INTRODUCTION
The first epoxidation of an unsaturated system was carried out by Prileschajew\textsuperscript{1-4} at the Polytechnic Institute in Warsaw in 1909 when he used peroxylbenzoic acid to convert diisobutylene to the corresponding epoxide. In forty years which have elapsed between Prileschajew’s discovery and its industrial utilization, the epoxidation reaction has been used primarily in the laboratory as a preparative method or as an analytical tool for the estimation of isolated ethylenic unsaturation. Research work during 1944-48 by Daniel Swern and co-workers\textsuperscript{5} has done most to focus attention on the commercial possibilities for the epoxidation reaction.

The reactivity of the epoxide ring makes epoxy compounds of interest in organic synthesis. They will add water to give glycols, halogen acids to give halohydrins. Nitric acid yields esters as do organic acids. Amino alcohols can be obtained from ammonia or amines. Hydrogen cyanide adds to give cyanohydrins. Phenols give phenyl ethers whilst Grignard reagents give alcohols, as does hydrogenation. Aldehydes or ketones yield acetals. Hydrogen sulphide yields hydroxythiols, and mercaptans give thioethers\textsuperscript{6}.

Epoxides are extremely valuable commercially because of the many reactions which they undergo. Their ability to donate electrons to hydrogen atoms in hydrogen bonding is important in such diverse applications as ulcer therapy and the stabilization
of poly (vinyl chloride) resins. The fact that epoxides polymerize under thermal, ionic, and free radical catalysis has encouraged considerable research on epoxy homopolymers and copolymers for industrial applications. The epoxides of long chain \( \alpha \)-olefins are potentially useful as detergent precursors. These samples show the commercial usefulness of epoxides, particularly as chemical intermediates.  

Epoxidation techniques employing peroxo acids, alkaline hydrogen peroxide, \( t \)-butylhydroperoxide, metal activated hydrogen peroxide and the mechanisms postulated for the epoxidation along with oxidative cleavage which occurs under these conditions are briefly discussed in the following sections.

A The Peroxy acid systems:

Epoxidation may be defined as the reaction in which olefinic unsaturation is converted to a cyclic three-membered ether by active oxygen agents

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{[O]} & \quad \text{C} \quad \text{C} \quad (1)
\end{align*}
\]

The products of epoxidation are 1,2-epoxides (\( \alpha \)-epoxides); they are also designated as oxiranes.

The discovery that oxiranes can be prepared from the ethylenic compounds by epoxidation with an organic peroxo acid is generally credited to the Russian chemist, Prideschajew, who showed that peroxycbenzoic acid is an efficient oxidizing agent
for epoxidation of isolated double bonds.

\[
\begin{align*}
- C = C - & \xrightarrow{\text{Organic}} C \xrightarrow{\text{Solvent}} - C & + C_{6}H_{5}CO_{2}H
\end{align*}
\]

The reactions proceed under mild conditions, and are generally conducted in a non-reactive organic solvents, such as CHCl₃, ether, C₆H₆, acetone or dioxane. As a rule the yields are high.

The reaction time is usually short, but it varies with the number and nature of the groups attached to the ethylenic system.

When epoxidation requires a long period of time for completion, monoperoxyphthalic acid has been employed with advantage. This reagent has been used extensively for the epoxidation of naturally occurring products, such as sterols and polyenes.

In a systematic study of the reaction of unsaturated compounds with peroxyacetic acid in acetic acid solution and in inert solvents, Arbuzow and Michailow observed that hydroxy acetates were formed in acetic acid while oxiranes were obtained in inert solvents. However to obtain good yields of oxiranes it is necessary to operate at moderate temperature (20--25°C is preferred), to keep the reaction time as short as possible and to exclude strong acids, which catalyze the opening of the oxirane ring by acetic acid. In the peroxyacetic acid epoxidation of compounds containing both an ethylenic and an acetylenic linkage, it has been reported that only the double bond is attacked. Acetylenic compounds react with peroxyacetic acid, but the rates of reaction are only about one-thousandth
as great as the rate of reaction of analogous ethylenic compounds. However, evidences for oxirane intermediates have been reported recently.\textsuperscript{13}

An important contribution in the epoxidation techniques employing peroxycetic acid, has been the Du Pont development of using polystyrene sulphonic acid exchange resins to catalyze H\textsubscript{2}O\textsubscript{2} in the epoxidation of unsaturated fats and oils.\textsuperscript{14,15}

Peroxyacamphoric acid has been employed to convert pinene and cholesterol to the corresponding oxiranes.\textsuperscript{16} Peroxyformic acid is generally considered not to be an epoxidation reagent because the high acidity of formic acid (employed either as solvent or formed during the oxidation) causes most oxirane rings to open rapidly. Hence yields of oxiranes were usually low. The peroxytrifluoroacetic acid systems of Emmons is also a likely laboratory reagent for epoxidation. Satisfactory procedures have been developed for the epoxidation of olefins and negatively substituted olefins with peroxytrifluoroacetic acid. These procedures are dependent on the presence of a buffer such as disodium phosphate, \textit{Na\textsubscript{2}CO\textsubscript{3}}, or \textit{NaHCO\textsubscript{3}} in the reaction medium.\textsuperscript{17} The fluorinated peroxy acid apparently exerts less acidity than either peroxyformic or peroxyacetic acid to catalyze epoxy cleavage.\textsuperscript{18} \textit{p}-Nitro and \textit{p}-nitro peroxybenzoic acids have been found to be much more reactive (8 times) than peroxybenzoic acid.\textsuperscript{19} \textit{p}-Nitroperoxybenzoic acid has been employed for the selective epoxidation of the allene function.\textsuperscript{20}
Among the commercially available peroxy acids, m-chloro-peroxybenzoic acid is stable, is soluble in a variety of common organic solvents and hence it is employed for epoxidation nowadays. The rate of epoxidation of unsaturated compounds with this peroxy acid is several times that with peroxybenzoic acid and it has a decided advantage in some cases, especially where isomerization is to be avoided.\textsuperscript{17,21}

The epoxidation of olefins with peroxy acids can be characterized as follows:

(1) the reaction is first order in olefins and in peroxy acid, (2) the primary product is the epoxide usually isolated in high quantitative yields (3) a wide variety of polar or non-polar organic solvents can be used (4) the reaction is often complete at or below room temperature in a few hours or less and (5) the reaction proceeds by \textit{cis} addition to double bond.

Since epoxidation is rapid in non-ionizing solvents and there is little or no salt effect or catalysis by acids, it has been usually assumed that ionic species or transition state cannot be involved. Furthermore, the high negative entropy of activation required a highly ordered transition state. The "molecular" mechanism first proposed by Bartlett\textsuperscript{22} and supported by others is consistent with the above facts, although there is no direct evidence for "spiro" transition state\textsuperscript{23}.
In this mechanism the transition state is non-ionic and oxygen transfer occurs by a concerted intermolecular process via the "spiro" transition state.

An alternate mechanism involving 1,3-dipolar addition to the \( \overset{1}{\overset{1}{C}} = C \overset{1}{\overset{1}{<}} \) as rate determining step has recently been suggested by Kwart and Hoffmann\(^{24}\) on the basis of the similarity between the reactivity parameters and general kinetic characteristics of epoxidation and 1,3 dipolar addition reactions.
The molecular mechanism is assumed to be more reasonable in nonpolar media and the dipolar mechanism in polar media.

A study of the substituent effects on reaction rates of peroxy acids on olefins shows that substitution of alkyl groups for the hydrogen atoms attached to the double bond increases the rate. Also, in compounds like isoprene, the more substituted double bond is attacked first, in spite of the greater steric hindrance.\(^5\) The rate is decreased when such electron-attracting groups as carbonyl or carboxyl groups are attached to, or are in close proximity to, the double bond.\(^2^5\) In the epoxidation of compounds containing conjugated double bonds, reaction proceeds at a much slower rate after 50% epoxidation has been effected. Thus peroxy acids can be used as analytical agents to differentiate between isolated and conjugated double bonds.\(^2^6\)

Therefore the organic peroxy acids are widely used oxidizing agents in organic chemistry because of their versatility, specificity, ease of preparation and the frequent production of excellent yields of desired product in a short time under mild conditions without the formation of difficult-to-remove by-products.

B Alkaline Hydrogen peroxide systems:

Alkaline \(\text{H}_2\text{O}_2\) systems for epoxidation were first used by Weitz and Scheffer\(^2^7\) in 1921 for the epoxidation of mesityl oxide and other \(\alpha,\beta\)-unsaturated ketones.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{CH} \cdot \text{CO} \cdot \text{CH}_3 + \text{H}_2\text{O}_2 + \text{CH}_3 & \quad \text{CH}_3 & \quad \text{C} = \text{CH} \cdot \text{CO} \cdot \text{CH}_3 + \text{H}_2\text{O} + \text{OH}^{-}
\end{align*}
\]  

(5)
The alkaline peroxide systems for epoxidation required the use of organic solvent under homogeneous reaction conditions. The use of aqueous alkaline medium, however, eliminated the need for the extraction of solvents and increased the yield of epoxide. Reactions conducted in aqueous mixtures also tend to give fewer by-products to contaminate the epoxide. Epoxy mesityl oxide, ordinarily considered unstable to heat, appeared to be very stable when prepared in aqueous alkaline medium. However, alkaline H₂O₂ solutions in methanol, ethanol, pyridine, and dioxane have proved satisfactory for epoxidation.

Relatively little work has been done in the past with H₂O₂ under controlled pH conditions. These reactions have been modified to such an extent that even a notoriously sensitive (to alkaline-induced polymerization) chemical such as acrolein could be epoxidized in 30% yield. By adopting the similar technique a variety of other α, β-unsaturated aldehydes like crotonaldehyde, cinnamaldehyde, citral etc. have been epoxidised.

There has been a useful study of the kinetic course of the oxidation by H₂O₂ in an alkaline medium by Bunton and Minkoff in 1949. The experimental order is in accord with the supposition that the rate-determining step of the reactions involves an attack by the ion HO₂⁻ on the β-carbon atom followed by ring enclosure and elimination of hydroxyl group.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{OH}^- & \quad \text{HO}_2^- + \text{H}_2\text{O} \\
\text{C} = \text{CH} - \text{CHO} & \quad \text{C} - \text{C} - \text{CHO} \\
\text{HO}_2^- & \quad \text{C} - \text{C} - \text{CHO} + \text{OH}^-
\end{align*}
\]
An interesting aspect of alkaline peroxide epoxidation is that, in contrast to electrophilic peroxy acid epoxidation, it is not stereospecific but rather "Stereoselective" as illustrated by the following example.

Both Cis and trans \( \text{C}_6\text{H}_5\text{CH} = \text{CHO} \cdot \text{C}_6\text{H}_5 \) yield the same stereoisomeric trans - epoxide. This stereoselectivity has been ascribed to a preferred conformation of the intermediate enolate anion.
The lower energy transition state which yields the epoxide with the unhindered carbonyl group is favoured because maximum over-lap is attainable in that transition state.

The reactions of alkaline $\text{H}_2\text{O}_2$ showed that the nucleophilic attack on $\alpha,\beta$ unsaturated ketones is hindered by electron accession to the reaction centre and the substitution of a methyl group for a hydrogen atom on the $\beta$-carbon atom decreases the rate by a factor of 5.6.\textsuperscript{30} This observation is in contrast to the reaction between olefins and peroxy acids, where the reaction involves electrophilic attack and is facilitated by alkyl substitution.

C tert-Butyl hydroperoxide systems:

The discovery that tert-butyl hydroperoxide (TBH) will cause the epoxidation of unsaturated ketones offers a convenient alternate method by which the epoxidation reaction may be carried out in a completely homogeneous, non-polar medium in the presence of a few mole per cent of Triton-B (benzyltrimethylammonium hydroxide). By this method mesityl oxide, methyl vinyl ketone, methyl isopropenyl ketone, cyclohexenone and chalcone were converted to their epoxides.\textsuperscript{33}

The reaction is envisioned as proceeding by the addition of an alkyl peroxy anion to the $\beta$-carbon of the activated double bond. This is followed by the elimination of alkoxide ion with the formation of the epoxide, a mechanism analogous to that suggested by Bunton and Minkoff (loc.cit.) for the epoxidation of
unsaturated ketones with alkaline H₂O₂. If the intermediate anion acquires a proton before cyclization occurs, the Michael adduct is formed. These transformations are illustrated by the reaction scheme.

\[ R \overset{\Theta}{\text{OO}} + R_2^1 \overset{\Theta}{\text{C}} = \text{CHX} \xrightleftharpoons{} R.O.O.C R_2^1 \overset{\Theta}{\text{C}} \text{CHX} \]  (9)

\[ R_2^1 \overset{\Theta}{\text{C}} \xrightarrow{\text{HB}} \text{CHX} \quad \xrightarrow{\text{OO.R}} \quad R_2^1 \overset{\Theta}{\text{C}} \text{CH}_X^2 + \overset{\Theta}{\text{O.O.R}} \]  (10)

\[ R_2^1 \overset{\Theta}{\text{C}} \xrightarrow{\text{CHX}} \overset{\Theta}{\text{O.R}} \]  (11)

The nature of group X, and consequently the stability of the intermediate anion, apparently determines which pathway is taken. When X is acyl or aroyl, the equilibrium concentration of the anion is sufficiently large to enable the elimination step (11) to compete favourably with the protonation step (10). In fact, since the elimination step is irreversible, the reaction is driven in the direction of epoxide formation. When X is nitrile or carbomethoxy, the concentration of the anions is small and the formation of the Michael adducts is favoured. These observations accord with the known relative stabilities of anion α to a carbonyl group and to a nitrile or ester group.34
The epoxidation of cinnamaldehyde was carried out using alkaline TBH in methanol at controlled pH.

\[
\text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{CHO} + t - \text{C}_4\text{H}_9\text{OH} \xrightarrow{\text{pH 8.5}} \text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{CHO} + t - \text{C}_4\text{H}_9\text{OH}
\]

(12)

In contrast to this result, the reaction of TBH with crotonaldehyde was not straightforward and resulted in only 7% yield.\textsuperscript{35b} Aldehydes, ketones and even nitriles have also been successfully epoxidized with quantitative yields, using hypochlorite anion (\(\text{OCl}^-\)) which presumably behaves analogous to the hydroperoxide and alkylhydroperoxide anions. A mechanism similar to that of hydroperoxide anion has been reported.\textsuperscript{36}

Recently mechanisms of borate ester induced decomposition of TBH have been studied.\textsuperscript{37} It has been shown that in the presence of phenyl borates, TBH will epoxidise olefins, but aralkyl hydroperoxides will preferentially undergo an acid catalyzed rearrangement.

D Metal - activated hydrogen peroxide systems:

In 1969 Payne carried out epoxidation of unsaturated systems involving metal catalyzed hydrogen peroxide.\textsuperscript{38} The system was operated by dissolving the epoxidizable substance in \(t\)-butyl alcohol - water mixtures to which was added a small quantity of tungstic or molybdoc acid catalyst. Excess hydrogen peroxide was then charged to the mixture held at 70 - 80°C until reaction was complete. Hydrogen peroxide used in this manner has transformed
the insecticide Aldrin to the epoxy insecticide Dialdrin in 95% yields. The tungstic acid method of epoxidation has been applied to maleic, fumaric and crotonic acids which are very resistant to attack by peroxycetic and peroxycbenzoic acids. These compounds were efficiently converted to their corresponding epoxides at pH 4 - 5.5.

More recently kinetic studies on the epoxidation of metal catalyzed hydroperoxide reactions have been carried out extensively. The mechanistic features of such epoxidations show that peroxo species of Mo, W and V act as the key intermediates in these oxidation reactions.

E. Epoxidative-cleavage reactions:

Additional information on the epoxidation mechanism, along with the rates and probable mechanisms of several competing reactions which occur under epoxidation conditions have been reported in recent times. α, β-epoxy ketones undergo oxidative cleavage under these conditions producing aldehydes. The alkaline peroxide treatment often yields products different from those obtained on cleavage with base alone. Treatment of α, β-epoxy ketone with base often leads to products of benzilic acid type rearrangement or Favorisk rearrangement.

The cleavage reaction of an epoxide has general synthetic utility in the preparation of dialcids, keto acids, and ketones from α, β-unsaturated ketones, α, β-unsaturated aldehydes and β-diketones.
Recently the oxidative carbon-carbon cleavage of simple epoxides with alkaline hydrogen peroxide have been reported. It was shown that cleavage proceeds through the \( \beta \)-hydroperoxy alcohols which were isolated in some cases. The substituent effect for the concerted fragmentation has been explained by (1) an acceleration by the phenyl group via resonance with developing carbonyl (2) a possible steric acceleration and (3) effect of acidity of the \( \text{HO}_2^- \) and \( \text{OH}^- \) anions.
THE PRESENT WORK

A comprehensive study of epoxidation of unsaturated systems with practically all peroxo acids in aqueous and non-aqueous solvents has already been carried out. When a carbonyl group is attached to \( \overset{\rightarrow}{C} = C \overset{\leftarrow}{\chi} \) bond, it confers electrophilic character and so the peroxo acids are not satisfactory for the epoxidation of \( \alpha, \beta \)-unsaturated carbonyl compounds. However they respond to epoxidation with alkaline hydrogen peroxide.

So far the kinetics of epoxidation of only a few \( \alpha, \beta \)-unsaturated ketones have been studied particularly in the aqueous medium. Hence a systematic study of the epoxidation of a large number of \( \alpha, \beta \)-unsaturated ketones, aldehydes and esters which are insoluble in water but soluble in organic solvent was found to be necessary. Such a study will give one an insight into the mechanism of epoxidation in non-aqueous solvents and would also permit a comparison of the reactivity of the \( \overset{\rightarrow}{C} = O \) group when attached to a \( \overset{\rightarrow}{C} = C \overset{\leftarrow}{\chi} \) linkage during epoxidation.

Also, very little investigation has been made regarding the epoxidation of unsaturated sulphones though a few \( \alpha, \beta \)-epoxy sulphones have been prepared from \( \alpha, \beta \)-unsaturated sulphones using alkaline hydrogen peroxide. However, to this date, there have been no reports in the literature on the study of the kinetics of epoxidation of \( \alpha, \beta \)- and \( \beta, \gamma \)-unsaturated sulphones.
and their cleavage reactions. Such studies are necessary to understand the effect of the sulphonyl group on the ethylenic linkage during epoxidation.

The kinetics of bromine addition to unsaturated sulphones reveal differences in the rate of addition to $\alpha$, $\beta$ and $\gamma$-unsaturated sulphones. Hence a comparison of rates of epoxidation could be made with the rate of bromination of such systems. Again such studies may serve to elucidate the structural and mechanistic features of epoxidation in the case of the unsaturated sulphones. The present investigation will also lead to a study of the relative chemical reactivity of the carbonyl and sulphonyl groups when attached to the ethylenic linkage during epoxidation and cleavage reactions.