  \hspace{1cm} (4)

Burkhardt\textsuperscript{68} and Hammett\textsuperscript{69} have found many linear free energy relationships in the reactions of substituted benzene derivatives and thus Hammett could systematize these relationships in the form of the two parameter equations.(Equations 1 and 2).

The equations 1 and 2 are often called the linear free-energy relationship between the free-energies of activation (in rate processes) for one homologous series of reactions and those of another. This can be shown by transforming the Hammett equation into the form, with the help of the Erying equation\textsuperscript{70}.

\[ \frac{-\Delta G^\#}{RT} = \frac{-\Delta G_0^\# + \rho \sigma}{RT} \]  \hspace{1cm} (5)
With the help of the Erying equation. In equivalent terms, equation (4) can be represented as

$$\Delta G^\# = \Delta G_o^\# - \rho \sigma RT$$  \hspace{1cm} (6)

Here $\Delta G_o^\#$, $\rho$ and $T$ are constants. For a second reaction series having the reaction constant, $\rho'$

$$\Delta G'^\# = \Delta G_o'^\# - \rho' \sigma RT$$  \hspace{1cm} (7)

Equations (6) and (7) lead to the relationship

$$\frac{\Delta G^\#}{\rho} - \frac{\Delta G'^\#}{\rho'} = \frac{\Delta G_o^\#}{\rho} - \frac{\Delta G_o'^\#}{\rho'}$$  \hspace{1cm} (8)

This may be written as

$$\Delta G^\# = \frac{\rho}{\rho'} \Delta G'^\# + \text{Constant}$$  \hspace{1cm} (9)

Equation (9) implies the linear free-energy relationship imbedded in the Hammett equation, because it is in the form of a linear equation and in it the free energy changes associated with the members of the reaction series are linearly related to free-energy changes associated with the correspondingly substituted members of another reaction series.

The reaction constant, $\rho$ is a measure of the susceptibility of the reaction centre to the influence of the substituents. A reaction which is facilitated by reducing the electron density at the reaction centre has a positive value of $\rho$ and the one facilitated by increasing the electron density at the reaction centre has a negative $\rho$ value. The $\rho$ scale covers roughly 0 + or - 4 and this may be taken as a measure of the extent of transmission of the electronic effects of substituents.
The electron density at the reaction site is determined by the ability of the substituents to withdraw or donate electrons and is measured by ‘σ’ constants. A positive value of ‘σ’ shows the greater ability of the substituent to attract electrons relative to hydrogen. A negative value of ‘σ’ indicates that the substituent is weaker electron attracting than hydrogen and it increases the electron density at the reaction site. While treating the applicability of the Hammett equation to a particular reaction, it is customary to plot log k (or) log K versus ‘σ’ constants appropriate to the applicability. The slope of the correlation line defines the values of the reaction constant, ρ.

In general there are three kinds of problem solved in any kinetic investigations. The first is the establishment of the relationship between the velocity and various factors such as temperature, pressure, concentration. The second is to arrive at an interpretation of the empirical laws in terms of reaction mechanism incorporating the possible intermediate and the product formed in the reaction. The third problem is to correlate the reactivity with structure. The present study deals with the kinetics and mechanism of oxidation of phenols and cyclicketones by benzyltriethylammonium chlorochromate (BTEACC) and chalcones and anilines by morpholinium chlorochromate (MCC). The reaction mechanism explains the all individual steps in the overall reaction. Kinetics is very useful in determining the individual steps of a reaction, it is rather limited in giving stereochemical details. The most important circumstantial evidence as to reaction mechanism is the identity of the products formed.
1.8 Literature survey on benzyltriethylammonium chlorochromate

The use of alkyl ammonium chromates for the oxidation of alcohols under mild, neutral conditions. They have the advantage of being much more soluble than pyridinium chlorochromate and pyridinium dichromate in standard organic solvents and are readily prepared from Cr(VI) oxide.

One of the Cr(VI) reagent is benzyltriethylammonium chlorochromate (BTEACC) which has emerged as a very useful and versatile oxidant deserving wide spread applications. BTEACC is an orange solid (m.p. 87 – 91°C). It is very soluble in water. It was demonstrated that this reagent (chromate or dichromate) shows good selectivity for benzylic and allylic alcohol.

![Structure of BTEACC](image)

Chouhan et al. studied the oxidation of six aliphatic aldehydes by benzyltriethylammonium chlorochromate (BTEACC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order each in BTEACC and the aldehyde. The reaction is catalyzed by hydrogen ions. The
hydrogen-ion dependence has the form: \( k_{\text{obs}} = a + b[H^+] \). The oxidation of acetaldehyde has been studied in 19 different organic solvents. The solvent effect has been analyzed using Taft's and Swain's multiparametric equations. A mechanism involving transfer of hydride ion has been suggested.

Kaur et al.,\(^7\) have reported the oxidation of several aliphatic secondary alcohols by benzyltriethylammonium chlorochromate in dimethylsulfoxide leads to the formation of corresponding ketones. The reaction is first order each in benzyltriethylammonium chlorochromate and the alcohols. The reaction is catalyzed by hydrogen ions. Hydrogen-ion dependence has the form: \( k_{\text{obs}} = a + b[H^+] \). Oxidation of 2-propanol has been studied in nineteen different organic solvents. The solvent effect has been analyzed using Taft's and Swain's multiparametric equations. A mechanism involving transfer of hydride ion from alcohol to the oxidant via a chromate ester has been proposed.

Oxidation of thirty six mono substituted benzaldehydes by benzyltriethylammonium chlorochromate in dimethyl sulphoxide, leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to chlorochromate and aldehydes. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form \( k_{\text{obs}} = a + b[H^+] \). The oxidation of duteriated benzaldehyde exhibits substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analyzed using Taft's and Swain's multi-parametric equations. The rates of the oxidation of para- and meta-substituted benzaldehydes showed excellent correlation in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes
were correlated well with tetrameramic LDRE equation. A suitable mechanism has been proposed by Sonu Barthora et al.,

The oxidation of glycollic, lactic, malic and a few substituted mandelic acids by benzyltriethylammonium chlorochromate (BTEACC) in dimethyl sulphoxide leads to formation of the corresponding oxyacids. The reaction is first order in BTEACC. Michaelis-Menten type of kinetics is observed with respect to the hydroxy acids. Polymerisation of acrylonitrile is not induced in this reaction. The oxidation of α-deuteriomandelic acid shows primary kinetic isotope effect ($k_{H^1}/k_{D} = 5.51$ at 298 K). The reaction does not exhibit the solvent isotope effect. The reaction is catalyzed by hydrogen ions and hydrogen ion dependence has the form: $k_{obs} = a + b [H^+]$. Oxidation of p-methyl mandelic acid has been studied in 19 different organic solvents. The solvent effect has been analyzed by using Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester was proposed.

The oxidation of nine aliphatic primary alcohols by benzyltriethylammonium chlorochromate (BTEACC) in dimethylsulfoxide (DMSO) leads to the formation of corresponding aldehydes. The reaction is first order with respect to both BTEACC and the alcohol. The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b [H^+]$. The oxidation of [1,1-2H2]ethanol (MeCD2OH) exhibits a substantial primary kinetic isotope effect. The reaction has been studied in nineteen different organic solvents. The solvent effect was analyzed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed by Mishra et al.,
Chouhan and Sharma\textsuperscript{78} reported that the kinetics and mechanism of oxidation of formic and oxalic acids by benzyltriethylammonium chlorochromate (BTEACC) in dimethyl sulphoxide. The main product of oxidation was carbon dioxide. The reaction is first order with respect to BTEACC. The reaction was acid catalyzed and the acid dependence has the form: $k_{\text{obs}} = a + b[H^+]$. The oxidation of $\alpha$-deuterioformic acid exhibits a substantial primary kinetic isotope effect ($k_{H}/k_{D} = 5.36$ at 298 K). The reaction has been studied in nineteen different organic solvents and solvent effect analyzed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate determining step.

1.9 Literature survey on morpholinium chlorochromate

Chromium(VI) complexes of heterocyclic bases have been reported as a mild and selective oxidizing reagent in the synthetic organic chemistry. Morpholinium chlorochromate (MCC), a mild and selective oxidant\textsuperscript{79}, stable, orange yellow solids.mp.215-217°C

![Structure of MCC](image)

Malani et al.,\textsuperscript{80} have studied the oxidation of thioglycollic, thiolactic and thiomalic acids by morpholinium chlorochromate was first order both in MCC and
thioacids. The hydrogen ion dependence takes the form $k_{\text{obs}} = a + b [H^+]$. The solvent effect has been analyzed by using Kamlet's and Swain's multiparametric equations. A mechanism involving the formation of a thioester and its decomposition in slow step is also proposed.

The oxidation of six aliphatic aldehydes by morpholinium chlorochromate (MCC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order each in MCC and the aldehyde. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{\text{obs}} = a + b[H^+]$. The oxidation of deuteriated acetaldehyde, MeCDO, exhibited a substantial primary kinetic isotope effect ($k_{H}/k_{D} = 5.95$ at 298 K). The oxidation of acetaldehyde has been studied in 19 different organic solvents. The solvent effect has been analyzed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's $\sigma^*$ values; reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested by Neelam Soni et al.\textsuperscript{81}

Malani and coworkers\textsuperscript{82} studied the oxidation of glycollic, lactic, malic and a few substituted mandelic acids by morpholinium chlorochromate (MCC) in dimethylsulfoxide (DMSO) leads to the corresponding o xoacids. The reaction is first order each in MCC and hydroxyacid. The reaction failed to induce the polymerisation of acrylonitrile. The oxidation of $\alpha$—deuteriomandelic acid shows a primary kinetic isotope effect ($k_{H}/k_{D} = 5.63$ at 298 K) but does not exhibit a solvent isotope effect. The reaction is catalyzed by hydrogen ions according to: $k_{\text{obs}} = a + b [H^+]$. The oxidation of $p$-methyl mandelic acid has been studied in 19 different organic solvents and the solvent effect analysed using
Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester is proposed.

Choudhary et al.\textsuperscript{83} studied the oxidation of thirty six monosubstituted benzaldehydes by morpholinium chlorochromate (MCC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to MCC. A MichaelisMenten type kinetics is observed with respect to benzaldehydes. The reaction is promoted by hydrogen ions; the hydrogen ion dependence has the form \( k_{obs} = a + b [H^+] \). The rates of the oxidation of para - and meta-substituted benzaldehydes showed excellent correlation in terms of Charton’s triparametric LDR equation; whereas the oxidation of ortho -substituted benzaldehydes were correlated well with tetra parametric LDRS equation. The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

Bishnoi et al.\textsuperscript{84} have reported the kinetics and mechanism of oxidation of formic and oxalic acids by morpholinium chlorochromate (MCC) in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to MCC. The reaction is acid-catalysed and the acid dependence has the form: \( k_{(obs)} = a + b[H^+] \). The oxidation of alpha-deuteroformic acid exhibits a substantial primary kinetic isotope effect \( (k(H)/k(D)= 5.58 \text{ at } 298 \text{ K}) \). The reaction has been studied in 19 different organic solvents and the solvent effect has been analyzed using the Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate-determining step. Suitable mechanisms have been proposed.
Oxidation of nine aliphatic primary alcohols by morpholinium chlorochromate (MCC) in dimethylsulfoxide leads to the transformation of alcohols to the corresponding aldehydes was found to be Choudhary et al., The reaction is first order with respect to both MCC and the alcohol both. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence has the form: \( k_{\text{obs}} = a + b[H^+] \). The oxidation of \[1,1-^2H_2\]ethanol (MeCD\(_2\)OH) exhibits a substantial primary kinetic isotope effect. The reaction has been studied in nineteen different organic solvents. The solvent effect was analyzed using Taft's and Swain's multiparametric equations. A suitable mechanism has been proposed.

Oxidation of benzyl alcohol and some ortho-, meta- and para-monosubstituted derivatives by morpholinium chlorochromate in dimethyl sulphoxide leads to the formation of corresponding benzaldehydes. The reaction is first order each in both morpholinium chlorochromate and the alcohol. The reaction is promoted by hydrogen ions; the hydrogen ion dependence has the form \( k_{\text{obs}} = a + b[H^+] \). The reaction has been studied in nineteen organic solvents and the effect of solvent analyzed using Taft's and Swain's multi-parametric equations. The rates of oxidation of para- and meta-substituted benzyl alcohols have been correlated in terms of Charton’s triparametric LDR equation whereas the oxidation of ortho-substituted benzyl alcohols with tetraperametric LDRI equation. A suitable mechanism has been proposed by Neelam Soni et al.,

1.10 Literature survey of oxidation kinetics of phenols

Phenols and phenolic compounds pose a significant threat to the environment and are commonly found as dilute contaminants in ground water and are commonly found as
dilute contaminates in ground water and surface water\textsuperscript{87-89}, whereas the oxidized product i.e. quinones possess pronounced bio-activity\textsuperscript{90} and consequently are important for medicine\textsuperscript{91}. Since many substituted phenols are readily available and usually quite inexpensive they serve as desirable starting materials for the synthesis of \textit{p}-benzoquinone, which constitute important oxidations in organic synthesis.

Phenol and ortho or \textit{p}-substituted phenols with groups like halogen, -OH, -OR, -Me and -t-Bu are oxidized to \textit{ortho}- or \textit{para}- benzoquinones by a variety of oxidizing agents like acid dichromate, lead tetraacetate, hydroiodic acid, atmospheric oxygen etc. For auto oxidation a free-radical mechanism is known to operate\textsuperscript{92}.

\[
\text{OH} \quad \text{[O]} \quad \text{OH}
\]

The oxidation by CrO\textsubscript{3}/t-BuOH in CH\textsubscript{2}Cl\textsubscript{2} at room temperature leads to the peroxidation at the \textit{para}-position of \textit{para}-substituted phenols\textsuperscript{93}. PDC instead of CrO\textsubscript{3} in the above reaction gives the same product.

\[
\text{OH} \quad \text{CrO}_3/t\text{-BuOH} \quad \text{CH}_2\text{Cl}_2, 25^\circ \text{C} \quad \text{O}
\]

Mare et al.,\textsuperscript{94} studied the kinetics and mechanism of phenol by the aqueous solutions of hypochlorous acids. Kinetics of chlorination of phenol by N-
chloroacetanilide has been studied by Hurst and Soper\textsuperscript{95}. The kinetic data indicated that N-chloroacetanilide, chlorinated phenol partly by preliminary hydrolysis to hypochlorous acid and partly by direct interaction with the phenoxide ion.

Chlorination of phenols and substituted phenols by peroxydisulphate and chloride ion has been reported by Radhakrishnamurthi and Sasmal\textsuperscript{96}. The reaction is first order in [peroxydisulphate] and fractional order in [phenols] and inverse fractional order in [acid].

Radhakrishnamurthi and Sahu\textsuperscript{97} have studied the kinetics of chlorination of phenol by N-chlorosuccinimide. The reaction is first order in the [haloginating agent] and zero order in the [substrate] in acetic acid medium.

Prasad Rao et al.,\textsuperscript{98} have studied the iodination of phenols and anisoles by iodine monochloride in the presence of mercuric acetate in aqueous acetic acid. Kinetics of chlorination of some substituted phenols by N-chlorosuccinimide.

Kinetics and mechanism of phenols and substituted phenols with NCP were followed by Ganapathy and Palaniappan a LFER study has been reported\textsuperscript{99}. Alexander and Tompkins\textsuperscript{100} reported the permanganate oxidation of nitrophenols.

Kinetics and mechanism of iodination of disubstituted phenols in aqueous acetic-acid medium by iodine monochloride has been reported by Vibhute and Dasharath\textsuperscript{101}. The order with respect to substrate and oxidant is one. A tentative reaction mechanism for these reactions have been proposed.
Khansoleet al.,\textsuperscript{102} have been reported that the oxidation of phenols by isoquinolinium bromochromate (IQBC) in aqueous acetic acid leads to the formation of corresponding quinones. The reaction is first order with respect to both phenol and IQBC and catalysed by hydrogen ion. The rate of oxidation decreases with increase in dielectric constant of solvent indicating ion-dipole interaction. The rate of oxidation decreases with increase in concentration of KCl, this may be due to the formation of less reactive species by interaction of $\text{Cl}^-$ and protonated IQBC. The specific rates of oxidizing phenol reaction correlate with substituents constants affording negative reaction constants. Hammett plot is found to be valid and the correlation between enthalpies and free energies of activation is reasonably linear with an isokinetic temperature of 320 K.

The kinetics of oxidation of phenols by pyridinium dichromate (PDC) in 60\% acetic acid-water (v/v) medium have been studied by Palaniappan et al.,\textsuperscript{103} The reaction shows unit order dependence each with respect to oxidant and substrate. The reaction is acid catalysed and the medium of low dielectric constant favours the reaction. Increase in ionic strength has no effect on the reaction rate. In the case of substituted phenols, the order with respect to substrate varies depending upon the nature of the substituent present in the ring. In general, the electron withdrawing substituents retard the reaction rate while the electron releasing substituents enhance the rate of the reaction.

Kinetics of oxidation of phenols such as $p$-hydroxy benzoic acid, $p$-chloro phenol, $m$-cresol, $p$-nitrophenol and $p$-cresol in glacial acetic acid as a solvent in the temperature range 25–45$^\circ$C, using pyridinium fluorochromate (PFC) as a mild oxidation agent have been investigated by Patil and Joshi\textsuperscript{104}. The overall order of oxidation of the phenols is
found to be two and the individual order as one in each reactant [the stoichiometry of the reaction is 1 : 1]. An increase in solvent polarity increases the reaction rate. The activation energy and other thermodynamic parameters are determined. A probable reaction mechanism was proposed.

The kinetic studies on the oxidation of some of the meta- and para- substituted phenols by QDC has been studied by ravishankar. Recently, Sekar and Anbarasu reported the linear free energy relationships in the Cr(VI) oxidation of phenols.

1.11 Literature survey of oxidation kinetics of anilines

Aniline is oily and, although colorless, it slowly oxidizes and resinifies in air, giving the sample a red-brown tint. It ignites readily, burning with a smoky flame. Chemically, aniline is a weak base. Aniline reacts with strong acids to form anilinium (or phenylammonium) ion (C₆H₅-NH₃⁺), and reacts with acyl halides such as acetyl chloride to form amides.

Anilines are the most widespread and principal contaminants of industrial waste waters. Since aniline is very harmful to the environment, its removal from the environment is the ultimate goal of basic research. For this purpose deep understanding of the mechanism of the process of aniline is needed.

Patwari, Khansole and Vibhut have been reported that the oxidation of anilines by isoquinolinium bromochromate(IQBC) in aqueous acetic acid leads to the formation of corresponding azobenzenes. The reaction was first order with respect to
both aniline and IQBC and it was catalysed by hydrogen ion. The rate of oxidation decreases with increasing dielectric constant of solvent, indicating the ion dipole interaction. The rate of oxidation decreases with increase in concentration of KCl. The specific rate of oxidizing species anilines reaction correlates with substituents constant affording a negative reaction constant. Hammett plot was found to be valid and the correlation between enthalpies and free energies of activation was linear with an isokinetic temperature of 401 K. Kaushik\textsuperscript{108} reported the periodate oxidation of anilines in acetone-water medium.

The imidazolium fluorochromate (IFC) oxidation of \textit{meta-} and \textit{para-}substituted anilines, in seven organic solvents, in the presence of \textit{p}-toluenesulfonic acid (TsOH) was first order in IFC and TsOH and was zero order with respect to substrate. The IFC oxidation of 15 \textit{meta-} and \textit{para-}substituted anilines at 299–322 K complies with the isokinetic relationship but not to any of the linear free energy relationships; the isokinetic temperature lies within the experimental range. The specific rate of oxidizing species-anilines reaction ($k_2$) correlates with substituent constants affording negative reaction constants have been observed\textsuperscript{109} and Correlation analysis of reactivity in the oxidation of anilines by nicotinium dichromate in nonaqueous media\textsuperscript{110} by Bhuvaneswari and Elango.

Subbiah Meenakshisundaram et al.\textsuperscript{111} have been performed that the mechanistic studies on the oxidation of 18 \textit{meta-}, \textit{para-}, and \textit{ortho-}substituted anilines by HOOSO$_3$\textsuperscript{-} in aqueous acetonitrile medium. The addition of \textit{p}-toluenesulfonic acid (TsOH) retards the reaction. The increase in the reactivity of anilines as the medium was made more
aqueous was interpreted. The reaction was enhanced by electron-donating groups on the amine in the series consistent with the rate-limiting nucleophilic attack of the amine on the persulfate oxygen. The proposed mechanism involves the conversion of phenylhydroxylamine to nitrosobenzene in a fast step. The ESR study reveals the absence of free radicals in the reaction. Various attempts have been made to analyze the experimental rate constants in terms of LFER plots.

Fan et al. reported that the reaction kinetics of aniline oxidation with chlorine dioxide in water. Results showed that the reaction was first-order with respect to both chlorine dioxide and aniline, and the entire reaction was of second-order. Oxidation pathways were proposed and discussed.

Panigrahi and Mahapatro have been observed the pyridinium chlorochromate (PCC) oxidizes aniline and substituted anilines except nitro anilines smoothly in chlorobenzene–nitrobenzene mixtures in the presence of dichloroacetic acid. The reaction has unit dependence on each of the aniline, PCC, and dichloroacetic acid concentrations. Electron-releasing substituents accelerate the reaction, whereas electron withdrawing groups retard the reaction, and the rate data obey Hammett's relationship. The reaction constant $\rho$ was -3.75. Azobenzene and $p$-benzoquinone have been obtained as products.

Sadagopa Ramanujam and Norman M. Trieff have been studied that the rates of reactions of aniline and substituted anilines with chloramine $\text{T(CAT)}$ to form $N$-chloroanilines. Each reaction showed first-order dependence on $\text{CAT}$ and fractional order dependence on the amine. The latter observation indicates that the reaction
involves formation of a complex in a fast equilibrium step followed by slow decomposition of the complex. The equilibrium constant \( K \) for the formation of the complex and its decomposition rate constant \( k_2 \) in each case have been calculated from the plot of \( 1/k_{obs} \) versus \( 1/\text{[amine]} \). In addition, the reaction constant \( p = -0.976 \), obtained from a Hammett plot) and thermodynamic parameters have been evaluated, and mechanisms were proposed.

Uma et al.,\(^\text{115}\) studied the kinetics of oxidation of substituted anilines with N-chlorosuccinimide in 100% acetic acid medium. Baier et al.,\(^\text{116}\) investigated the oxidation of aniline with bromate in \( \text{H}_2\text{SO}_4 \). The kinetics of chromic acid oxidation of aniline in 10% aqueous acetic acid medium has been studied by Shrivastava and Ranver\(^\text{117}\).

1.12 Literature survey of oxidation kinetics of cyclic ketones

The carbonyl group plays a central role in organic chemistry as well as in biochemistry by the number of important reactions it may undergo, by its potential utilization for generating stereochemistry and molecular asymmetry and its function as a building block in the construction of natural and synthetic molecules and biopolymers. The chemical properties of carbonyl compounds depend markedly upon the nature of remaining two bonds to the carbonyl carbon.

The chemistry of alicyclic compounds is of interest the primarily because of the stereochemical properties inherent in the ring system. In the cyclic organic compounds, the six-membered ring has been a source of both challenge and entertainment to the
stereochemist. Quite apart from the frequency of its occurrence in isolable compounds, it appears to be one of the most highly preferred forms in transition states. As such it has come to be looked upon as one of the most intrinsically strain-free systems in organic chemistry and it is not surprising that since the inception of modern stereochemistry the monocyclic six-membered ring has been under intensive investigation.

**I-Strain effect in ring compounds**

The six membered ring derivative cyclohexanone is highly reactive towards carbonyl reagents, cyanide ion and semicarbazide where as cyclopentanone and cyclooctanone are surprisingly inert towards these reagents. The difference in reactivity between 5- and 7-membered ring compounds on the one hand and the 6-membered ring compounds on the other are quite large and involve factors of the order of 100. The difference in reactivity points to an important effect of ring size on chemical behavior, i.e., I-strain. I-strain is that change in internal strain which results from change in coordination number of a ring atom involved in chemical reaction.

Marigangaigh et al. studied the kinetics and mechanism of acidic permanganate oxidation of cyclohexanone. They found that the acid permanganate oxidation of cyclohexanone was autocatalytic. The oxidation of cyclohexanone by acidified potassium permanganate in the presence of perchloric acid and sodium fluoride resulted in the formation of mainly cyclohexane-1,2-dione which was isolated as its Ni(II) dioxime complex and identified.

Littler has studied the kinetics and mechanism of oxidation of cyclohexanone by chromic acid in aqueous perchloric acid.
The kinetics of the oxidation of ketones by quinolinium dichromate (QDC) in acid medium has been investigated by Das et al., The rate of the reaction was proportional to the concentration of the ketone, QDC and acid. The order of reactivity for the cycloketones was cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone. The thermodynamic parameters and suitable mechanism was proposed.

Krishnapillay and Kasthuri studied the kinetics of oxidation of cyclohexanone, cyclooctanone, cyclopentanone and cycloheptanone by pyridinium fluorochromate in acetic acid medium. The reactions were found to be acid catalyzed. A first order rate dependence each on [O],[S] and [acid] has been inferred.

The kinetics of oxidation of cyclohexanone, cyclooctanone, cyclopentanone and cycloheptanone by quinolinium fluorochromate has been studied by Sekar. The reaction shows first order dependence with respect to oxidant as well as substrate and second order with respect to [H+] ion. The added Mn2+ ion has a noticeable catalytic effect and the retardation of the rate by the addition of Al3+ ion confirms the three electron transfer process involved in the reaction. The product was 1,2-cyclohexanedione. A suitable mechanism was proposed. Srinivasan has also studied the kinetics of oxidation of cyclanones by NDC.

1.13 Literature survey of oxidation kinetics of chalcones

Chalcones or phenyl styryl ketones are of interest because they have a unique structural feature of having a C=O functional group in conjugation with C=C and the whole molecule is in conjugation.
It exhibits various biological activities. They have been reported to possess antioxidant, antimalarial, antiflammatory, antitumour and antibacterial activity\textsuperscript{123,124}. The presence of a reactive $\alpha$-$\beta$-unsaturated keto function in chalcones is found to be responsible for their antimicrobial activity which may be altered depending on the type and position of substituent on the aromatic rings.

Chalcones were oxidized by different oxidizing agents and in all these reactions either the C=C or C=O group of the chalcone was attacked by the oxidant\textsuperscript{125-127}.

The kinetics of the oxidation by chromic acid of chalcone (phenyl styryl ketone) and several substituted chalcones have been investigated in 95 \% (v/v) acetic acid by Khandual et al.,\textsuperscript{128} The reaction is overall of the second order, first order in each reactant. The parameters of Arrhenius and transition state theories have been computed. The effect of substituents on the rate of oxidation has been evaluated. A Hammett-type correlation with Brown's $\sigma^+$ values has been established with $\rho^+ = 1.2$. The datas are consistent with a mechanism which involves electrophilic attack of chromic acid at the carbon–carbon double bond resulting in the formation of an epoxide.

Srinivasulu et al.,\textsuperscript{129} studied the kinetics of OsO$_4$ catalyzed oxidation of chalcones by Ce$^{4+}$ in aqueous acetic-sulfuric acid medium in the temperature range 313 to 338 K. The order in [oxidant] is zero while the order with respect to [substrate] and [catalyst] are fractional. The rate of the reaction decreased with increase in percentage of acetic acid.
The rates of various substituted chalcones (with substituents in the phenyl ring attached to the moiety) are in the order $p$-CH$_3 > m$-CH$_3 > H > p$-Cl $> m$-Cl $> m$-NO$_2 > p$-NO$_2$.

Manikyamba and Aruna$^{130}$ reported that the kinetics of oxidation of chalcone by quinolinium dichromate in aqueous acetic acid medium in the presence of H$_2$SO$_4$. The reaction is first order each in [chalcone] and [oxidant]. The reaction is acid catalyzed and increase in the percentage of acetic acid in the solvent mixture increases the rate. A mechanism involving a slow attack of (QH)$H_2^+CrO_4$ on chalcone molecule is giving benzoic acid and phenyl acetaldehyde was proposed.

Komal Reddy et al.,$^{131}$ have been reported that the kinetic results of the oxidation of chalcones, by N-bromo acetamide in 70% (v/v) acetic acid – water-perchloric acid medium at various temperatures. The reaction was first order in [NBA] and fractional order in [chalcones] and [H$^+$] and inhibited by the addition of acetamide. The rate of oxidation is susceptible to change in the composition of acetic acid - water mixture. The negative value of $\rho$ (reaction constant) indicates the reaction is facilitated by high electron density at the reaction site. The possible mechanism was also proposed.

The kinetics and mechanism of oxidation of chalcone and some substituted chalcones by trichloroisocyanuric acid (TCICA) at 313 K in HOAc-HClO$_4$ medium has been investigated by Anilkumar and Sondu$^{132}$. The reaction has been found to be first order each in [TCICA] and [Chalcone] and fractional order in [H$^+$]. There is no kinetic or spectral evidence for the formation of complex between TCICA and Chalcone. The rate increases with increase in percentage of acetic acid and [Cl$^-$]. The products of oxidation have been identified as phenyl acetaldehyde and benzoic acid. The reactive species of
oxidant have been established as HOCI and H₂OCl⁺. The rate increases with electron releasing groups in the benzaldehyde moiety and vice versa with a Hammett's p value of -0.45. A suitable mechanism involving the chalcone molecule and the reactive species of TCICA in the rate determining step has also been proposed.

The kinetics of oxidation of substituted styryl 4-biphenyl ketones and substituted styryl 2-fluorenyl ketones by pyridinium chlorochromate (PCC) in 90% acetic acid medium containing perchloric acid and NaClO₄ at 100, 200, 300 and 40 °C have been studied by Dae Dong Sung and Ananthakrishna Nadar. The reactions were first order in styryl ketones and PCC. The effects of varying [HClO₄] and the percentage of acetic acid on the reactions have also been analysed. A mechanism involving nucleophilic attack of PCC leading to an unsymmetric intermediate from which epoxides were formed.

Chawta et al. studied the kinetics of epoxidation of chalcones and substituted chalcones by perbenzoic acid. A correlation of substituent constants and rate constants has obtained from the substituents. The effect of substituents discussed in terms of the reactivity-selectivity relationship.