I. INTRODUCTION

I. 1. Redox Reactions:

Redox reactions play a vital role in chemical, biochemical and industrial processes. Their usefulness is much varied. In synthesis involving chemical transformations and in a host of biological processes, electron transfer occupies a key position. For example, most of the metabolic energy generated in the tissues comes from the oxidation of carbohydrates and triglycerols. The remainder is furnished by the oxidation of amino acids.

Thus, in view of their many-faceted involvement and applications, an understanding of the mechanism of redox reactions is obviously significant. Redox processes are complementary in nature that an oxidation is accompanied by a simultaneous reduction. These processes may be simple or complex, involving at least two species, oxidant and reductant. The species accepting an electron or electrons is termed the ‘oxidant’ and the one losing electrons is referred to as the ‘reductant’. Research investigations involving redox processes have been carried out over the years. Due to the advent of many sophisticated experimental techniques (fast reaction methods, electron spin resonance etc.) and of the relevant theories, a clear understanding of the mechanistic aspect of electron transfer reactions (redox processes) has become possible.
I.2. Classification of redox reactions:

In a simple way, redox reactions can be classified as:

(a) Reactions involving simple electron transfer and

(b) Reactions involving breakage and formation of covalent bonds

The following reactions,

\[ \text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+} \] (exchange reaction)

\[ \text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+} \]

\[ \text{Tl}^{3+} + 2\text{Fe}^{2+} \rightarrow \text{Tl}^{+} + 2\text{Fe}^{3+} \]

belong to the first category. Simple electron transfer may include (i) outer-sphere and (ii) inner-sphere electron transfer reactions.

I.2. (i) Outer-sphere electron transfer reactions.

This type of reaction may involve exchange process like,

\[ \text{MnO}_4^{2-} + \text{MnO}_4^- \rightarrow \text{MnO}_4^- + \text{MnO}_4^{2-} \]

\[ \text{Mo(CN)}_6^{4+} + \text{Mo(CN)}_6^{3-} \rightarrow \text{Mo(CN)}_6^{3-} + \text{Mo(CN)}_6^{4+} \]
or net reactions like:

\[ \text{Fe(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{3+} \rightarrow \text{Fe(bpy)}_3^{3+} + \text{Ru(bpy)}_3^{2+} \]

The significant aspect in these reactions is that the coordination spheres of either the oxidant or the reductant remain intact during electron transfer.

1.2. (ii) **Inner-sphere electron transfer reactions:**

This type consists of two step processes, formation of the bridged intermediate followed by the electron transfer.

Since all inner-sphere reactions are two step changes, either the formation of the intermediate or the electron transfer may be the rate-determining step in the redox process.

\[ \text{Cr(H}_2\text{O)}_6^{2+} + \text{Co(NH}_3)_5\text{Cl}^{2+} \rightarrow [(\text{NH}_3)_5\text{-Co-Cl-Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \]

\[ [(\text{NH}_3)_5\text{-Co-Cl-Cr(H}_2\text{O)}_5]^{4+} \rightarrow \text{CrCl}^{2+}_{(\text{aq})} + \text{Co(NH}_3)_2^{2+}\text{H}_3\text{O}^+ \]

\[ \text{Co(NH}_3)_5^{2+} \rightarrow \text{Co}^{2+}_{(\text{aq})} + 5\text{NH}_4^+ \]
The above reaction affords an easy method of testing for the operating mechanism. In presence of $^{36}\text{Cl}^-$ion, one expects the isotope to be incorporated into the final CrCl$_2^{2+}$ (aq) if the redox reaction involves an outer-sphere mechanism.

$$\text{Cr}^{3+} (aq) + \text{Cl}^-(^{36}\text{Cl}^-) \rightarrow \text{CrCl}^{2+} (aq) + \text{Cr}^{36}\text{Cl}^{2+} (aq)$$

If, however, the reaction proceeds by an inner-sphere mechanism, then no $^{36}\text{Cl}^-$ should be incorporated since the cl'ion never breaks free of atleast one of the metals. In a classic investigation, Taube$^6$ found no incorporation of $^{36}\text{Cl}^-$ into the CrCl$_2^{2-}$ (aq) formed, thus giving strong evidence for the inner-sphere process.

Since Taube's work$^6$, most redox investigators have attempted to characterize their particular reaction as either inner - or outer - sphere type reactions. The assignment is frequently straightforward, but sometimes difficult. The mechanisms may be distinguished by inspection of the products as is exemplified in the preceding example. Another method is by detecting a bridged complex comparable to that described previously. The detection of a bridged complex should not be taken as a proof for an inner-sphere process since the bridged complex may be involved in a side equilibrium while the products are formed directly from reactants by an outer-sphere process.
Schemes invoked in the oxidation of organic substrates by Ce(IV) frequently involve a fast complexation step between the metal ion and the substrate prior to electron transfer\(^7\), implying an inner-sphere process. Evidence for such complexation comes from several observations. For example, the change of yellow color of Ce(IV) to red on adding a reductant has long been attributed to complex formation\(^8\). Additional evidence for complexation comes from kinetic studies where the observed non-linear dependence of the rate constant on substrate concentration may indicate complex formation\(^9\).

Following are some examples in which the oxidant and the reductant separately undergo bond-cleavage respectively:

\[
\begin{align*}
\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} & \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+} \\
\text{Co}^{3+} + \text{RCH}_2\text{OH} & \rightarrow \text{Co}^{2+} + \text{RCHOH} + \text{H}^+
\end{align*}
\]

The reductant may be a metal ion or metal complex in its low valence state such as Fe\(^{2+}\), Mn\(^{2+}\), Fe(CN)\(_6\) \(^{4-}\), etc., or organic compound containing oxidisable groups like aldehyde, alcohol, amine or a facile \(\pi\) - system (double bond). The oxidant may be a metal ion or metal complex in its higher valence state like Ce\(^{4+}\), Mn\(^{3+}\), Mn\(^{7+}\), Cr\(^{6+}\), \(\nu^{5+}\) etc., or compounds containing peroxo linkage, -O-O-, such H\(_2\)O\(_2\), S\(_2\)O\(_8\) \(^{2-}\), HSO\(_5\)\(^-\), P\(_2\)O\(_8\) \(^{4-}\), C\(_6\)H\(_5\)CO\(_3\)H.
Viewing from the multi-faceted applications, it is clear that an investigation of the kinetics and mechanism of redox reactions (Organic or inorganic) is an important one. It will not only help to enlighten the pathway of a particular reaction but also to identify newer reactions and hence the associated mechanisms.

Reaction rate is of great practical interest in both laboratory and industrial practice. No reaction that takes years to become sensibly complete is useful in making its product, but reactions that are complete in fractions of a second include hazardous explosions. It is clearly necessary to understand the factors controlling the rate at least to some extent before a reaction becomes useful on almost any scale. A study of reaction mechanism allows a more informed extension of the scope of the reaction to new but mechanistically related cases. One important outcome of mechanistic studies has been the chemistry of unstable intermediates, of compounds that are normally not isolable. Thus it is clear that a study of reaction mechanism is of much significance.

The need for information regarding the factors which influence the role of metal ions in complexation and in oxidation-reduction requires little justification. This is especially true in view of the growing awareness of the importance of metal ions in various biochemical systems. Metal ions have been shown to be important in a variety of systems, e.g., coordination with proteins, metal-ion catalyzed decarboxylations, the conversion of solar energy into biochemical
energy\textsuperscript{13}, and the oxidation of organic matter to produce carbon dioxide, water and energy\textsuperscript{13}. Several metal ion couples are involved in biological oxidation-reduction, e.g., Fe(II)-Fe(III) in cytochrome c, Cu(I)-Cu(II) in cytochrome a, and Co(II)-Co(III) in vitamin B\textsubscript{12}\textsuperscript{14}.

I.3. Reactions involving Ce(IV): 

In the following, a review of the earlier works on the oxidation of organic and inorganic compounds by Ce(IV) is provided:

I.3. A. Oxidation of organic compounds by Ce(IV)

(i) Oxidation of p-chloromandelic acid\textsuperscript{15}:

The kinetics of the oxidation of p-chloromandelic acid by Ce(IV) in H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4} solutions was carried out by Grover et al. No kinetic evidence in support of a complex formation between the reactants was obtained\textsuperscript{15}. The values of $E_\text{a}$ and $\Delta S^\text{f}$ obtained were 19.8 kcal mol\textsuperscript{-1} and 1 cal mol\textsuperscript{-1}deg\textsuperscript{-1} respectively.
(ii) Oxidation of methanol and ethanol\textsuperscript{16}:

Ce(IV) oxidation of methanol and ethanol was studied by Gopala Rao et al. The reaction was carried out in both nitric and perchloric acid media. A difference in the behaviour of the system in these media was noticed and attributed to the different specie of Ce(IV)\textsuperscript{16}.

(iii) Oxidation of propane-1,3 and butane-1,4-diols\textsuperscript{17}:

A kinetic study of this title reaction was made by Sankla\textsuperscript{17} et al. The reaction was found to have a first order dependence both on Ce(IV) and [diol] and an inverse dependence on [H\textsubscript{2}SO\textsubscript{4}]. The reaction was catalyzed by H\textsuperscript{+} at constant HSO\textsubscript{4}\textsuperscript{−}. Two reaction pathways, one involving the bimolecular collision of the reactants and another involving an intermediate complex were suggested. The rate-determining step was noticed to be C-H fission.

A mechanism as below was given:

\[
\begin{align*}
K_1 \\
CeSO_4^{2+} + HSO_4^- & \rightleftharpoons Ce(SO_4)_2 + H^+ \\
& \quad k \\
CeSO_4^{2+} + \text{diol} & \longrightarrow Ce(\text{III}) + H^+ + R
\end{align*}
\]
Ce(SO\(_4\))\(_2\) + diol $\xrightarrow{\text{K}'}$ Ce(SO\(_4\))\(_2\)-dil

Ce(SO\(_4\))\(_2\)-dil $\xrightarrow{\text{k}''}$ Ce(III) + H\(^+\) + \cdot R

Ce(IV) + \cdot R $\xrightarrow{\text{k}''}$ Ce(III) + H\(^+\) + P

and a rate law consistent with the above was given\(^\text{17}\) as:

$$\text{rate} = \frac{d[\text{Ce(IV)}]}{dt} = \frac{2 (k'+k K_2 K_1 [\text{HSO}_4^-] [\text{H}^+]^{-1}) [\text{Ce(IV)}][\text{dil}]}{1+K_1 [\text{HSO}_4^-] [\text{H}^+]^{-1} + K_2 K_1 [\text{HSO}_4^-] [\text{H}^+]^{-1} [\text{dil}]}$$

(iv) Oxidation of p-methylmandelic acid\(^\text{18}\): Specific cation effects

A kinetic study on the oxidation of p-methylmandelic acid by Ce(IV) in H\(_2\)SO\(_4\)-MHSO\(_4\) (M\(^+\) = Na\(^+\), K\(^+\)) and H\(_2\)SO\(_4\)-MCIO\(_4\) (M\(^+\) = Li\(^+\), Na\(^+\)) was performed by Arcoleo et al. The kinetic data indicated that the hydrogen ion dependence of the reaction rate observed when H\(^+\) was replaced by Na\(^+\) and K\(^+\) at constant ionic strength arises from a medium effect. The activation parameters were not significantly altered by the type of the cation used\(^\text{18}\).
(V) Oxidation of mandelic acid: Ionic strength and specific cation effects

The kinetics of the redox reaction between mandelic acid (MA) and ceric sulphate was studied in aqueous sulfuric acid solutions and in $\text{H}_2\text{SO}_4$-M$\text{ClO}_4$ ($M^+ = H^+, Li^+, Na^+$) and $\text{H}_2\text{SO}_4$-MHSO$_4$ ($M^+ = Li^+, K^+$) mixtures at various ionic strengths. The oxidation reaction was found to occur via two paths obeying the rate law:

$$\text{rate} = k[\text{MA}] [\text{Ce(IV)}],$$

$$k_1 + k_2$$

Where $k = \frac{(1+a)^2[\text{HSO}_4^-]^2}{(1+1/a)^2[\text{SO}_4^{2-}]^2}$

"a" being a constant.

The cations were shown to exhibit negative specific effects upon the overall oxidation rate.

(vi) Substituent effects on the kinetics of oxidation of mandelic acids:

Anomalous kinetic behavior of methoxy derivative

The kinetics of the Ce(IV) oxidation of p-nitro and p-methoxymandelic acids was studied. The oxidation of p-nitromandelic acid proceeded through two [H$^+$]-independent paths. The kinetic behavior of the p-methoxy derivative
differed from that of the other mandelic acids in that the reaction occurred via two \([H^+]\)-dependent paths, the reaction rate being anomalously high and the activation enthalpy and entropy markedly lower. A hint on the operation of a different mechanism was made\(^{20}\).

(vii) **Oxidation of alkylbenzenes**: -

The oxidation of styrenes and other alkenylbenzenes by Ce(IV) ammonium nitrate was found to take place either by an electron-transfer mechanism or by a free-radical addition depending on the structure of the substrate\(^{21}\). It was suggested that the reaction was initiated by the attack of \(\cdot NO_3\) at the double bond.

The following mechanism was suggested:

\[
\text{ArCH} = \text{CH}_2 + \text{Ce}^{IV} \text{NO}_3 \rightarrow (\text{ArCH} = \text{CH}_2)^{\cdot} \text{Ce}^{III} \text{NO}_3 \\
(\text{ArCH} = \text{CH}_2)^{\cdot} \text{Ce}^{III} \text{NO}_3 \rightarrow \text{ArCH-CH}_2(\text{ONO}_2) + \text{Ce}^{III} \\
\text{ArCH-CH}_2(\text{ONO}_2) + \text{Ce}^{IV} \text{NO}_3 \rightarrow \text{ArCH(ONO}_2)\text{CH}_2(\text{ONO}_2) + \text{Ce}^{III}
\]

(viii) **Oxidation of \(\alpha\)-ketoacids\(^{22}\)**:

The rates of oxidation of the \(\alpha\)-keto acids, glyoxylic, pyruvic, phenylglyoxylic and 2-oxobutyric acids by cerium(IV) in sulfuric acid-perchloric
acid media was carried out by Sarac. The active species of the oxidant was \( \text{CeSO}_4^{2-} \). The oxidation reaction was proposed to be a one-electron process with the rate-determining step being the decomposition of \( \alpha \)-keto acid-Cerium(IV) complex to a free radical and \( \text{CO}_2 \).

(ix) Oxidation of methylnaphthalenes:

Naphthalenes with an \( \text{CH}_3 \) group in the 1-position gave aldehydes in good yields when oxidized with Ce(IV) ammonium nitrate in 50% acetic acid at 85°C.

(x) Ce(IV) catalyzed iodination at \( C_5 \) of uracil nucleosides:

Asakura et al. observed that the treatment of uridine derivatives with elemental iodine in presence of ceric ammonium nitrate gave the corresponding 5-iodouridine products in high yields.

(xi) Oxidation of thioethers:

Baciocchi et al. carried out a product and kinetic study on the oxidation of thioethers by cerium(IV) ammonium nitrate in acetic acid. The dialkyl, alkyl and diaryl sulphides were oxidized to the corresponding sulphonyl oxides. The rate of the
reaction was very sensitive to the electronic effect of the substituent \( \rho = -3.3 \) and was well correlated with the oxidation potential of the substrates. An electron transfer mechanism involving the formation of a sulfur radical cation was proposed:

\[
\text{ArSR} + \text{Ce}^{IV}\text{ONO}_2 \xrightleftharpoons{} \text{ArSR} + \text{Ce}^{III}\text{ONO}_2 \\
\downarrow \text{ArSOR}
\]

(xii) Kinetics of Ceric ion oxidation of naphthalenes:

The kinetics of oxidation of naphthalene by ceric ammonium sulfate was studied by Bhatt et al. The product was shown to be 1,4-naphthaquinone. From the kinetic investigations, a reaction taking place through initial formation of 1:1 complex of naphthalene and cerium(IV) in an equilibrium step followed by slow decomposition of the complex to naphthalene radical cation was proposed. This radical cation then reacted in a fast step forming the product.

The following mechanism:
and the rate law:

\[
\frac{d[Ce^{4+}]}{dt} = \frac{kK[Naphthalene][Ce^{4+}]}{1 + K[Naphthalene]}
\]

\[
k_1 = \frac{kK[Naphthalene]}{1 + K[Naphthalene] + 1}
\]

\[
1/k_1 = \frac{kK[Naphthalene]}{k}
\]

were proposed to explain the data.

(xiii) Ce(IV) assisted chemical preparation of polyaniline and its derivatives:

Polyanilines widely used as positive electrode in secondary batteries were prepared by oxidizing 3,5- and 2,3-dimethyl-aniline with Ce(IV) sulfate. An improved yield of the products was noticed with this oxidant as compared to other commonly used oxidants.
(xiv) Ru(III) catalyzed oxidation of amines by Ce(IV)\(^{28}\):

Ruthenium(III) catalyzed oxidation of methyl, ethyl, propyl, butyl, dimethyl and trimethyl amines by Ce(IV) in nitric acid was carried out by Nageshwar Rao et al. The mechanism was explained in terms of formation of 1:1 complex between Ru(III) and amine which later reacted with Ce(IV) giving ammonia and the corresponding aldehyde or ketone as the products.

(xv) Oxidation of 2,2'-azinobis(3-ethylbenzo-thiazole-6-sulfonate) (ABTS)\(^{29}\):

Ce(IV) promoted oxidation of ABTS was carried out by Maruthamuthu et al.\(^{29}\) and was found to form the radical cation of ABTS, Viz ABTS\(^{+}\) and further oxidation gave ABTS\(^{2+}\). The reaction was followed using stopped-flow technique. Both the formation and decay of ABTS\(^{+}\) were found to obey a total second order kinetics, first order each with respect to [ABTS] or [ABTS\(^{+}\)] and [Ce(IV)].

The mechanism was suggested as
$\text{ABTS}^+ + \text{Ce(IV)} \rightarrow \text{ABTS}^{2+}$

Decomposed product
(XVI) Enormous acceleration by Ce(IV) for the hydrolysis of certain nucleosides:

It was observed by Sumaoka et al. that at pH7 and 30°C, 3'5'-cyclic monophosphates of adenosine and guanosine were promptly hydrolyzed by Ce(IV) under physiological conditions. This investigation was performed using reversed-phase HPLC. The pseudo first order rate constant was 6.1 min⁻¹.

I.3. B. Oxidation of Inorganic Compounds by Ce(IV):

(xvii) Oxidation of hydrogen peroxide:

The reaction of H₂O₂ with Ce⁴⁺ was found to be very fast in the pH range: 0-0.7. At pH > 0.7, the reaction was very slow. The order of the reaction with respect to [Ce⁴⁺] and [H₂O₂] was found to be one and zero respectively. The first order rate constant was 2.8 x 10² s⁻¹ at 25°C for [HClO₄] = 0.2-2 M.

(xviii) Oxidation of halide ions:

The oxidation of iodide and bromide ions were both first order in [Ce⁴⁺]. However, whereas the oxidation of Br⁻ is second order in both [Br⁻] and [H⁺],
that of I' is first order in both [I'] and [H+]. The second order term in Br with a direct second order in [H+] indicated that intermediate Ce4+-Br complexes are involved34,35.

(xix) Oxidation of pentaamminecobalt(III) complexes of malonic & methylmalonic acids36:

Ce(IV) induced electron transfer in \((\text{H}_3\text{N})_5\text{Co}^{\text{III}}\) complexes of malonic acids was found to yield nearly quantitative amounts of Co(II), CO2 and formic acid. A synchronous electron transfer in the binuclear complex formed between Ce(IV) and Co(III) complex was suggested.

1.4. Reactions involving pyrimidines:

In the following, a brief coverage of the reactions of certain pyrimidines is provided:

(xx) Oxidation of pyrimidines with m-Chloroperbenzoic acid37:

Oxidations of 1,3-dimethylthymine, 3',5'-diacetylthymidine etc., with m-chloroperbenzoic acid was reported by Harayama et al.37. The corresponding hydroxy ester was formed as the product.
(xxi) Permanganate ion oxidation of 2,4(1H,3H)-Pyrimidinediones:\textsuperscript{38,39}

The oxidation of uracil, thymine and 6-methyluracil by MnO$_4^-$ was reported by Freeman et al.\textsuperscript{38,39}. Uniquely stable manganese intermediates were identified showing absorption in the 285-296 nm region ($\varepsilon_{\text{max}} \approx 4500$ M$^{-1}$ cm$^{-1}$).

The kinetic studies were carried out with stopped-flow spectrophotometer. The relatively moderate $\Delta H^\circ$ values and large negative $\Delta S^\circ$ values were attributed to the oxidation of carbon-carbon double bonds by MnO$_4^-$ consistent with an electrocyclic addition of MnO$_4^-$ to the olefinic linkage.

(xxii) Oxidative damage of thymine and thymidine derivatives with superoxide ion:\textsuperscript{40}

The oxidation of thymine and thymidine derivatives with potassium superoxide (KO$_2$) was investigated. The following compounds (1) and (2), in which their active hydrogens were protected by alkylation, reacted with KO$_2$ in presence of 18-crown-6 under argon giving the corresponding ring contracted imidazolone derivatives (3) and (4) in 15-53% yield. This ring contraction is a novel type of reaction in nucleic acid chemistry.
The following mechanism was proposed:

\[
\begin{align*}
\text{R}^1 & \text{N} \rightarrow \text{R}^2 \text{O}^\cdot \\
\text{R}^1 & \text{N} \rightarrow \text{R}^2 \text{O}^\cdot \\
\text{R}^1 & \text{N} \rightarrow \text{R}^2 \text{O}^\cdot \\
\text{R}^1 & \text{N} \rightarrow \text{R}^2 \text{O}^\cdot \\
\end{align*}
\]
In connection with an understanding of the damage of nucleic acids by peroxides and superoxides, the oxidation of certain thymines and uracils by \( S_{2}O_{8}^{2-} \) was carried out by Itahara et al.\(^{41} \). Isolation of the products formed was achieved. The selective oxidation of the 5-methyl group of thymines and uracils forming the corresponding 5,6-dihydropyrimidines was noticed.

Oxidation of thymine by sodium peroxodisulfate in water at 85°C gave the corresponding 5-(hydroxymethyl)uracils and 5-formyluracils. It was noticed\(^{42} \) that the reaction proceeded through cation radicals. The oxidation of thymines by potassium peroxomonomosulfate\(^{42} \) in water gave the corresponding cis-5,6-dihydroxy-5,6-dihydrothymine and 5-hydroxy-5-methyl-barbituric acids.

The reactions of pyrimidines like, e.g., uracil with the radicals produced in the radiolysis of water, i.e., \( e^{-} \), \( \cdot H \), and \( \cdot OH \) have been intensively investigated\(^{44} \). With the use of pulse radiolysis with optical detection, the isomer
distribution of the radicals formed by addition of \( \cdot \text{OH} \) to \( \text{C}_2\text{-C}_6 \) double bonds of uracil, thymine, 3- and 6-methyluracil, orotic and isoorotic acids was determined by Fujita and Steenken\(^43\). The reactions of the radical intermediates involved were studied in detail\(^45\).

(xxvi) \( \text{TiO}_2 \) mediated photooxidation of pyrimidines:

The heterogeneous photooxidation of uracil, thymine and 6-methyluracil etc. mediated by irradiated (365nm) \( \text{TiO}_2 \) has been carried out. The involvement of radical intermediates of the pyrimidines formed by the attack of \( h^+_{\text{vb}} \), \( \cdot \text{OH} \) and \( \text{O}_2^- \) was implicated\(^46\).