

**KINETICS AND MECHANISM OF ELECTRON TRANSFER  
REACTIONS OF MIXED –VALENCE DI - $\mu$ - OXO TETRAKIS  
(1,10-PHENANTHROLINE) DI MANGANESE (III,IV) ION AND  
ROSANILINE HYDROCHLORIDE WITH SOME REDUCING  
AGENTS**

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ZARIA, NIGERIA.**

**JULY, 2005**

## DECLARATION

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources have been acknowledged by means of references.

ABIODUN.

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DATE.

## CERTIFICATION

This thesis titled “KINETICS AND MECHANISM OF ELECTRON TRANSFER REACTIONS OF MIXED –VALENCE DI -  $\mu$ - OXO TETRAKIS (1,10-PHENANTHROLINE) DI MANGANESE (III,IV) ION AND ROSANILINE HYDROCHLORIDE WITH SOME REDUCING AGENTS”. by Babatunde, Oluwayemisi Abiodun, meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello University Zaria, Nigeria and is approved for its contribution to knowledge and literary presentation.

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## **DEDICATION**

This work is dedicated to

- 1 Almighty God for his love, care and gift of life through Jesus Christ.
- 2 The memory of my father Chief David Adeyemi Olowookere Omole, who has always prodded me to strive harder. Daddy, what a sad time to say Good-bye!

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## ABSTRACT

The kinetics and mechanism of the electron transfer reactions of a mixed-valence manganese complex ( $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$ ) with four different reductants ( Ascorbic acid ( $\text{H}_2\text{A}$ ), 1, 3 dihydroxybenzene ( $\text{H}_2\text{R}$ ),  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ ) have been studied in acid medium at  $28 \pm 1^\circ\text{C}$ . The reactions were found to obey second order kinetics with the following general rate law

$$-\frac{3}{2} \frac{d[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = k_2 [\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] [\text{Reductant}].$$

The experimental data for three of the reaction systems were found to exhibit first order dependence on acid concentration with this general rate law.

$$-\frac{3}{2} \frac{d[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = (a + b [\text{H}^+]) [\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] [\text{Reductant}].$$

For  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}} / \text{H}_2\text{A}$  system

$a = 3.50 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 2.13 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at constant  $[\text{H}^+] 0.50 \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^3$  (NaCl),  $T = 30^\circ\text{C}$  and  $\lambda = 580\text{nm}$ .

For  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}} / \text{H}_2\text{R}$  system

$a = 0.70 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 0.02 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at  $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$  (NaCl),  $T = 28 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 580\text{nm}$ .

For  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}} / \text{SO}_3^{2-}$  system

$a = 1.22 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 7.83 \times 10^{-7} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at  $[\text{H}^+] 5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl),  $T = 28 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 580\text{nm}$ .

while the rate law for the  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}} / \text{S}_2\text{O}_3^{2-}$  system is

$$-\frac{3}{8} \frac{d[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = (a + b [\text{H}^+]) [\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] [\text{S}_2\text{O}_3^{2-}]$$

where  $a = 7.01 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $b = 0.92 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at  $28 \pm 1^\circ\text{C}$   $[\text{H}^+] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ).

There were no spectroscopic and kinetic evidences for the formation of an intermediate complex in any of the reaction systems. This is not in favour of inner sphere mechanism. Therefore, the electron transfer must probably occur by the outer sphere mechanism in these systems.

In  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}/\text{H}_2\text{A}$  and  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}/\text{SO}_3^{2-}$  systems, the reactions were catalysed by cation and anion species. This is in support of the outer sphere mechanism but in the  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}/\text{H}_2\text{R}$  and  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}/\text{S}_2\text{O}_3^{2-}$  systems, no catalysis was observed and free radicals were also not important in the redox processes. Therefore, the results obtained are in support of proton coupled electron transfer (PCET) mechanism and is hereby proposed for the two reaction systems.

The kinetics and mechanism of the electron transfer reaction of rosaniline hydrochloride (referred to as Ros) with reductants ( $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{IO}_4^-$ ,  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$ ) have also been studied in aqueous medium at  $30^\circ\text{C}$ ,  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaCl}$ ,  $\text{CH}_3\text{COONa}$  or  $\text{NaClO}_4$ ),  $[\text{H}^+] = 1 \times 10^{-4} \text{ mol dm}^{-3}$  except for  $\text{OH}^-$  system that does not involve  $[\text{H}^+]$ .

The stoichiometry is 1:1 in all the five systems investigated. The reaction is first order in both the [oxidant] and [reductant] for  $\text{OH}^-$ ,  $\text{NO}_3^-$  and  $\text{S}_2\text{O}_6^{2-}$  systems respectively therefore the overall order for the system is second order with the following rate law

$$-\text{d}/\text{dt}[\text{Ros}] = k_2[\text{Ros}][\text{reductant}]$$

In the  $\text{IO}_4^-$  and  $\text{SO}_3^{2-}$  systems, the reaction is first order in the [oxidant] and zero order in the [reductants] hence the overall order is first order with the rate law

$$-\text{d}/\text{dt}[\text{Ros}] = k_0 [\text{Ros}]$$

The rates of the redox reactions showed direct dependence on acid concentrations for Ros/ NO<sub>3</sub><sup>-</sup> system and an inverse dependence on acid concentration for Ros/SO<sub>3</sub><sup>2-</sup> and Ros/S<sub>2</sub>O<sub>6</sub><sup>2-</sup> systems while in Ros/IO<sub>4</sub><sup>-</sup> system, acid concentration have no effect on the rate of the reaction. The overall rate equation for the reactions can be given as

$$-d/dt[\text{Ros}] = (a+b [\text{H}^+]) [\text{Ros}][\text{NO}_3^-] \text{ for Ros/NO}_3^- \text{ system}$$

$$-d/dt[\text{Ros}] = (a+b [\text{H}^+]^{-1}) [\text{Ros}][\text{reductant}] \text{ for Ros/SO}_3^{2-} \text{ and Ros/S}_2\text{O}_6^{2-} \text{ systems}$$

The rate of the reaction displayed negative salt effect for Ros /OH<sup>-</sup> system and a positive salt effect for Ros /NO<sub>3</sub><sup>-</sup> system and the rate also was sensitive to changes in the di-electric constants.

Spectroscopic investigation showed the presence of short-lived intermediate complex formation in the Ros/IO<sub>4</sub><sup>-</sup> and Ros/ SO<sub>3</sub><sup>2-</sup> systems. This suggested that both systems are proposed to take place by inner sphere mechanism. In Ros/ OH<sup>-</sup>, Ros/NO<sub>3</sub><sup>-</sup>, and Ros/S<sub>2</sub>O<sub>6</sub><sup>2-</sup> systems, there was no evidence for the formation of an intermediate complex of significant stability and free radicals are absent therefore the mechanisms of their reactions are discussed in terms of outer sphere mechanism.

On the basis of the experimental results obtained, the outer sphere mechanism has been proposed for Ros/ OH<sup>-</sup>, Ros/NO<sub>3</sub><sup>-</sup> and Ros/S<sub>2</sub>O<sub>6</sub><sup>2-</sup> systems respectively and inner sphere mechanism for Ros/IO<sub>4</sub><sup>-</sup> and Ros/SO<sub>3</sub><sup>2-</sup> systems.

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## Abbreviations

<b>Abbreviation</b>	<b>Name</b>
A	Absorbance
aq	Aqueous
ATP	Adenosine triphosphate.
B.D.H.	British Drug House
Calc.	Calculated.
$D_{\text{mix}}$	Dielectric constant of mixture.
$E_{\text{mad}}$	Madelung Energy.
env	Environment.
$E_{\text{op}}$	Energy for optical electron.
ET	Electron transfer.
Eth transfer.	Energy for thermal electron
$H_2A$	L-ascorbic acid
$H_2R$	1, 3- di hydroxy benzene.
I.S	Innersphere.
I	Ionic strength.
IT	Intervalence transfer
K	Equilibrium constant
EXAFS	Extended x-ray Absorption fine structure Spectra.
EPR	Electron Paramagnetic Resource
$k_{\text{red}}$	Rate constant for redox process
$k_{\text{sub}}$ process	Rate constant for substitution
NADPH diphosphate	Nucleic acid hydrogen
O.S	Outer sphere
Obs	Observed.
Oes	Oxygen-evolving centre
PCET transfer.	Proton coupled electron
Phen	1, 10 phenanthroline
PQ	Plastoquinone
PS II	Photo system II
Redox	Oxidation-reduction
Ros	Rosaniline hydrochloride.

Sub  
UV  
□  
λ

Substitutions.  
Ultraviolet.  
Concentration  
Wavelength.

# CHAPTER ONE

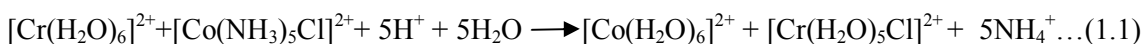
## 1.0 INTRODUCTION

After a period of quiescence in the early part of the 20<sup>th</sup> century, inorganic chemistry has again become an exciting area of research. The most interesting developments in inorganic chemistry bridge the gap with other disciplines. These include organometallic chemistry with bias towards catalysis, coordination chemistry and bioorganic chemistry (Purcell and Kotz, 1977)

Many organometallic compounds play important roles in industrial chemistry as catalysts. Some success has been achieved in the use of such catalysts for converting natural gas to related but more useful chemical substances.

Chemists have also synthesized large inorganic molecules that contain a core of metal atoms, such as manganese, surrounded by a shell of different chemical units. Some of these compounds, referred to as metal clusters, have characteristics of metals, while others react in ways similar to biological systems. Although organic molecules were once thought to be the distinguishing chemical feature of living creatures, it is now known that inorganic chemistry plays a vital role as well. Trace amounts of metals such as manganese in biological systems are essential for processes such as photosynthesis, respiration, nerve function, and cell metabolism. Processes of this kind form the object of study of bioinorganic chemistry. (Cotzias, 1962)

A great deal of work in inorganic reaction mechanism came from the research efforts of Taube and co-workers (Taube et al; 1953; Taube and Meyers 1954). They started with the study of reduction of substitutionally inert amine complexes of Co<sup>III</sup> by substitutionally labile Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and established the ultimate details of how electron transfer reactions occur. (Taube et al 1953; Taube, 1970). Using isotopic labelling techniques, they were able to suggest that the reaction can be represented by equation (1.1)



Significant advances have been recorded in the synthesis and characterization of transition metal complexes of mono-, di- and poly nuclear centers. (Arulsamy et al, 1994; Cooper and Calvin, 1977; Dave and Czernuszewicz; 1994 (a and b)). The reactions of these complexes are being studied continuously, particularly the electron transfer processes (Monzyk and Holwerda, 1992. Ghosh et al, 1994).

These electron transfer reactions gave insight into the actual process of transfer. They also have found application in chemical synthesis, histological techniques, biological systems and electron transfer catalysis. (Bugress, 1978, Wilkin, 1974)

Various reactions in inorganic and biological systems (biological reactions that involve organic catalysts or enzymes) involve transfer of electrons at one stage or the other. In addition, the need for industries to have a new set of stable polymers particularly those that could withstand extremes in thermal and physical stress aroused great interest in inorganic polymers with skeletons consisting of boron, aluminium silicon and phosphorus atoms. The formation of such inorganic polymers demands good knowledge of inorganic reactions kinetics. (Armtage, 1972)

Iyuu in 1982 also highlighted the fact that the knowledge gained from these reactions will constitute an inevitable prerequisite to the understanding, development and eventual effective control of a wide area of science and technology.

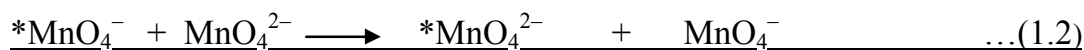
## 1.1 OXIDATION – REDUCTION (REDOX) REACTIONS

Redox reactions are among the most common types of reactions in chemical and biological processes (Yoshihana et al, 1995). They are usually spontaneous and often accompanied by changes in oxidation state of at least two of the reactants. (Purcell and Kotz, 1977). These reactions are basically of two types;

- i) Reactions involving electron transfer (ET) which play important roles in chemical, biological and technological processes.
- ii) Reactions involving atom transfer with or without electron transfer.

The simplest of all these redox reactions are those that involve the transfer of electrons. An example is the reaction between  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  which was studied by the use of an isotopic tracer (Horning et al, 1950) and is represented by

equation (1.2)



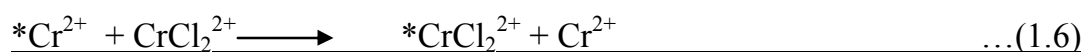
### 1.1.1 Electron Transfer Reactions

Electron transfer reaction mechanisms are inherently of interest because of the insight they give into the actual process of transfer. (Sheldon and Kochi, 1981; Meyer and Taube, 1987).

Electron transfer is very important in different types of molecular and bimolecular systems. It is also important in polymerization reaction, photography, electrochemistry, photosynthesis, metabolism and many other processes of individual and industrial applications. (Yoshihana et al, 1995). Electron transfer reactions can be classified in two main types on the basis of thermodynamic parameters. These are homonuclear electron exchange reactions and heteronuclear electron exchange reactions (Lawal, 1997)

#### 1.1.1.1 Homonuclear (or Isotopic Exchange) Reactions

In homonuclear electron exchange reactions, electron transfer takes place between two ions of the same element existing in different oxidation states.

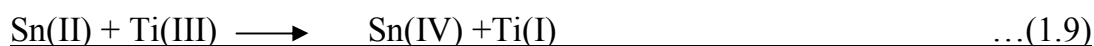
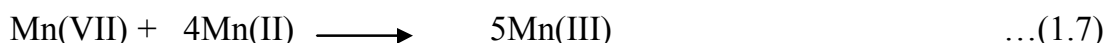


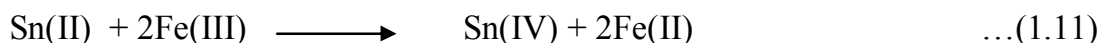
where \* is an isotopically labelled species.

In all of the above reactions, there is no net chemical change and the rate constant for the forward and backward reactions are equal. The reactant and product concentrations are the same. Therefore the equilibrium constant =1. The only change in free energy is that due to mixing and therefore the overall free energy change  $\Delta G \approx 0$

### 1.1:1.2 Heteronuclear Electron Exchange or Cross Reactions

These reactions involve transfer of electrons between different metal ion centres and the products are chemically distinct from the reactants. The rate can be measured by chemical methods. Examples are equations (1.7–1.11).





In equations (1.7) and (1.8), the net change in free energy in most cases is less than zero ( $\Delta G < 0$ ).

In equations (1.8) and (1.10), the stoichiometry is 1:1 and the reactions is complementary in which case the oxidant and reductant undergo equal changes in oxidation states. However in equation (1.11), the stoichiometry of these types of reactions is usually not 1:1 and they are non-complimentary in that the oxidant and reductant undergo unequal changes in oxidation states. These reactions certainly involve the formation of reactive intermediates in which unstable oxidation states of the metal are formed.

## **1.2 THEORIES OF ELECTRON TRANSFER**

### **1.2.1 Franck – Condon Principle**

Franck – Condon principle state that “the motion of nuclei is so slow ( $10^{-13} \text{ s}^{-1}$ ) when compared to that of electrons ( $10^{-15} \text{ s}^{-1}$ ) and that electron transfer occurs without an appreciable movement of the nuclei” (Platzmann and Franck, 1954; Sutin, 1966). The principle shows that the position of the nuclei remains virtually frozen (intact) during the process of electron transfer. There are two important consequences of the electron transfer processes from the Franck - Condon principle.

Firstly, no angular momentum can be transferred to or from the transition state during the act of electron transfer and a restriction is also imposed on the change in spin angular momentum.

Secondly, the oxidant and the reductant must undergo reorganization before electron transfer in such a way that their energies in the transition state become identical thus minimizing the energy change on electron transfer.

The total change in free energy involved in the process can then be represented by equation (1:12) (Marcus 1956)

$$\underline{\underline{\Delta G^{\#} = \Delta G_t^{\#} + \Delta G_i^{\#} + \Delta G_o^{\#} \dots(1.12)}}$$

Where

$$\underline{\underline{\Delta G_t^{\#} = \text{Activation free energy}}}$$

$$\underline{\underline{\Delta G_i^{\#} = \text{Inner-sphere reorganization energy}}}$$

$$\underline{\underline{\Delta G_o^{\#} = \text{Outer-sphere reorganization energy}}}$$

### **1.2.2. Electron Tunnelling Theory**

Tunneling is a term often associated with electron transfer, which involves transfer of a particle between electronically coupled chemical sites through a tunneling process. In that sense, every electron transfer process involves electron tunneling with tunneling frequency given in the classical limit by equation. (1.13).

$$\underline{\underline{V_e = \frac{2\pi V^2}{h} \left[ \frac{\pi^2}{\lambda RT} \right]^{\frac{1}{2}} \dots(1.13)}}$$

$$\underline{\underline{V_e = \text{Electron transfer frequency}}}$$

$$\underline{\underline{V = \text{Electronic coupling}}}$$

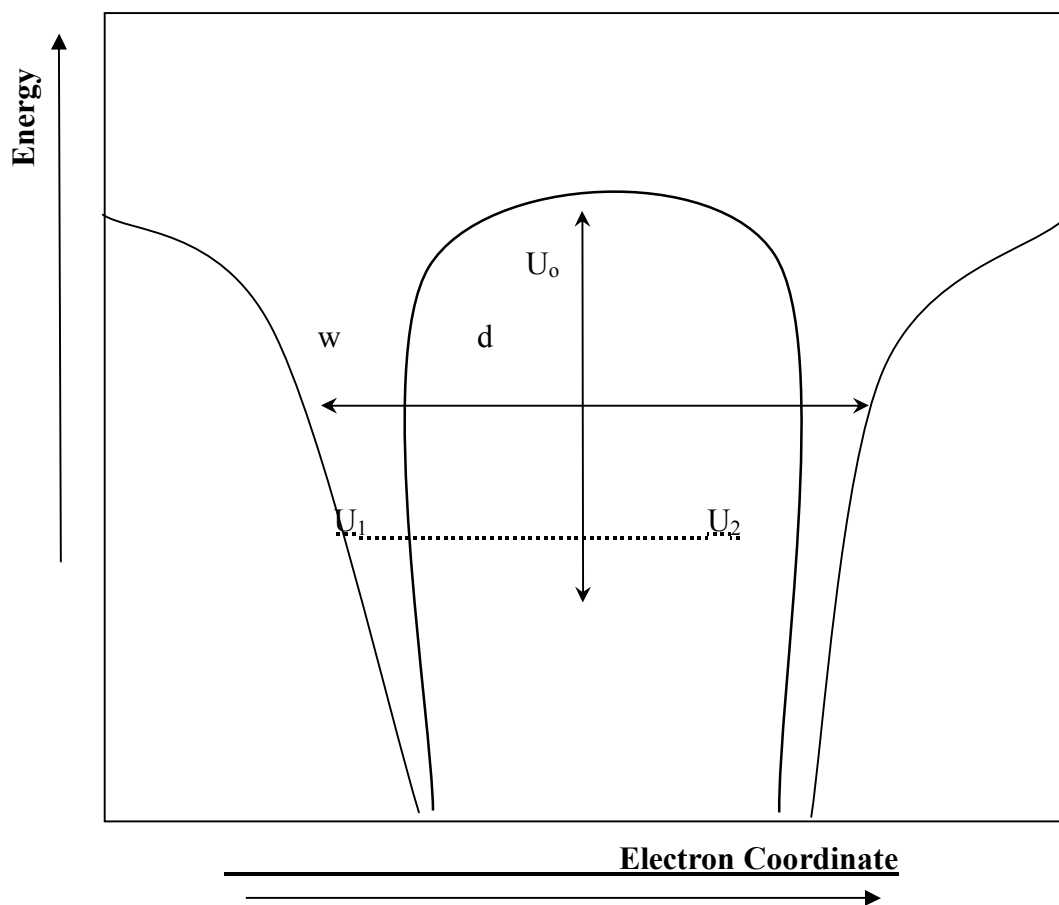
$$\underline{\underline{h = \text{Boltzman constant}}}$$

$$\underline{\underline{T = \text{Absolute temperature}}}$$

$$\underline{\underline{R = \text{Gas constant}}}$$

The electron tunneling theory was developed by some workers (Weiss 1954; Marcus et al, 1954). They concluded that the electronic energy in the reactants and products is not as high as would ordinarily be expected from the classical point of view. Under this condition, electron transfer process was then viewed as a tunneling process in which electron passes through the potential energy barrier rather than over it (Basolo and Pearson, 1967). The outcome of the tunneling process is that electron can be moved to a longer distance beyond the distance of

actual collision of the reactants. The potential energy barrier leakage is illustrated in Figure- 1.1



**Fig.1.1 ELECTRON TRANSFER BY PENETRATION OF A POTENTIAL ENERGY BARRIER.**

$U_1$  and  $U_2$  = Ground states of electron in cation 1 and 2 respectively.

$$\begin{aligned} \underline{d} &= \text{Width of barrier at height of penetration} \\ \underline{w} &= \text{Kinetic energy of the electron.} \\ \underline{U_0} &= \text{Height of the barrier} \end{aligned}$$

A theoretical basis was developed to explain this electron transmission model (Marcus et al, 1954; Marcus, 1956) and their results were expressed in terms of transition state theory of chemical kinetics and could be written in the form

$$\underline{k} = \frac{K_T}{h} k' \exp\left(\frac{\Delta G_r^*}{RT} - \frac{\Delta G_e^*}{RT}\right) \dots (1.14)$$

$$\underline{K_T} = \text{Equilibrium constant at constant temperature.}$$

$$\underline{k} = \text{Rate constant}$$

$$\underline{k'} = \text{Electron transmission co-efficient}$$

$$\underline{h} = \text{Boltzman constant}$$

$$\underline{T} = \text{Absolute temperature}$$

$$\underline{G_e^*} = \text{Activation energy}$$

$$\underline{G_r^*} = \text{Hydration energy for inner co-ordination shell arrangement}$$

$$\underline{R} = \text{Gas constant}$$

As the exchanging partners come close, transmission coefficient increases, while the energy of activation also increases as a result of electrostatic repulsion between the reactants. Both effects tend to decrease the rate constant. The rate at an optimum distance between the reactants, a maximum exchange rate is obtained. Taube (1959) and Lewis (1980) then suggested that electron tunnelling is probably involved in most electron transfer processes and that the tunnelling step might not necessarily be the rate-determining step.

### 1.2.3. Marcus Theory

The approach is to calculate the rate of an outer-sphere electron transfer reaction from the first principle. In the outer-sphere mechanism, the weak interaction between reactants during electron transfer, enables theoretical treatment and correlations between the kinetic and the overall thermodynamic parameters. (Sutin 1966, Diebler and Sutin, 1964). The most widely used of such treatment was developed by Marcus (Marcus, 1956) and is commonly known as Marcus theory.

Marcus theory was initially used for the calculation of absolute rate constants for homonuclear exchange reactions which was later extended to cross reactions and related processes (Marcus, 1956, 1957 a–c, 1963, 1965 a–c, 1968 a and b 1977). He assumed in his theory that when the work term is small, then little reorganization is involved prior to electron transfer. Therefore:

- i. There is small electronic interaction between the reacting species (which are treated as rigid spheres of radii  $a_1$  and  $a_2$ ) and that there is no change of inter-atomic distance between the species during the electron transfer reaction.
- ii. The probability of electron transfer within the activated complex is unity.
- iii. The work terms of the self-exchanging and cross-reaction are the same.
- iv. The motion of the inner coordination spheres are harmonic with

breathing forces having the reduced value  $\frac{2f_i f_r^p}{f_r + f_i^p}$

where  $f_i$  and  $f_i^p$  are force constants for the symmetrical breathing vibration of the species in the reactant and product respectively.

It is necessary to estimate the contribution of  $\Delta G^*$  made by the various steps by which the reaction is thought to occur. Those terms include the free energy

required to bring reactants to within reactant distance and to re-organize bond distance in each reactant so as to bring each to a common state prior to electron transfer and finally the free- energy change of the net reaction,  $\Delta G^*$ .

The free energy  $\Delta G^*$  can therefore be represented by equation

$$\underline{\Delta G^* = \frac{\lambda}{4} + \frac{(\Delta G^{*p} - w^p - w^r)}{2} + \frac{(\Delta G^{*p} - w^p - w^r)^2}{4\lambda} \dots (1.15)}$$

$$\underline{\text{where } \lambda = \lambda_p + \lambda_i \dots (1.16)}$$

$\lambda_p$  and  $\lambda_i$  are given as follows

$$\underline{\lambda_p = (ne)^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{D_{op}} - \frac{1}{D} \right) \dots (1.17)}$$

$$\underline{\lambda_i = \frac{f_i f_i^p}{f_i + f_i^p} (\Delta a_1)^2 + \frac{f_2 f_2^p}{f_2 + f_2^p} (\Delta a_2)^2 \dots (1.18)}$$

where

$w^r$  and  $w^p$  –are work terms required to bring the reactants to their mean separation distance ( $a_1 + a_2$ ) and then remove the products to infinity.

$\lambda_p$  and  $\lambda_i$  –are the free energies required to reorganize the solvent molecules around the reactants (the outer-sphere coordination shell) and to reorganize the inner coordination shell of the reactants.

$\Delta G^*$  – is the standard free energy of the reaction at the separation distance.

$n$  – is the number of electron transferred which is based on the assumption that

$$\underline{\frac{a_1 + a_2}{2} = (a_1 a_2)^{\frac{1}{2}} \text{ and } a_1^a = a_1 - a_1^p \text{ is the difference in the radius of the}$$

specie i when it is a reactant and its radius when it is a product.

$D_{op}$  and  $D_r$  are the square of the refractive index and dielectric constant for the medium respectively.

The free energy  $\Delta G^*$  is related to the free energy of activation as follows.

$$\Delta G^* = \Delta G^\ddagger + RT \ln \frac{hZ}{kT} \quad \dots(1.19)$$

$$\text{or } \Delta G^* = \Delta G^\ddagger - 10.2256 \text{ Jmol}^{-1}\text{K}^{-1} \quad \dots(1.20)$$

So that the rate constant becomes

$$k = Z \exp \frac{-\Delta G^*}{RT} \quad \dots(1.21)$$

where  $Z = 10^{11} \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}$  ( for homogeneous reaction).

Iyun in 1982 reported that from the above equation the activation parameters for electron transfer reactions can be predicted. Therefore equation (1.15) can be re written as

$$\Delta G^* = \frac{\Delta G_{11}^* + \Delta G_{22}^*}{2} + \Delta G_{12} \left( \frac{1 + \alpha}{2} \right) \quad \dots(1.22)$$

where  $\Delta G_{11}^*$ ,  $\Delta G_{22}^*$  and  $\Delta G_{12}^*$  are the free energy for the exchange reactions respectively.

This relationship can also be written for entropy and enthalpy.

$$\Delta S^* = \frac{\Delta S_{11}^* + \Delta S_{22}^*}{2} \left( (1 - 4\alpha^2) + \frac{\Delta S_{12}^*}{2} (1 + \alpha) \right) \quad \dots(1.23)$$

$$\Delta H^* = \frac{\Delta H_{11}^* + \Delta H_{22}^*}{2} \left( (1 - 4\alpha^2) + \frac{\Delta H_{12}^*}{2} (1 + 2\alpha) \right) \quad \dots(1.24)$$

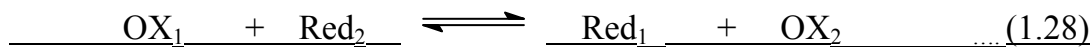
From the expressions in equations (1:20)–(1:23) above, the activation parameters can be calculated using the appropriate equations below

$$\Delta G^* = \Delta G^\ddagger + RT \ln \frac{hZ}{kT} \quad \dots(1.25)$$

$$\Delta S^* = \Delta S^\ddagger + RT \ln \frac{hZ}{kT} - \frac{1}{2}R \quad \dots (1:26)$$

$$\Delta H^* = \Delta H^\ddagger - \frac{1}{2}RT \quad \dots (1:27)$$

For a cross reaction (1:28), and (1:29). Marcus theory predicts that the rate of the electron exchange is given by equation (1.31)



$$\underline{k_{12} = (k_{11} k_{22} K_{12} f)^{\frac{1}{2}}} \quad \dots (1.31)$$

$$\underline{\text{where } \log f = \frac{(\log k_{12})}{4 \log \left( \frac{k_{11} k_{22}}{Z^2} \right)}} \quad \dots (1.32)$$

$k_{12}$  and  $K_{12}$  are the rate constant and equilibrium constant respectively for the cross reaction  $k_{11}$  and  $K_{22}$  are appropriate rate constants for the isotopic exchange reactions.  $Z$  is the collision frequency for the hypothetically unchanged reaction ions.

However, the theoretical rate constants for electron transfer reactions can be calculated from equation (1:33) below by considering the solvent reorganization occurring outside the inner coordination shells

$$k = Z \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \text{ of each of the reactant} \dots(1:33) \Delta G^\ddagger$$

$\Delta G^\ddagger$  = Change in free energy of cross reaction

R = Gas constant

T = Absolute temperature

A reasonable agreement between the rate calculated and rate observed is taken as evidence that the reaction is of the outer-sphere type. This relation has been used to:-

- i) Affirm that the experimental and calculated values of  $k_{12}$  are in accord; when the values of  $k_{11}$ ,  $k_{12}$ ,  $K_{12}$  are known; compilation of observed and calculated rate constants has been documented (Pennington, 1978) and comparing the different oxidants with the same series of reductant.
- ii) Check for gross deviations from the theory, which signal a change in mechanism and can be used to estimate the self-exchange rate constant for one reactant when the value is unknown, based on measured values for one or more cross reactions. (Pladziwicz and Espenson, 1973).

### 1.3 IMPORTANCE OF ELECTRON TRANSFER REACTIONS

Electron transfer is important in reactions of metal ion complexes. They often involve ligand substitution or electron transfer or both. In some redox reactions, ligand substitution occurs and this provides a low energy pathway for electron transfer as shown in the oxidation of both metal ion and non-metallic substrates by chromium (VI) (Beagle and Haight, 1972).

Various reactions in organic and biological systems involve the transfer of electrons at one stage or the other especially in biological redox reactions involving organic catalysts

More recently, it has become increasingly obvious that many reactions in inorganic chemistry once thought to be concerted in nature also occur via sequential one electron step. (Thompson and Meyer, 1982)

In view of the obvious importance of electron transfer reactions; further investigations on these reactions are necessary. Since the main approach to reaction mechanism is the kinetic study, it is necessary that emphasis be placed on rate measurements and their interpretations.

#### **1.4 MECHANISM OF ELECTRON TRANSFER REACTIONS**

The mechanism of a reaction is the detailed stepwise process involving molecules, atoms, radicals or ions that occur simultaneously or consecutively and culminates in the observed overall reaction. Therefore in studying a redox reaction mechanism, one needs to investigate the following parameters and apply it appropriately.

The first set of parameters to be investigated are the stoichiometry of the reaction and the nature of the activated complex, whether the given chemical reaction occurs in a single molecular process or several processes. If the latter occurs, one should consider whether the molecular steps occur as concurrent alternatives or in succession along a single pathway.

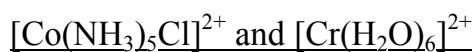
In addition, the stereochemical arrangement of the activated complex, the state of maximum potential energy through which the system passes in its key phase is the rate determining step and the presence or absence of intermediate(s) in the reaction must also be considered.

The effects of acid or base (pH), anions and or cations, dielectric constant, ionic strength and activation parameters  $E_a$ ,  $\Delta H$ ,  $\Delta S$  e.t.c on the rate of the reaction must be considered. However, when the reaction is accompanied by transfer of electrons or atoms, the nature of all these parameters can be rationalized in terms of two distinct mechanisms that have been established for

reactions i.e. the outer-sphere and the inner-sphere mechanisms These two mechanisms were first proposed by Taube and his co-workers (Taube et al, 1953, Taube 1959).

### **1.4.1 Inner-Sphere Mechanism:**

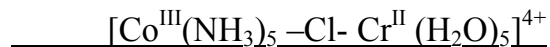
An inner-sphere mechanism is one in which the reductant and oxidant share a ligand in their inner or primary coordination spheres and the electron is transferred across a bridging group. That is, the two reactants are linked together by at least one bridging ligand common to the coordination shell. The essential feature of this mechanism is that substitution takes place at one of the metal centres to give binuclear ligand bridged specie prior to the transfer of an electron. The first redox reaction that demonstrated this type of mechanism was the reaction between



This reaction involves a binuclear ligand -bridged intermediate of



which leads to transfer of electron



and forming a product of



The reaction product will then indicate that there was transfer of electron from cobalt to the chromium through the ligand which is usually but not always transferred from one reactant to another. The bridging ligand X may be F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and group VI etc. The only essential feature for a bridging ligand is that it

should have at least one lone pair of electrons available for bonding to metal cation that is at least one lone pair electron beyond the electron pair needed to bond to cobalt in the first place in equation (1.34) above. For example, ligands such as NH<sub>3</sub> and other Group 5 bases have only one lone pair of electron available for bonding to a cation and they use this to coordinate with the first metal. They therefore cannot act as bridging ligand in inner-sphere redox reaction.

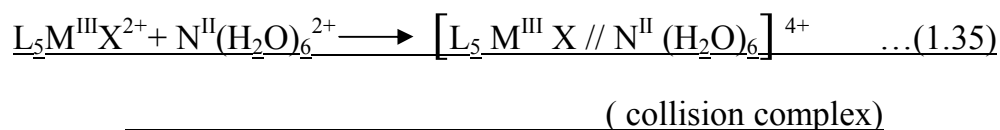
The prerequisite for inner sphere mechanism includes:

(i) One of the reactants (usually the oxidant) should possess at least one ligand capable of bonding simultaneously to two reaction centres (metal ions). Although this bridging ligand (atom) is frequently transferred from the oxidant to the reductant in the course of electron transfer, it is not always the case.

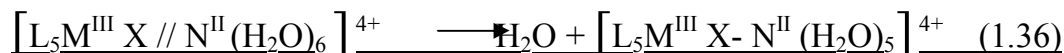
(ii) One ligand of the reactants (usually the reductant) should be substitutionally labile i.e. capable of being replaced by a bridging ligand in a facile substitution process

The basic step in this type of reaction may be summarized by the sequence below as proposed by Sutin, (1968), Bennet, (1972), and Linck, (1972).

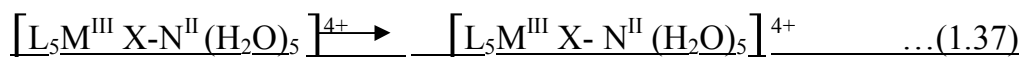
Step 1: - Formation of an Encounter or Collision Complex.



Step 2: Formation of a bridged precursor complex



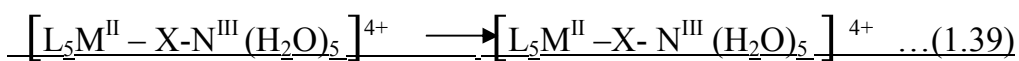
Step 3: Formation of activation of the precursor complex



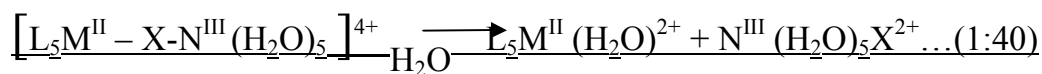
Step 4: Formation successor complex and electron transfer.



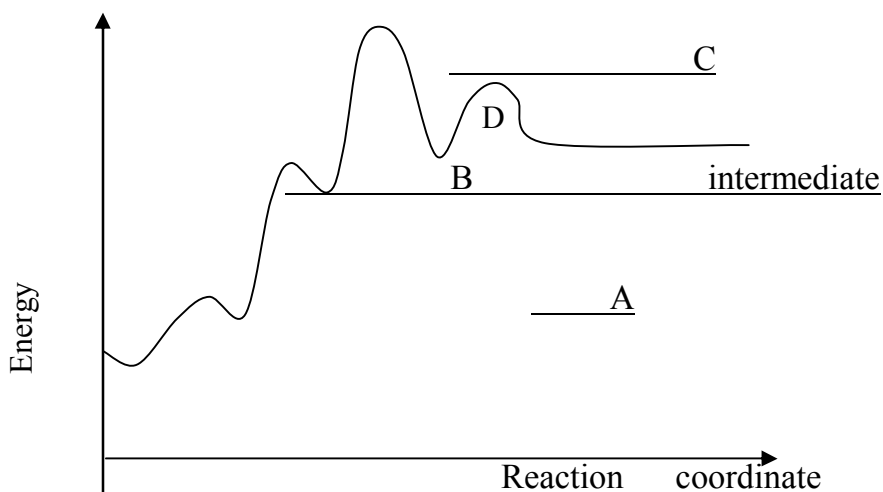
Step 5: Deactivation of the successor complex



Step 6: Decomposition of the successor complex



A typical energy profile for a redox reaction which occurs by the inner-sphere mechanism is often illustrated as below

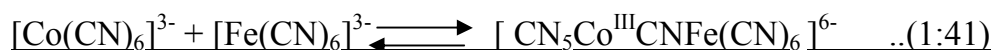


**Fig.1.2 Energy profile diagram for a redox reaction which occurs by the inner-sphere mechanism**

- A. = Collision complex
- B. = Bridged precursor complex formation
- C. = Successor complex formation and act of electron transfer.
- D. = Decomposition of successor complex giving the products

Any of the reaction steps could be the rate-determining step but there are three special steps that are practicable.

- i. Formation of successor complex is the rate-determining step. This is found in substitution controlled redox reactions.
- ii. Electron transfer within the bridged complex is the rate-determining step. This is the most commonly observed result in inner- sphere mechanism.
- iii. The decomposition of the successor complex is the rate-determining step e.g



The successor complex has been identified as a solid.

However, in 1972, Linck reported that the reaction usually encountered rate-determining step that involves the actual transfer of electron(s) i.e the transition states are

- 1) systems in which the highest point on the free energy-reaction co-ordinate diagram corresponds to the acts of electron transfer itself
- 2) systems in which the precursor complex formation dominates the process.
- 3) systems in which the successor complex destruction is of importance

He then reported that the composition of all the three transition states are the same and can be schematically illustrated as in Fig 1:3.

## Scheme 1

This involves the formation of the precursor complexes with their rates of transformation to successor complexes relatively slow. For example, the reduction of  $[\text{Co}(\text{en})_2\text{H}_2\text{OCl}]^{2-}$  by  $\text{Fe}^{2+}$ . This reaction proceeds by substitution on the  $\text{Fe}^{2+}$  ion followed by electron transfer with subsequent rupture of the Co–Cl bond to give  $\text{FeCl}^{2-}$  and  $\text{Co}^{2-}$  (Linck, 1972). The binuclear complex formed must be stable so that this reaction will dominate.

## Scheme II

In Scheme II, the rate of electron transfer occurs rapidly as soon as the precursor complex is formed. For example, oxidation of  $\text{Co}^{\text{III}}$  by series of reductants as shown in Figure 1:3.

## *Scheme III*

Here the reactants and the successor complexes are in equilibrium with the overall reaction rate dependent on the rate of bond rupture in the successor complex. The reduction of  $\text{Cis-}[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ ,  $\text{Cis-}[\text{Ru}(\text{NH}_3)_4\text{H}_2\text{OCl}]^{2-}$  and  $[\text{Ru}(\text{NH}_3)_3\text{Cl}]^{2-}$  by  $\text{Cr}^{2+}$  proceeds by Scheme III. (Basolo and Pearson, 1967, Linck 1972).

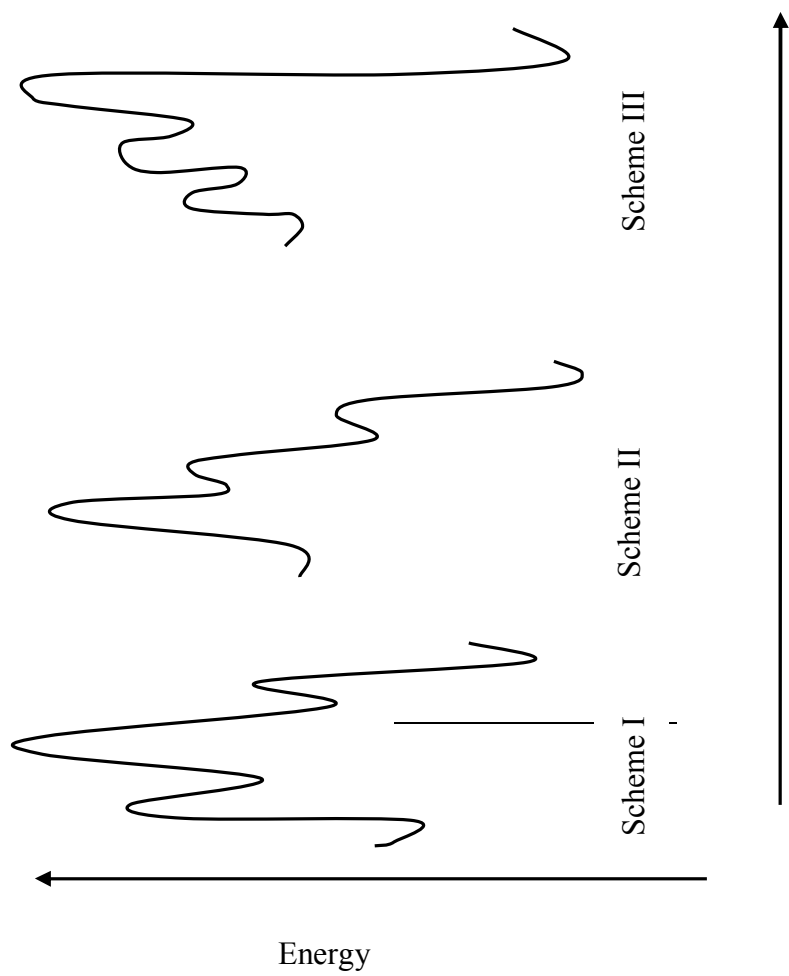


Fig 1.3: - The three pathways for achieving and destroying the activated complex in inner-sphere electron transfer process (Linck, 1981)

### 1.4.2 Outer-Sphere Mechanism:

Outer-sphere electron transfer constitutes one large, well-recognized and extensively studied group of reactions. It is one in which the reactants do not form an intermediate with bridging functional group to provide a pathway for electron transfer.

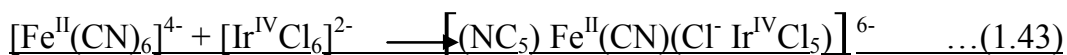
In principle, outer-sphere mechanism involves electron transfer from reductant to oxidant with the coordination sphere of each staying intact throughout. Both reactants are inert with respect to substitution or one is relatively inert and does not present site for the labile reactants.

This mechanism also takes place when the energy barrier involved is low or is zero. The mode of activation of outer-sphere mechanism can be illustrated as shown below for the reaction between

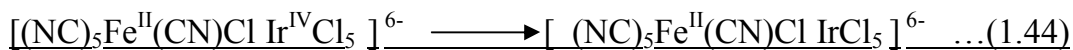


This mechanism occurs in four steps as shown below.

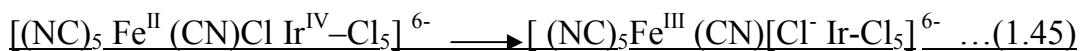
Step I:- Formation of precursor complex



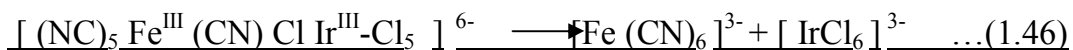
Step 2:- Activation of precursor complex



Step 3:- Electron transfer and formation of the successor complex



Step 4:-Decomposition of the successor complex to give final products



In the above, any of the steps can be rate determining step but it is important to mention the following points:-

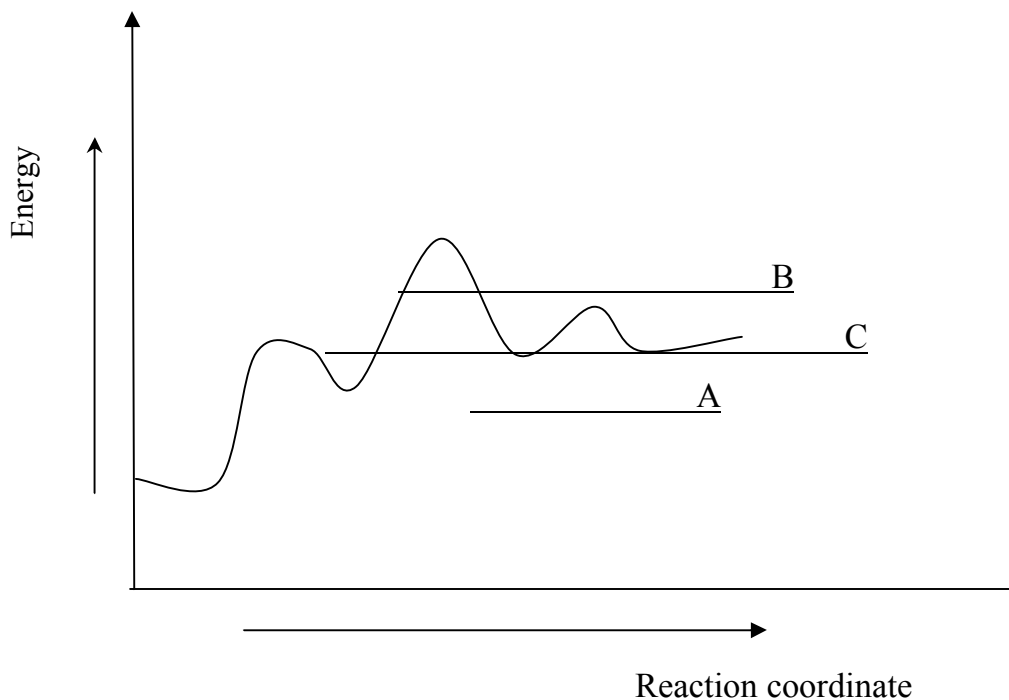
The first step is known as the formation of precursor complex, wherein the distance between the reactant centers is approximately that required for electron transfer, but their relative orientations and internal structures do not yet permit electron transfer. (Purcell and Kotz, 1977)

The second and third steps involve structural changes in the precursor to accommodate the electron transfer. Within the precursor, there must be both a reorganization of the oxidant and reductant complexes and within those complexes, structural changes that define the chemical activation process for electron transfer.

As the transition is passed, there follows the completion of the electron transfer and final relaxation of the oxidant and reductant structure.

The fourth and final step is the separation of the products, ions or molecules

A typical energy profile for a redox reaction which occurs by the outer sphere mechanism is illustrated in Fig 1:4



**Fig:1.4 Energy profile diagram for a redox reaction which occurs by outer sphere mechanism**

where A. Formation of precursor complex

B. Electron transfer and formation of successor complex

C. Separation of the successor complex to give final product

Theoretically any of the above steps can be the rate-determining step, but the most usual rate-determining step is B that is the electron transfer and formation of the successor complex increases the energy of the reaction.

However, several chemists have developed theoretical treatments of outersphere redox reaction. Probably the best known theory is the version proposed and developed by Marcus (1956)

Marcus theory determines the rate of outer-sphere redox reaction as the rate of electron transfer between the oxidized and reduced forms of each of the couples that make up the redox reaction.

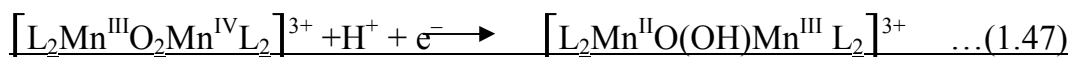
### 1. 4.2.1 Proton Coupled Electron Transfer (PCET) Mechanism

This is the mechanism that involves the simultaneous transfer of proton and electron under the outer-sphere mechanism. Here, it is also possible for three-species to come together in the form of an ion pair leading to the final products. The situation is such that an open coordination will act as an electron-proton acceptor (Meyer and Taube, 1987). This mechanism has been observed for a number of reactions (Ghosh et al, 1994, Arabel et al, 1997, Iyun and Lohdip, 1999, 2001).

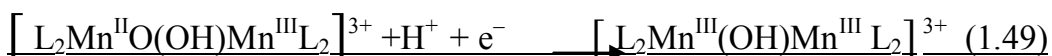
The requirement for the occurrence of the PCET pathway is that the molecule or substrate must contain

- (i). a protonable moiety,
- (ii). be capable of accepting an electron or contain acidic proton(s)  
\_\_\_\_\_ or
- (iii). have easily removable electron(s)
- (iv). have easily oxidisable group(s) or easily removable electron(s). (Chaudhuri et al, 1995, Arabel et al, 1997, Iyun et al, 1997)

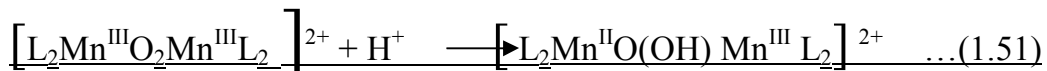
It has been found that mixed valence manganese complexes fulfill two of the above conditions as shown in the equations (1.47)–(1.51).



L = bipyridine (bpy)



L=Phenanthroline (phen)

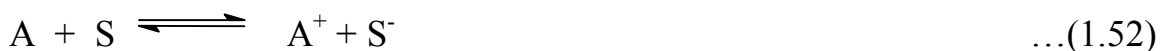


L = N, N-bis (2- methyl pyridyl) ethane-1,2-diamine.

The redox reactions of these systems have been shown to occur by PCET pathway (Chaudhuri et al 1995, Arabel et al, 1997 Iyun et al, 1997). Other substrates which have been shown to promote the PCET mechanism include thiols and hydroxy-acids because both groups of compounds contain acidic protons and easily oxidisable groups.

### **1.4.3 Solvated Electron Theory**

In addition to the two mechanisms for electron transfer reactions, another possibility is the solvated electron concept (Latimer 1952). In this theory, the reducing agent is assumed to eject an electron into the solvents which solvate it and holds it until the oxidizing agent picks it up. The redox process involved in this model is thought to occur by the following steps equations (1.52)–(1.54).



Where A = reductant, B= oxidant and S = Solvent.

This process has been found to occur readily in non-aqueous solvents. (e.g. liquid ammonia and liquid halides), but it is unlikely to occur in aqueous medium. There is no available evidence to show that in aqueous solutions, the electron from a reducing agent is released and becomes solvated before reacting with an oxidizing agent (Cooke, 1979). This is because the aquated electron ( $E_0 = -2.7V$ ), will rapidly reduce water to hydrogen (Latimer, 1952) as in equation (1.55).



## **1.5 FACTORS AFFECTING OUTER-SPHERE REACTIVITY**

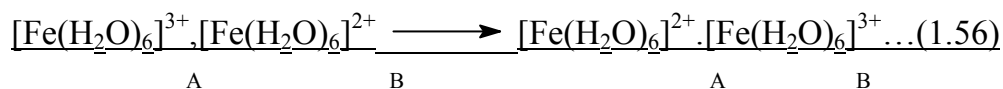
In reactions occurring by the outersphere mechanism, it is possible to assess the factors (at the molecular level) that determine rate of electron transfer. The outer-sphere reaction is far easier to treat than reactions occurring by inner-sphere mechanism because of its relative simplicity and the absence of bond-making or bond-breaking steps. (Wilkinson, 1987)

There are three main factors that play important roles in determining the rate of electron transfer.

### **1.5.1 Intramolecular Vibrational Trapping**

A commonly used example for illustrating intra molecular vibrational trapping induced by structural changes is  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{3+}$  self-exchange reactions. X-ray crystallographic studies in solution show that the most significant structural difference between the aquated  $Fe^{II}$  and  $Fe^{III}$  ions is a

symmetrical decrease in the Fe-OH<sub>2</sub> bond distance upon oxidation. Electron transfer is accompanied by net structural changes at each redox site since both change their electron content during the reaction e.g the site labelled B in equation (1:56) will have the equilibrium structure of Fe<sup>II</sup> before electron transfer and the equilibrium structure of Fe<sup>III</sup> after electron transfer.



The changes in structure that must occur create barriers to electron transfer. In order to understand the origin of the barrier and to treat it quantitatively, it is necessary to recall that the structural changes at each reactant can be resolved into a linear combination of its normal vibrational modes.

The normal modes constitute a complete, orthonormal set of molecular motions into which any changes in intramolecular structure can be resolved. From the essentially symmetrical decrease in all six Fe-O bonds between Fe<sup>II</sup> and Fe<sup>III</sup>, it can be concluded that the only significant normal mode contributing to the structural change between Fe<sup>II</sup> and Fe<sup>III</sup> is the totally symmetric (Fe-O) iron – oxygen breathing mode.

### **1.5.2 Solvent Trapping**

The solvent plays a role in trapping the exchanged electron on one site similar to that of intramolecular structural changes. An ion can be thought of as creating a polarization field in the surrounding solvent. At the molecular level, there are three ways that the solvent molecules respond to the electrostatic field of the ion.

- a. orientation of permanent solvent dipole
- b. electrostatically induced structural distortions within the molecules.
- c. induced electrostatic polarization of electronic clouds including bounding and non-bounding electron density.

The strength of the ion-solvent interaction depends on the charge on the ion, when electron transfer occurs, changes must also occur in the orientation of the surrounding solvent dipoles since in the electron transfer act, the polarization field at the reactants are interchanged. The necessary re-orientation of solvents are closely related to rotations of molecules in the gas phase but are necessarily collective in nature because of molecule-molecule interaction in the condensed phase of the solution.

The orientation component arising from solvent dipoles must adopt a non-equilibrium distribution before electron transfer can occur. The orientation of solvent dipoles contributes to the energy of activation through the time scale for dipole re-orientation. It can also contribute to the pre-exponential or frequency factor for electron transfer.

### **1.5.3 Electron coupling:-**

For electron transfer to occur between reactants, an electronic Interaction must exist which tends to delocalise the exchanging electron between sites. Neglecting the overlap, the magnitude of interaction is given by equation (1.57)

$$v = (Q_D/v/Q_A) \quad \dots(1.57)$$

where

$v$  = electrostatic operator that describes the electronic perturbation between the electron donor and acceptor and causes electron transfer to occur.

$Q_A$  = electronic wave function for the acceptor

$Q_D$  = electronic wave function for the donor.

The electronic interaction leads to two new electronic states, an upper state and a lower state that combine to give bonding and anti bonding

molecular orbital. If the overlap between  $Q_D$  and  $Q_A$  is negligible, the energies of the two new states including the electronic interaction but neglecting the vibrational energies are given by equation (1.58)

$$U_e + V \text{ and } U_e - V \quad \dots(1.58)$$

where  $U_e = U_e^P = U_e^R$  for a self-exchange reaction.

The existence of vibrational trapping creates an unusual situation compared with other molecular orbital-type problems. If electronic coupling between the two sites is weak, the effect of vibrational trapping will be to localize the exchanging electron either on the electron donor site or on the acceptor site. The delocalization of the exchanging electron is in fact the electron transfer process itself.

If the electronic coupling is weak, electron transfer becomes an occasional event that can only occur at an appreciable rate from electron donors and acceptors having the non-equilibrium vibrational distributions and solvent dipole orientations appropriate for maximizing the electron transfer rate.

## **1.6 CRITERIA FOR ASSIGNING THE MECHANISM OF ELECTRON TRANSFER REACTIONS**

Kinetic studies of electron transfer reactions try to assign the system under study to one of the two established reaction mechanisms. i.e. the outer-sphere and inner-sphere mechanism. The following criteria discussed below have been used for assessing and distinguishing the types of mechanisms for electron transfer reactions.

### 1.6.1. Rate of redox process versus rate of substitution ( $k_{\text{red}}$ vs $k_{\text{sub}}$ )

For the inner-sphere mechanism to take place, there must be substitution of a ligand into the co-ordination shell of one of the metal ions before the electron transfer process. This is to form ligand bridged precursor complex.

If the rate of redox process is greater than rate of substitution, then the reaction cannot proceed through the inner-sphere mechanism. The outer-sphere mechanism must be presumed to be operating.

An example of a reaction with outer sphere mechanism is as given in equation (1.59).



$$k_{\text{red}} = 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$



$$k_{\text{sub}} = 7.8 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

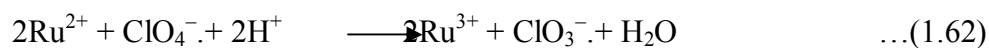
Because  $k_{\text{red}} \gg k_{\text{sub}}$ , the electron transfer in the above reactions cannot occur via formation of a binuclear intermediate hence the reaction has been classified as occurring by the outer-sphere mechanism. (Rosenhein et al, 1974)

According to Larsen and Wahl in 1965, electron exchange reaction between  $[\text{Fe}(\text{phen})_3]^{2-}$  and  $[\text{Fe}(\text{phen})_3]^{3-}$  can also serve as another example.



The rate constant for the substitution of phen are  $7.5 \times 10^{-5} \text{ s}^{-1}$  for  $[\text{*Fe(phen)}_3]^{2-}$  and  $5.01 \times 10^{-5} \text{ s}^{-1}$  for  $[\text{Fe(phen)}_3]^{3+}$  while  $k$  for the exchange is  $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is another example where the outersphere mechanism is operative because  $k_{\text{red}} \gg k_{\text{sub}}$ .

When  $k_{\text{sub}} \gg k_{\text{red}}$ , the reaction will follow inner-sphere mechanism for example, the reduction of  $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$  by  $\text{Cr}^{2+}$  as reported by Taube et al (1954). When  $k_{\text{red}} = k_{\text{sub}}$ , such reaction is said to be substitution controlled. An example of such reaction is the oxidation of  $\text{Ru}^{2+}$  by  $\text{ClO}_4^-$ .



$$\text{Rate} = k[\text{Ru}^{2+}][\text{ClO}_4^-] \quad \dots(1.63)$$

This reaction is believed to be substitution controlled, the rate constant  $k$  and activation parameters being similar to those of halide / anion reactions.

### 1.6.2 Reactivity Pattern.

#### i) Reactivity pattern with a wide range of reactants .

If a wide variety of complexes such as  $[\text{Co(NH}_3)_5\text{X}]^{2+}$  ( $\text{X} = \text{Cl}^-, \text{F}^-, \text{Br}^-, \text{NO}_3^-$ ) is reacted with another metal ion, the rate of the reactions for inner-sphere mechanism would be expected to be sensitive to the nature of  $\text{X}$  (the bridging ligand), while in the case of outer-sphere mechanism, the rate will be similar irrespective of the identity of  $\text{X}$  (Sykes, 1967, Shea and Haim, 1973, Adegite et al, 1977).

#### ii) Relative rates of reaction of hydroxyl and aquo complexes.

The hydroxyl group ( $\text{OH}^-$ ) is a better bridging ligand than  $\text{H}_2\text{O}$  so it is expected that the hydroxo complexes react faster via the inner-sphere mechanism. Thus where  $k_{\text{OH}} \ll k_{\text{H}_2\text{O}}$  the outer-sphere mechanism is said to be operating while the converse is true when  $k_{\text{OH}} \gg k_{\text{H}_2\text{O}}$ .

iii) The effect of added anions and cations gives clue to the type of mechanism in a given redox reaction (Pennington and Haim, 1967; Priztas and Sutin, 1973 and Adegite et al, 1977). Effect of added anions on inner-sphere redox reactions are much smaller than that of outer-sphere reactions. Anion catalyzed reactions are presumed to be operating via outer-sphere mechanism. Thus an examination of the dependence of redox rate on added anion such as chloride ion has been used for the identification of the mechanism.

**iv) The use of ambidentate bridging ligand.**

The distinction between the inner sphere and outer sphere mechanism can be made on the basis of the difference in the rate of electron transfer observed with symmetrical and unsymmetrical bridging ligands e.g. azide, thiocyanate and isothiocyanate complex. If the ratio of the rate constant for the reduction of azide

complex to that for reduction of the thiocyanate complex  $\frac{k_{N_3^-}}{k_{NCS^-}}$  or for

isothiocyanate and thiocyanate complex  $\frac{k_{SCN^-}}{k_{NCS^-}}$  shows no difference or are

similar, then the outer sphere mechanism should be operating while the converse is true for reactions of the inner sphere mechanism (Sutin, 1968, Wang and Esperson; 1965, Candlin et al; 1964, Fay, 1970).

**1.6.3 Identification of binuclear intermediate.**

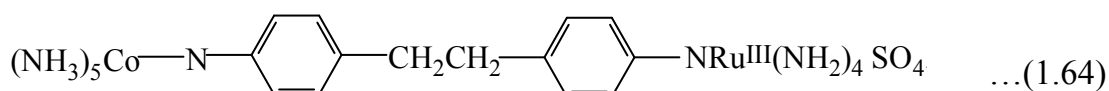
The presence of binuclear intermediate confirms that the reaction proceeds via an inner sphere mechanism. The identification of the binuclear intermediate in the inner sphere mechanism is however possible if the reduced oxidant and the oxidized reductant are relatively inert and the rate of decomposition of the intermediate is slower than the rate of electron transfer. In some cases, where the binuclear intermediate has transient

nature, their presence can be inferred indirectly from kinetic data or from empirical rate law. An example of such indirect identified binuclear intermediate includes  $\text{CrOHV}^{5+}$  (Espenson 1965) and  $\text{OHTi}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (Orhanovic and Earley 1975).

At times, the intermediates are kinetically stable enough to be detected during the reaction studies which provides a convincing evidence for the interpretation of the inner-sphere mechanism.

An example is the reaction  $\text{VO}^{2+}$  with  $\text{Cr}^{2+}$  in which an intermediate,  $\text{VOCr}^{4+}$ , was characterized (Espenson 1965). Its rate of decomposition showed hydrogen ion dependence. If the intermediates are long lived the detection is by spectroscopy while for the short-lived intermediates, fast techniques have been used to isolate it or its presence inferred from the form of the rate law.

Although the detection of a bridged species suggests that it may be an inner-sphere mechanism, it is not however, a sufficient condition for diagnosing the inner-sphere mechanism, such intermediate could actually exist and yet the products are formed directly from reactants. Taube et al (1976) demonstrated such possibilities when they prepared a stable analog of an inner-sphere complex and concluded that electron transfer occurred independent of the connecting chains.



Kinetic evidence from pH dependence term shows the existence of the intermediate. A strong dependence of rate on  $[\text{H}^+]^{-1}$  is generally observed for known inner-sphere reactions especially reactions of aquo complexes.

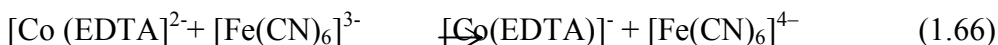
#### 1.6.4 Product Analysis

Inner-sphere mechanism occurs by transfer of electron between two metal centers through a bridging ligand common to both metals when the bridging ligand

is transferred from one metal (reaction) centre to another after the redox process. It provides an evidence in support of the inner-sphere mechanism. An example is reduction of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  by  $\text{Cr}^{2+}$  (Taube et al, 1953)



The product  $\text{CrCl}^{2+}$  was isolated with a binuclear intermediate of  $[(\text{NH}_3)_5\text{Co}-\text{Cl}-\text{Cr}]^{4+}$  and an inner-sphere mechanism was proposed for the reaction. These criteria however must be used with caution since atom transfer does not occur in all inner-sphere reactions. For example, the reaction,



is an example of electron transfer reaction, which occurs by inner-sphere mechanism. This reaction is not accompanied by ligand transfer (Huchital and Hodges, 1973).

### 1.6.5. Activation Parameters.

There seems to be no direct correlation between activation parameters  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  or  $\Delta G^\ddagger$ , the type of mechanism, their signs and magnitudes that can be used in support of or against a particular mechanism. For example, despite the differences in mechanism the  $\Delta S^\ddagger$  for the reaction of  $\text{Cr}^{2+}$  and  $\text{V}^{2+}$  with Ru complexes are almost the same. Lawal, (1997) and Wilkins,(1974,1991). The negative value of  $\Delta H$  indicates the formation of a precursor complex as in inner-sphere mechanism. The use of volume of activation ( $\Delta V^\ddagger$ ) in mechanistic diagnosis has been suggested, but its applicability is narrow This criterion is of little use. The volume of activation is expected to increase in case of inner-sphere mechanism because the effective volume of free water molecule is more than that of a coordinated water molecule.

### 1.6.6 Marcus theory correlation

Marcus theory has been utilized to predict the theoretical correlation between kinetic and thermodynamic parameters of redox reactions which follow the outer-sphere mechanism (Marcus, 1956, Diebler, Sutin, 1964 and Sutin, 1966,).

Marcus theory can be used as an aid to assigning a mechanism to a particular electron transfer reaction. For example a reasonable agreement between calculated and observed rate constants are usually taken as evidence in support of the outer-sphere mechanism.

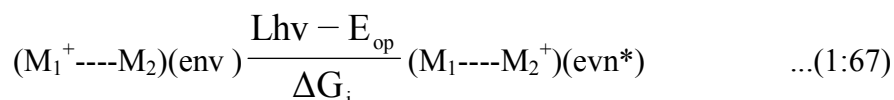
### 1.7 INTERVALENCE TRANSFER (IT)

The study of the rate of intermolecular transfer within binuclear complexes revealed that the act of electron transfer follows two processes i.e optical electron transfer and thermal electron transfer processes (Krentzien and Taube, 1976).

#### 1.7.1. OPTICAL ELECTRON TRANSFER PROCESS.

In this process, the reaction is initiated by bombarding the sample with light of appropriate wavelength. Optically induced electron transfer is an allowed process in which the metal-to-metal charge-transfer bands can be obtained at relatively low energies in the absorption spectra of mixed valence complexes. This type of transfer is termed inter-valence transfer (Hush, 1967, Tom et al, 1975). Inter-valence transfer is defined as an optical transition which involves transfer of electron from one nearly localized site to an adjacent one, the donor and acceptor being metal ions which possess more than one accessible oxidation state (Hush, 1967).

The optical electron transfer process can be represented by the following general equation



(P)

(S\*)

where

(env) = the metal ion in solvent environment.

M<sub>1</sub>---M<sub>2</sub> can be rigid binuclear complexes or reactive pairs in systems undergoing a binuclear reaction where the metal centers differ by one electron.

L = Avogadro number

v = a measure of the molar energy, enthalpy and free energy of the process

$Lh\nu \approx \Delta G$

The electron configuration of S\* is different from that of P but it still retains the ligand environment of P.

### 1.7.2 THERMAL ELECTRON TRANSFER

Thermal electron transfer can be explained in terms of electronic coupling between metal ion sites which are sufficiently separated specially to ensure that direct overlap between pure metal-based d-orbitals is reduced. (Meyer and Taube, 1987) Variations in electronic coupling can lead to profound change in properties and this is what is responsible for the usual physicochemical properties of mixed valence systems (Tom et al, 1975, Iyun, 1982). This can be illustrated by considering the series (bipy)<sub>2</sub>ClRu(pz)RuCl(bipy)<sub>2</sub><sup>3+</sup>, (NH<sub>3</sub>)<sub>5</sub>Ru(pz)(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> and (bipy)<sub>2</sub>ClRu(O)RuCl(bipy)<sub>2</sub><sup>3+</sup> (Meyer and Taube, 1987).

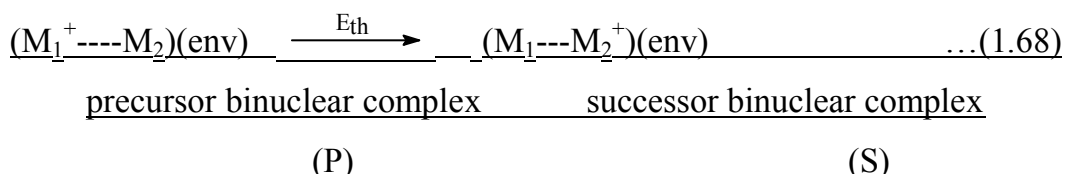
In (bipy)<sub>2</sub>ClRu(pz)RuCl(bipy)<sub>2</sub><sup>3+</sup>, there is a clear evidence for localization of the excess electron on the vibrational time scale. In (bipy)<sub>2</sub>ClRuORuRuCl(bipy)<sub>2</sub><sup>3+</sup>, the excess electron appears to be delocalisation over both metal sites while in (NH<sub>3</sub>)<sub>5</sub>Ru(pz)(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> the system appears to be poised between the localized and delocalised limits.

The transition energy of the optical electron transfer process and the activation energy of the thermal electron transfer process are each dependent on the electron affinity differential of the donor and acceptor sites and the ability of the reactant sites to satisfy the Frank Condon restriction in terms of

the non-equilibrium state of the electrically excited species with respect to atomic motion (Iyun, 1982 and the refs there in).

The thermal electron transfer process can be represented by equation

(1.68)



(env) = the metal ion-solvent environment,  $M_1 \cdots M_2$  can be rigid binuclear complexes or reactive pairs in systems undergoing a binuclear reaction where the metal centres differ by one electron.

Hush (1967) concluded that for symmetrical homonuclear binuclear complexes undergoing one electron transfer, the energies of the optical and thermal electron transfer processes are related by equation (1.69–1.70)

$$\Delta E_{op} = 4 \Delta E_{th}^{\#} \quad \dots(1.69)$$

and

$$\Delta E_{op} = h\nu_{max} - (16 \ln 2kT)^{-1} \Delta E_{\frac{1}{2}}^{2-} \quad \dots(1.70)$$

where  $k$  = Boltzman's Constant

$T$  = Temperature (in degrees absolute)

$\Delta E_{\frac{1}{2}}$  = Band width at half height

### 1:8 Mixed Valence Compounds

Mixed valence compounds have been shown to exhibit properties different from those of the individual metal ions taken separately. This is because the interactions between the metal ions involved in the mixed valence systems tend to change the physico-chemical properties of the compound (Iyun 1982). Tom et al in 1975, reported that a mere change in the oxidation state on the part of the metal ions, in the mixed valence system by a unit

or more can change a paramagnetic substance into a ferromagnetic or even diamagnetic type.

Many mixed valence compounds contain an intense absorption in the visible region, which is not observed in the compounds containing either of the valence state alone. According to Robin and Day (1967), mixed valence compounds are classified into four different groups on the basis of the strength and symmetry of the ligand fields around the metal ions and the extent of delocalisation of excess electrons ( $\alpha$ ).

Group I has the following characteristics;

- i) Metal ions in ligand fields of very different symmetry and or strength i.e tetrahedral versus octahedral
- ii)  $\alpha = 0$  localized valencies, valencies very firmly trapped.
- iii) Insulators, resistivity of  $10^{10}$  Ohm  $\text{cm}^{-1}$  or greater.
- iv) No mixed valence transitions in the visible region.
- v) Clearly shown spectra of constituent ions (IR or UV)
- vi) Magnetically dilute, paramagnetic or diamagnetic at very low temperatures.

Electrons which distinguish the valence of one ion from another are so firmly trapped that virtually no magnetic coupling between partly filled shells on adjacent metal ions is possible, the visible spectra are merely the sum of the spectra of the constituent ions so that they are mostly colourless compounds with absorption bands greater than  $27000\text{cm}^{-1}$ . For example  $[(\text{bpy})_2\text{Cl Ru}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$  where  $X = \text{ClO}_4^-$  or  $\text{PF}_6^-$  belongs to this class.

## Group II

- i) Metal ions in ligands field of nearly identical symmetry, differing from one another by distortion of only a few tenths of  $A^\circ$ .**
- ii)  $\alpha > 0$ , Valencies distinguishable but with slight delocalization.
- iii) Semi-conductors, resistivity in the range  $10-10^7$  Ohm  $\text{cm}^{-1}$ .
- iv) One or more mixed-valence transition in the visible region.

- v) Shows spectra of constituent ions at very nearly their normal frequencies.
- vi) Magnetically dilute with ferromagnetic and anti-ferromagnetic interactions at low temperatures.

This group absorbs between  $14000\text{--}27000\text{cm}^{-1}$  and these are absent from the spectra of constituents. The energy of transition is given by equation

$$h\nu = E_A + E_B + E_{\text{mad}} \quad \dots(1.71)$$

$E_A$  and  $E_B$  are changes in internal energy at metal ion sites A and B respectively and  $E_{\text{mad}}$  = Madelung energy expended in moving the optical electron from A and B in the electrostatic field. In this system, there is no evidence for metal electronic interaction, this is a situation where the metal sites A and B do not mix, so that the precursor and successor states have two maxima of a mixed valence complex.

The excitation from the precursor (P) state to the successor (S) state has zero probability. The two metal energy terms correspond to the ionization potential and electron affinity of the sites A and B for example  $\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$  and  $\text{Cs}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_2$

#### Group III<sup>A</sup>.

- i) Metal ions indistinguishable but grouped into polynuclear cluster
- ii)  $\alpha$  -maximal locally
- iii) Probably insulating
- iv) One or more mixed-valence transitions in the visible region.
- v) Spectra of constituent ions not discernible
- vi) Magnetically dilute.

Members of this group are referred to as polynuclear mixed valence anions, cations and neutral species in which the sites of all metal ions are equidistant. An example of this compound is  $[(\text{bpy})_2\text{Cl Ru}(\text{Py})\text{Ru}(\text{bpy})_2\text{Cl}]^{2+}$

**Here, there is weak metal-metal interactions through bridging ligand, local valence exists where the  $d \rightarrow p$  S. Transition produces inter valence transfer band. The extent and resonance of this band can be estimated from transition dipole.**

### **GROUP III<sup>B</sup>**

- i. All metal ions indistinguishable
- ii. Maxima, complete delocalization over cation sub-lattice.
- iii. Metallic conductivity, resistivity- the range  $10^{-1}$ ,  $10^{-6}$  ohm  $\text{cm}^{-1}$
- iii. Absorption edge in the infrared opaque with metallic reflectivity in the visible region.
- iv. Spectra of constituent ions not discernable.
- v. Either ferromagnetic with high Curie temperature or diamagnetic depending upon the presence or absence of local moments.

Example of this group 111B is  $[(\text{bpy})_2\text{RuClORuCl}(\text{bpy})_2]^{2+}$ . For a system with strong metal-metal interaction either through a space or through a bridging ligand like in this group, the ground state can be appreciable mixing of the  $(A^+ \leftrightarrow B)$  and  $(A \leftrightarrow B^+)$  configuration. [Systems  $(A^+ \leftrightarrow B)$  &  $(A \leftrightarrow B^+)$  may be binuclear complexes of more or less fixed geometry or they may be reactive pairs in systems undergoing binuclear reaction. These configurations are equivalent to the precursor and successor states respectively.

When there is a strong, direct metal – metal bonding in this group, this is a situation where the resonance energy exceeds the critical value so that states P and S coalesce giving rise to a complex termed “average valences” complex. This complex will then be characterized by electronic transition and no longer has inter–valence transfer.

## **1.9 PHOTOSYNTHETIC PROCESS**

Photosynthesis is a well known process that proceeds by a complicated mechanism of electron transfer from a special form of chlorophyll to an acceptor. This leads to oxidation of the chlorophyll and the reduction of acceptor molecule.



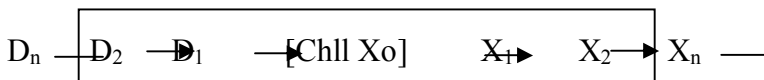
Electrons are donated from different sources to the oxidized chlorophyll, reducing it and allowing the process to be repeated. The essential nature of the photosynthetic process is therefore a chemical oxidation-reduction process, catalysed by proteins, driven against the thermodynamic energy gradient by the energy of light captured by green plant.

### 1.9.1 PHOTOSYNTHETIC REACTION CENTRE

The photosynthetic reaction centre can be found in the chloroplast of green plants and some photosynthetic bacteria. Gregory in 1989 reported that photosynthetic reaction center helps in driving electron transfer system.

During photosynthesis, there is a chlorophyll molecule (Chll) in close proximity to an electron acceptor (X). When the chlorophyll becomes excited (directly or indirectly) by absorption of light, it leads to ejection of an electron which passes from the chlorophyll to the acceptor without any molecular movement within an electron transport chain. (Lawlor 1993). The electrons pass from a higher to lower energy state along a chain of electron acceptors ( $X_1$ ) and donors ( $D_1$ ) in the reaction-centre complex which alternatively are reduced and oxidized in the process until a stable reduced compound is formed ( $X_n$ ). The positive charge left on chlorophyll (Chll) is filled by an electron from a donor ( $D_1$ ) which may or not be part of the complex (Gregory 1989).

The restoration of the  $\text{Chll}^+$  to Chll is however a slow and temperature dependent process. This is why absorption of light energy is needed during photosynthesis. The effect of the absorption of the quantum of light energy in the complex has been identified as the production of oxidized  $D_n$  and reduced  $X_n$  as indicated in Figure 1:5



**Fig1:5 Generalized diagram of a Photosynthetic reaction centre**

Four types of photosynthetic reaction centers have been identified and described in literature (Lehninger, 1975, Lubert 1981, Danks et al, 1983, Gregory

1989, Lawlot 1993). The four photosynthetic reaction center complexes indicating the identities of the  $D_n$  and  $X_n$  are given in Table 1:1.

**Table 1.1: Four types of photosynthetic reaction centres (Gregory 1989).**

<b>TYPE</b>	<b>DESIGNATION</b>	<b>ELECTRON DONOR</b>	<b>ELECTRON ACCEPTOR (<math>X_n</math>)</b>
Green nm-sulphur bacteria	-	Cytochrome (C553)	
Green sulphur bacteria	-	Cytochorome (C553)	Ferredoxin
Green plant <u>Green</u> <u>Plant</u>	PS I PS II	Plastocyanin or Cytochrome C553 water	Ferredoxin Plastoquine

Where PS I is photo system I

PS II is photosystem II.

The reaction centers may be regarded as enzymes, catalyzing the oxidation of the donor and the reduction of the acceptors by means of light energy (Gregory, 1989) Note that the reverse reaction is effectively prevented.

Electron transfer in the reaction center complex ultimately leads to the formation of metabolically useful products (the reduced co-enzyme Nicotinamide Adenosine Diphosphate (NADPH) and the production of adenosine triphosphate (ATP). The hydrolysis of ATP or other related phosphorylated adenylate compounds provides the energy required to carry out the biological catalytic reactions leading to the re-

organisation of the primary reactants into complex products. (Lawlor 1987). The electron transfer is very fast (in pico seconds) and occurs at over liquid helium temperature as long as chlorophyll are part of the same protein complex.

## 1.9.2 PHOTOSYSTEM II

The Photosystem II (PS II) is a short-waved absorbing photosystem and is a protein chlorophyll complex (in thylakoid of chloroplast) that carries out the light-driven reaction catalysed by water plastoquinone reductase (Ogawa et al, 1966, Thornber, 1986).

The primary photochemical reaction of PS II reduces pheophytin, a high potential proton acceptor, by transferring an electron from a very high potential donor, thus generating a strong reductant and a strong oxidant.

The reaction center chlorophyll and primary electron donor of PS II can be observed at a wavelength of 680 or 820 nm. It is generally accepted that the bond manganese (5-8 mn/400 chlorophylls) is an essential co-factor for the water-splitting system. (Radmer and Cheniae 1977).

Some models of the oxygen evolving mechanism suggest that there are as few as two manganese atoms per water-splitting enzyme. In thylakoid, Mn exists in a mixture of oxidation state i.e.  $Mn^{2+}$  and at least one higher oxidation state (Govindjee and Wydroznski 1981). Another major characteristic of PS II is the regulatory cap, which is involved in the splitting of water (Lawlor, 1993). The cap may also regulate the passage of ions ( $Ca^{2+}$  and  $Cl^-$ ) and water into the water splitting manganese complex.

During the process of the water splitting, oxygen is evolved in the lumen of the thylakoid while the plastoquinone (PQ) pool diffuses freely in the lipid matrix of the membrane. The production of oxygen is a  $4e^-/4H^+$  process according to Gregory, (1989) and Iyun et al, (1997) (equation 1.73)

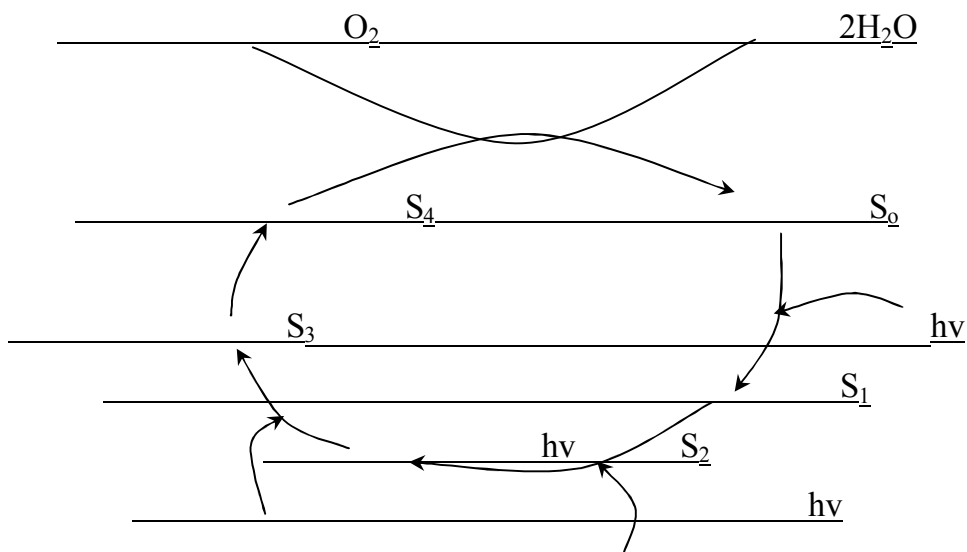


However, Renger in 1978 reported that this reaction does not occur in a single step and that the four positive charges generated by the turn over of p<sub>680</sub> must accumulate before oxygen can be evolved.

Ghosh (1995) reported that this oxygen production is accomplished through four manganese atoms in the PS II constitution. The existence of a four-electron gate has been confirmed by experiments. (Joliot et al, 1969, Kok et al, 1970).

The results of investigations revealed that store in the system will accumulate positive charges by donation of electrons one at a time to P680<sup>+</sup> directly or indirectly (P denotes pigment while 680 nm is the absorption peak of PS II).

When the store has accumulated four positive charges, it would react to produce oxygen and thus return to its original state (Gregory, 1989). These S-states (S<sub>0</sub> to S<sub>4</sub>) are directly from one another by successive absorption of light quanta and delivery of single electrons (Ghosh et al, 1994). The electron transfer is coupled in some instance, by transfer of H<sup>+</sup> (proton) to the associated photosynthetic acceptor site, with the release of oxygen, occurring only from S<sub>4</sub>, which is then reverted to S<sub>n</sub>. The stages can be represented in Fig 1:6 and is referred to as kok clock (kok et al, 1970)



**Fig 1:6: - The kok-clock hypothesis for the storage of oxidizing equivalents in photosystem II.**

This process has earlier been referred to as proton coupled electron transfer (PCET)

Mn is an essential component of the complex with four atoms per PS II with two Mn atoms tightly bound to PS II which are most probably involved in the accumulation of charges and the other two loosely bound. (Lawlor 1993).

Mn exists in a mixture of oxidation state i.e. Mn<sup>2+</sup> and at least higher oxidation state. It also exists in clusters at two binding sites linked by the oxygen and nitrogen of the protein matrix. Approximately, two thirds of the Mn is only loosely bound to the membrane. This is not detected by ESR at room temperature and is at least a part directly involved with oxygen-evolution. The remainder of the Mn is either tightly or very loosely bound and some of this may be associated with the light harvesting chlorophyll a and b binding proteins. (Gonvindjee and Wydryznski; 1981)

The photosystem II is sensitised by several types of chlorophyll a in protein complexes and by chlorophyll b which is also present in a pigment in protein complex. In all oxygen- evolving organism, the pigment sensitising PS II absorb only up to 680 nm (Ruben et al, 1941). It is also called P<sub>680</sub>.

This arrangement is similar to the multinuclear manganese complex of interest in this work. In addition, studies carried out on the multinuclear manganese complexes have shown that the oxo- bridged mixed valence manganese complexes have similar properties to those of PS II. For example, EXAFS, spectra show similar Mn –Mn distance, their multi line EPR signals are similar and they have similar redox behaviour. (Lawlor, 1993)

### **1.10. DYES**

A dye is an organic compound, which contains chromophoric and auxochromic groups attached to benzene rings. The colour of the substance is attributed to chromophores and the dyeing property to the salt-forming auxochrome. They are intensely coloured substances used for the colouration of various substances including paper, leather, hair food, drugs cosmetics, waxes, greases, petroleum products, plastics and textile materials e.t.c. Dyes are retained in these substrates either by physical adsorption of salt, metal complex formation, and mechanical retention or the formation of covalent chemical bond.

To the biologist, biological stains are dyes that are adapted for very special purposes. They are used for making microscopic objects more clearly visible than they would be if unstained. (Conn, 1961)

#### **1.10.1 CHEMISTRY OF DYES (ARTIFICIAL DYES)**

All coal-tar dye (artificial dyes) are organic compounds of aromatic series (derivatives of the hydrocarbon, benzene). The double bonds in benzene are not localised but delocalised between adjacent carbon atoms making it possible to react with other radicals and elements forming compounds of extreme complexity.(Trotman, 1984)

If two oxygen atoms replace two of the hydrogen atoms and the substitution takes place simultaneously on opposite sides of the benzene ring, re-adjustment of the

double bond takes place and a new compound quinone ( $C_6H_4O_2$ ) is formed.

(Figure 1.7)

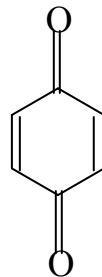


Fig 1:7. Quinone.

In quinone, the two double bonds in the ring are not delocalised as in the case of benzene. Quinoid compounds are obtained from quinone. Quinone compounds absorb light from the bands in the visible spectrum and possess colour.

The chemical groups that confer colour are known as chromophores. The fundamental groupings involved in these chromophores are C=C, C=S, C=N, N=N, N=O and NO<sub>2</sub>, and the more of these that occur in the same compound the more pronounced the colour.

In order to exhibit colour, a substance must absorb light from wavelength in the visible spectrum. Benzene and its derivatives are colourless because they absorb light only in the ultraviolet region, but some benzene compounds are chromogen because they contain chromophore radicals. A pigment although coloured is not a dye, in that they possess no affinity for fibres or tissues. It may coat them, but only mechanically and it will be easily removed by a mechanical process. (Trotman, 1984)

For a substance to be a dye, it must contain in addition to the chromophore group, a group which imparts to the compound the property of electrolytic dissociation. Such auxiliary groups are known as auxochromes. They may slightly alter the shade of the dye but are not the cause of the colour. Their function is to furnish salt-forming properties to the compound.

The auxochrome groups of atoms also determine whether a dye will be acidic or basic. Auxochrome like – NH<sub>2</sub> yield hydroxyl ions and enables the compound to ionize and act as a cation in forming salt; such a dye is a basic dye. The auxochrome (-COOH) is acidic as it can furnish hydrogen ions by electrolytic dissociation.

### **1.10.2 CLASSIFICATION OF DYES**

Dyes can be classified into two main groups, the natural dyes and the synthetic or aniline dyes.

#### **i) NATURAL DYES**

Natural dyes such as carmine, madder, indigo, saffron, hematoxylin, cochineal, brazilin and orcein are employed in the textile industry for dyeing wool and cotton and by the tanning industry long before they are applied to sections of tissues as biological stains. These groups of dyes are very few when compared to artificial dyes. Today many of these natural dyes can be produced artificially. However some, particular extracts from logwood and cochineal, are still valuable as biological stains. These include

(ii) SYNTHETIC DYES: -The first artificial dyes were produced from aniline. This class is often called aniline dyes. Although a large number of them bear no relationship with aniline and they are not derived from it.

Aniline dye is now replaced by coal-tar dyes since all of them are made by chemical transformation from one or more substances found in coal tar.

Artificial dyes can further be sub divided into the following sub-groups.

(a) REACTIVE DYES: - These are dyes that form a covalent bond with the fibre usually cotton wool or nylon. This class of dyes was first introduced commercially in 1956. It made it possible to achieve extremely high wash fastness properties by relatively simple dyeing methods.

A marked advantage over direct dyes is that their chemical structures are much simpler. Their absorption spectra show narrower; absorption bands and

dyeing are brighter. The principal chemical classes of reactive dyes are azo and anthraquinone.

(b) FLOURESCENT BRIGHTNESS DYES:- These are colourless compounds that absorb incident ultra-violet light and re-emit it in the visible (blue) region of the spectrum. Strictly speaking these compounds are not dyes. However because of their widespread application to textile and other materials a C.I. classification has been assigned.

(c) DISPERSE DYES:- Disperse dyes are substantially water insoluble non-ionic dyes for application to hydrophobic fibres from aqueous dispersion . They are used in polyester, nylon, cellulose diacetate, and acrylic fibres because of their use in synthetic materials, they are the fastest growing class of dyes.

(d) DIRECT DYES: - These are water-soluble anionic dyes which dyed from aqueous solution in the presence of electrolytes are substantive to cellulosic fibres. The principal use is the dyeing of cotton and regenerated cellulose paper, leather and to a lesser extent nylon. Most of the dyes in this classes are azo compounds, stilbenes, thiazoles and oxazines.

(e) VAT DYES:- Vat dyes are water insoluble dyes that are applied mainly to cellulose fibres as soluble leuco –salts after reduction in an alkaline bath, usually with sodium hydrosulphite the principal chemical classes of the vat dyes are anthraquinone and indigoid.(Conn, 1961)

(f) SULPHUR DYES:- Sulphur dyes are dyes that are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent. Numerically, this is a relatively small group. However the low cost and good wash fastness properties of the dyeing make this class important from an economic stand point.

(g) ACID DYES:- An acid dye is a salt of a coloured acid usually in sodium salt but occasionally a salt of potassium, calcium or ammonium. They are water-soluble anionic dyes for application to nylon, wool, silks and modified acrylics. They are also used to some extent for paper, leather, food and cosmetics.

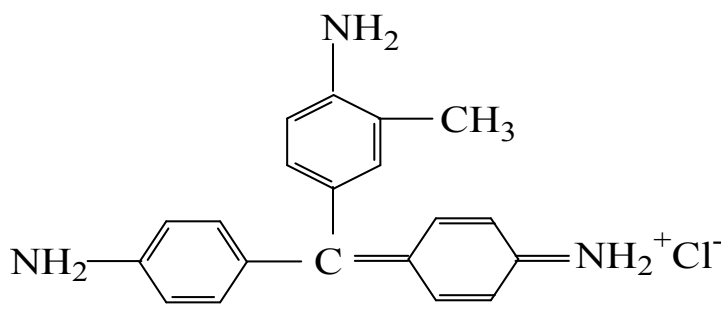
The original members of this class all had one or more sulphonic or carboxylic acid groups in their molecules. Chemically the acid dyes consist of azo, anthraquinone and triarylmethane compound with a few azine, xanthene, ketone, imine, nitro, nitroso and quinoline compounds. (Oguntona,1983)

(h) BASIC DYES / FUCHSIN: - The dyes ordinarily known commercially as basic fuchsin are mixtures of pararosaniline, rosaniline and magenta II. They are among the most powerful nuclear dyes and find many biological uses. They are valuable stains for mucin, elastic tissues and for bringing out the so-called fuchsinophile granules.

Basic fuchsin is the main constituent of Schiffs reagent and restores colour after contact with aldehydes. Its violet rather than red colour seems to indicate that some other changes in the dye take place in addition to its reduction

### Rosaniline (Magenta 1)

(C.I. Base violet 14) Colour index No. 42510.

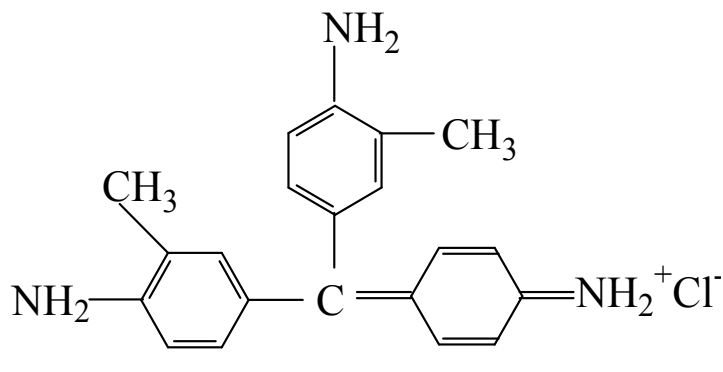


C<sub>20</sub>H<sub>20</sub>N<sub>3</sub>Cl, mol.wt 337.84

This compound is monomethyl fuchsin or tri-amino-toly diphenylmethane chloride the absorption maximum is about 550nm. It is not a textile dye, and is not found free from pararosaniline unless specially prepared.

**C      MAGENTA II**

This theoretical constituent of basic fuchsin is never encountered pure except as specially prepared in the laboratory. Probably, it is present in commercial samples of the dye. It is dimethyl fuchsin of triaminoditoly phenyl-methane chloride.

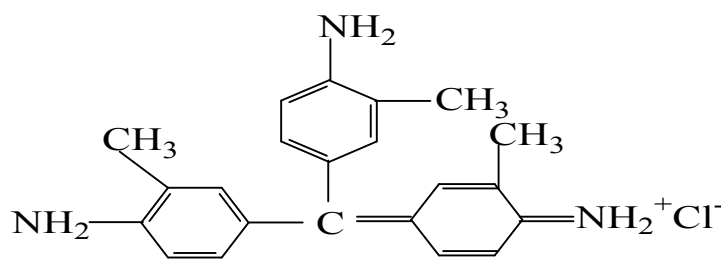


C<sub>21</sub>H<sub>22</sub>N<sub>3</sub>Cl : mol.wt 351.867

**D      MANGENTA III**

(C.I. Basic violet 2). Colour index NO. 42520. Synonyms. Isorubin, fuchsin NB.

This compound is trimethyl fuchsin or triaminotritolyl-methane chloride.



C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>Cl. Mol wt 365.89.

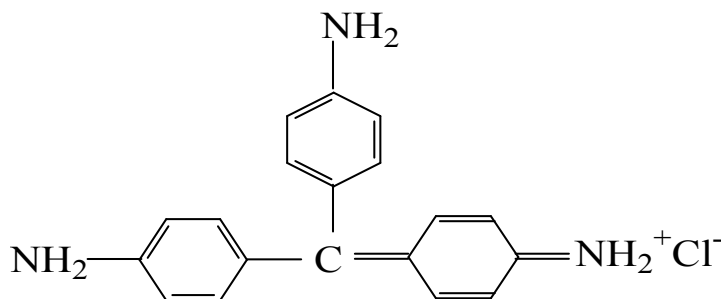
The absorption maximum is about 556, solubility at 26°C in water is 1.13% and in alcohol is about 3.20%

From the general rule concerning alkyl substitution, magenta III is the deepest in shade of these four dyes while pararosaniline is the least .

**E PARAROSANILINE**

Synonyms: - Basic rubin, parafuchsin, paramagenta  
(C:I Basic Red 9) colour index N0. 42500.

This compound is triaminotriphenylmethane chloride.



$\text{C}_{19}\text{H}_{18}\text{N}_3\text{Cl}$  : mol.wt 323.815

Pararosaniline is metallic green lustrous crystals that decomposes above 200°C .

Its solution is carmine red in colour, it is a basic dye. It has an absorption maximum at 545nm, solubility at 26°C, in water 0.26% in alcohol 5.93%. It is the chief constituent of the majority of samples of basic fuchsin. It is sometimes present as the chloride or as the acetate

A basic dye is a salt of a coloured base usually a chloride, but sometimes a sulphate or acetate. They are sometimes available as free bases in which case the name is ordinarily followed by the word 'base'. Examples are azo, athraquinone, triphenylmethane, methine, triazine, oxazine and quinoline.

**1:10.3: – USES OF DYES AS STAINS.**

- i. Plant Histology:- Stains are very useful in botany as seen in plant histology. Hematoxylin stains are used for general tissue and woody tissue for botanical microtechnics. Safranin is the best nuclear stain employed in

botanical work. With a green or blue counter stain, very effective pictures are obtained.

Various combinations of stains such as thionin, orange G, martius yellow have been employed for certain more highly specialized purposes. Such as staining fungi in tissues or for demonstrating pollen tubes in the styles.

(Conn, 1961)

- ii. **Microbiology:-** Another very important field in which biological stains are employed is the study of bacteria and related micro organisms such as fungi and protozoa. Examples of these groups of dyes are methylene blue, crystal violet and basic fuchsin. In microbiology, dyes are used not only as stains but as constituent of culture media. They are used as indicators and in the differentiation of species.

An important aspect of bacterial staining in the laboratory is diagnosis of disease of which tuberculosis and diphtheria are the most conspicuous examples.

- iii. **Plant Cytology:-** There is a very considerable variety of staining procedure in plant cytology. Hematoxylin methods and Flemming triple stain, safranin and orange G are employed for fresh smears of anthers. It is interesting to note that although there are many dyes used in both plant and animal microtechnic, there are others that are important in one of these fields but not in the other (Conn, 1961).

- iv. **Animal Microtechnics:-** Stains were first used extensively in animal histology, most especially as general tissue stains. This involves the use of one, two or three dyes in staining sections of general animal tissue designed primarily to differentiate nuclei from cytoplasm of cells and to permit distinctions between the various types of tissue.

Dyes used include Hematoxylin, Eosin Y, Congo Red and Safranin. There is also a specialized application known as connective tissue stains, which is similar to general tissue stains. Neurological staining methods are numerous and all are

highly specialized. Many of them are not actually dyeing procedures, but depend on the use of silver salts with which tissue elements are impregnated so that the desired structures are made visible when the salts are converted into metallic silver. In addition to these three groups of procedures, there are stains for other types of tissue and body fluids.

Fats for example are stained by special oil soluble dyes such as Sudan IV Both blood and bones have their own different methods of staining.

### **OBJECTIVE OF THIS RESEARCH WORK**

The chemistry of oxo-bridged Mn complexes have received considerable attention in the recent years, due to their redox activities in the biosystem like manganese containing superoxide dimutase, pseudo catalysed reductase and photosynthetic water oxidation catalyst, photosystem II (PS II).

Kinetics of reduction of oxo-bridged manganese complex  $Mn^{III}O_2Mn^{IV}$  by  $HSO_3^-$ ,  $NO_2^-$  and  $H_2C_2O_4$ ,  $SCN$ , and 2-methionine ions has been studied and reported by previous workers as cited earlier. The results of the reactions indicated a second order rate constant and a proton coupled electron transfer mechanism was proposed. It was also reported that Mn complexes have similar properties to those of PS II. For example, EXAFS spectra show similar Mn-Mn distance (2.7–3.3 $^{\circ}$ A), their multi line EPR signals are similar and they have similar redox behaviour.

In this work, the kinetics and mechanisms of the redox reaction of di- $\mu$ -oxo-tetrakis(1,10-phenanthroline)dimanganese(III,IV)perchlorate,  $[(Phen)_2MnO_2Mn(Phen)_2](ClO_4)_3$  with ascorbic acid, 1,3-dihydroxybenzene, sulphite and thiosulphate were studied in acidic medium

This work was done to provide a better understanding of related biochemical activities in other systems. It is hoped that the knowledge that will be gained will be utilized in the development of biochemical catalytic phenomena involving this system and will aid in the design of new molecular materials.

Rosaniline hydrochloride being a basic dye is also used as a biological stain. It is used as constituents of culture media, indicators and bacteriostatic effect.

Most bacteria stain well when subjected to basic dyes (eg rosaniline hydrochloride) due to the affinity of the nucleic acid contained in the bacteria for the dye. In Africa, the staining technique plays a prominent role in diagnosing diseases such as tuberculosis and diphtheria (Conn, 1961)

Literature reveals that kinetic studies of rosaniline monochloride with  $\text{NO}_2^-$ ,  $\text{ClO}_3^-$  and  $\text{S}_2\text{O}_4^{2-}$  ions ( Iyun and Onu ; 1998,1999,2001) have been done and an outer sphere mechanism was proposed. Therefore, the other part of this work involves investigating the redox reactions of rosaniline hydrochloride with  $\text{SO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{S}_2\text{O}_6^{2-}$  and  $\text{IO}_4^-$  in acidic medium except  $\text{OH}^-$ . These reactions have been studied in order to obtain a better understanding of the kinetics of the dye, to give an insight to the mechanism of the reaction and also be a useful tool in improving on the uses of the dye as a biological stain and indicator. It will also give room for improvement on its application in textile industry particular its fading and fastness property

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 KINETICS AND MECHANISMS OF OXY-ANION REACTIONS

Shakhashili and Gordon (1969) investigated the kinetics, mechanism and activity pattern of redox reactions involving complex ions and oxy- anions. They reported that most reactions involve the transfer of oxygen atom(s) from one atom to another and that the oxygen atoms are held tightly together and therefore direct transfer processes are very slow. For example in equations (2.1) and (2.2).



The rate of oxygen exchange and redox reactions of the oxy-anions were found to depend strongly on acid concentration (Birk and Kozub,1973) and their rate terms is generally expressed in the form of  $k[\text{XO}_n^{m-}][\text{H}^+]$  and  $k[\text{R}][\text{XO}_n^{m-}][\text{H}^+]$  for the reduction of species R, (X = Cl, Br, I, S, N,

n =2, 3 or 4 and m = 1 or 2) as reported for  $\text{ClO}_3^-$  (Hoering et al, 1958),  $\text{ClO}_4^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_4^-$ ,  $\text{IO}_3^-$  (Birk and Kozub,1973),  $\text{NO}_3^-$  (Anbar and Taube, 1954)and  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  (Hoering and Kennedy,1957)

Edwards (1964) reported that because of the hydrogen ion dependence, the protons enhance the cleavage of the bond between the oxide ions from the central atoms and for the oxy-anions that are derived from small and or highly charged central atoms. The predominant rate law is

$k[\text{XO}_n^{m-}][\text{H}^+]^2$  and this has been observed for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$  and  $\text{BrO}_3^-$ . For example, chloride ion has been found to catalyze the oxygen exchange between water and  $\text{NO}_3^-$  and  $\text{BrO}_3^-$  with Rate =  $k[\text{XO}_3^-][\text{Cl}^-][\text{H}^+]^2$ .

However, Baloga and Earley, (1963) reported that when the central atom is large and or less highly charged, the second order dependence of rate on hydrogen ion is no longer characteristic and the rate becomes

$k[\text{XO}_n^{m-}][\text{H}^+]$  which was observed when  $\text{XO}_n^{m-}$  is  $\text{OCl}^-$ ,  $\text{OBr}^-$ ,  $\text{ReO}_4^-$  and  $\text{IO}_3^-$  (Anbar and Taube, 1958; Murman, 1961; Anbar and Guttaman, 1961)

The charge on the central atom of an oxy-anion is very important in determining reactivity. The lower the charge, the higher the reactivity (for a series of closely related species, atomic charge is a function of formal charge and of oxidation state) (Jolly, 1976). Thus the rates for reactions of the chlorine oxy-anions increase in the order  $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}^-$

The rate of oxygen exchange with water increases in the order  $\text{ClO}_4^- < \text{SO}_3^{2-} < \text{HPO}_4^{2-} < \text{H}_2\text{SiO}_4^-$ . The size of the central atom is also important in that the larger the size, the higher the reactivity. For example, the iodate reactions are fast, chlorate reactions are slow while bromate reactions are intermediate rate. Both inner sphere and outer sphere mechanisms have been postulated depending on the nature of the metal ion complex or organic substrate and the oxy-anion.

The oxy-anion of interest in this work are  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{IO}_4^-$  and a more detailed review is considered below

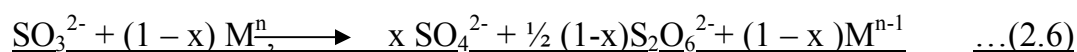
## **2.2. REDOX REACTIONS OF SULPHITE IONS**

The sulphite ions have received a lot of attention as a powerful reductant in the past few decades and continue to receive attention. Russel and Yost (1944) reported that the sulphite ions have been known to reduce metal ions and other oxidants by a variety of mechanisms and with varying stoichiometry. The stoichiometry of the products of the reaction allow a distinction to be made between one-equivalent and two-equivalent oxidizing agents as shown by

equations (2.3) and (2.4). The products are dithionate ( $S_2O_6^{2-}$ ) and sulphate ( $SO_4^{2-}$ ) ions respectively. (Higginson and Marshall, 1957, Davies et al 1969).



Substitution of inert complexes which behave as one- equivalent oxidants, give  $SO_4^{2-}$  as product while substitution of labile ones react with a lower non-integral stoichiometry, giving  $S_2O_6^{2-}$  as an addition product.



where x is between zero and unity. Higginson and Marshall (1957) went further in reporting that free  $SO_3^{2-}$  ions are always oxidized to  $SO_4^{2-}$  without  $S_2O_6^{2-}$  while Veprek-Siska et al, (1966) reported that the oxidation can take place with very negligible amount of  $S_2O_6^{2-}$ .

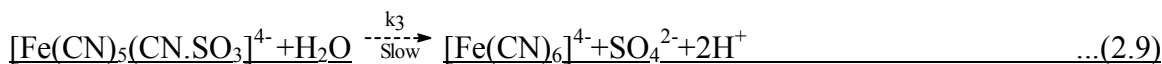
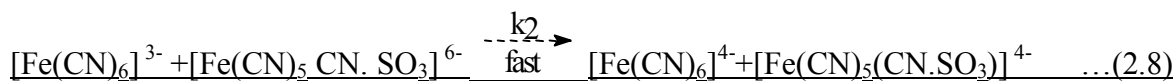
Recently, the formation of the dithionate ( $S_2O_6^{2-}$ ) in addition to the sulphate ion ( $SO_4^{2-}$ ) as oxidation products of sulphite ions ( $SO_3^{2-}$ ) has been established (Dennis et al, 1983) confirming earlier reports (Haight et al, 1965, Lister and Roseblum 1963).

The most intensively studied oxidation reaction of  $SO_3^{2-}$  is that involving hexacyanoferrate (III) (Murray, 1968, Lanncaster and Murray, 1971). This reaction was believed to involve the intermediate  $[Fe(CN)_5SO_3]^{4-}$  with subsequent formation of  $SO_4^{2-}$  (Veprek-Siska and Wagnerova, 1995; Veprek-Siskas et al 1966]. But this proposed mechanism was later disproved by Swinehart (1967),

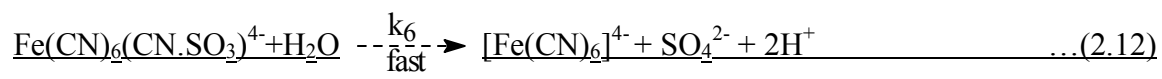
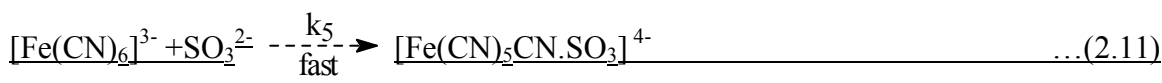
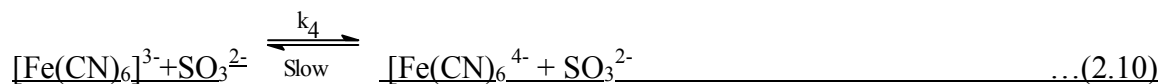
when he prepared and analysed the species  $[\text{Fe}(\text{CN})_5\text{SO}_3]^{4-}$ . Its reactivity was found to be different from that predicted by Veprek-Siska and so the outer sphere formation of  $\text{SO}_3^{2-}$  radical ion was favoured.

Two reaction schemes have been proposed for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  by  $\text{SO}_3^{2-}$  in aqueous solution.

### Scheme I.



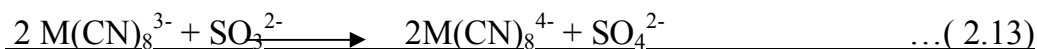
### Scheme II



Scheme II has been substantiated and found to be similar to the mechanism proposed earlier for the reaction between  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{NO}_2^-$  (Davies and Stedman, 1968).

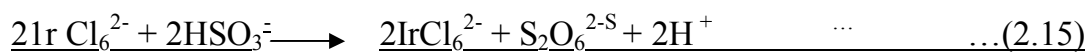
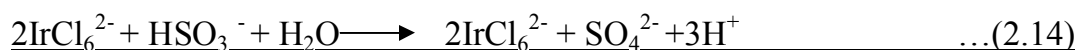
In an effort to give more insight into the mechanisms of the reaction of sulphite ions, Dennis and co-workers (1983) investigated on  $\text{Mo}(\text{CN})_8^{3-} - \text{SO}_3^{2-}$

and  $W(CN)_8^{3-} - SO_3^{2-}$  system and were able to establish the occurrence of outer sphere mechanism in both cases with the following stoichiometry.



$M=M_0(V)$  and  $W(V)$

A similar mechanism has also been proposed to operate in the reaction between  $SO_3^{2-}$  and  $IrCl_6^{2-}$  (Strapp and Carlyle, 1974). The net reaction can be described by equation (2.14) below.



$$\frac{-d[IrCl_6^{2-}]}{dt} = k[H^+] \quad \dots(2.16)$$

The rate does not however suggest the product of the rate determining step, the products could be  $IrCl_6^{3-}$  and  $SO_3^{2-}$  or  $IrS^{VIII}$  complex as indicated in equation below



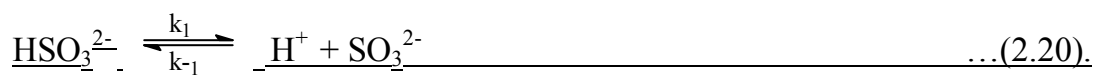
Based on evidence from the rate law, stoichiometry and inertness of  $IrCl_6^{2-}$ , the outer sphere mechanism was proposed for this system. This is consistent with the earlier report by Brown and Higginson (1972), Strapp and Carlyle, (1974), Dennis et al; 1983; Sengupta, (1987) Lohdip, (1989), reported that sulphate ions in aqueous solution exist in equilibrium system illustrated below



$$K = 1.0 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

The major species in aqueous solution is  $\text{HSO}_3^-$ .

Lohdip, (1989) investigated the  $\text{SO}_3^{2-}$  reduction of Ruthenium oxo-bridged dimer, and observed a shift in  $\lambda_{\text{max}}$  and an intercept for the Michaelis-Menten plot. Based on this finding the inner-sphere mechanism was proposed with the scheme represented by equation (2.20) to (2.23)



Where  $\text{RuORu}^{4+}$ : -Diaquotetrakis (2,2'-bipyridine)- $\mu$ -oxodiruthenium (iii) ion.



But, anion catalysis was observed for the same reaction and the researchers proposed an outer-sphere mechanism.

Various groups of researchers studied the interaction of transition metal complexes with  $\text{SO}_2$ ,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  in aqueous solution. For example, Harris and co-workers (1986) reported that non-labile octahedral metal hydroxo species can take  $\text{SO}_2$  to produce oxygen-bonded sulphito complexes. The process is reversible and acidification rapidly releases  $\text{SO}_2$  without metal-oxygen bond cleavage (Kraft and Eldik;1989). Oxygen-bonded sulphito complexes undergo various subsequent reactions including substitution, linkage isomerization and

electron transfer. In contrast labile metal complexes tend to directly produce s-bonded sulphito species during the reaction with the SO<sub>x</sub> system.

Kinetic traces of the redox decomposition of Iron(III)-sulphito complexes exhibit a peculiar break in the presence of oxygen (Eldik et al, 1994). This step is a result of the sulphite-induced autoxidation of produced Iron (II) in the presence of oxygen. The kinetics was interpreted in terms of a first order decay of the Iron(III)- sulphito complexes and a reversed pseudo-zero order oxidation of Iron(II) by SO<sub>3</sub><sup>2-</sup>, HSO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. These species are

generated in solution via the reaction of SO<sub>3</sub><sup>2-</sup>, produced during the reduction of Iron(III) by sulphite, with oxygen. However, in the investigation of Iron III catalysed auto-oxidation of sulphur (IV) oxides Kraft and Eldik, (1989) reported that the reaction is characterized by the rapid formation of a yellow to red species with absorbance far in the visible region, which slowly decomposes to a colourless product. The overall reaction can be subdivided into four consecutive steps, of which two accounts for the formation and the other two for the decomposition of Fe (III) – S (IV) transients.

The redox kinetics of excess SO<sub>3</sub><sup>2-</sup> with HOCl and OCl<sup>-</sup> in HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> buffer was investigated by (Margerum et al, 1989) and they reported that the rate constant for the reaction of HOCl and SO<sub>3</sub><sup>2-</sup> was so large (7.6x10<sup>8</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, at 25°C, μ =0.5) that the rate of proton transfer from water to OCl<sup>-</sup> can limit the reaction velocity. A mechanism with Cl<sup>-</sup> transfer to sulphur is proposed via the reactive intermediate, HOCl.SO<sub>3</sub><sup>2-</sup>, that decomposes by itself to form ClSO<sub>3</sub><sup>-</sup>. The subsequent hydrolysis of ClSO<sub>3</sub><sup>-</sup> to give Cl<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> was so slow by comparison (270 s<sup>-1</sup>)

In view of this fact and the continuing interest in the electron transfer reactions of this important reductant, we investigated the reaction of this reductant with rosaniline hydrochloride and [Mn<sup>III</sup>O<sub>2</sub>Mn<sup>IV</sup>]<sup>3+</sup> complex. It is expected that the result of this investigation will provide additional data on the reactions of rosaniline hydrochloride and enhance its applicability. We

also hope that the reaction with  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]^{3+}$  complex will enable a comparison of the results with those of previous workers.

### 2.3 REDOX REACTIONS OF THIOSULPHATE ION

The oxidation of thiosulphate ion ( $S_2O_3^{2-}$ ) with various substrates has been investigated in the last few decades (Edmonds et al, 1970; Howlett et al, 1976).

In most of the systems studied, the oxidation exhibited second order kinetics, with first order each in concentration of thiosulphate and the concentration of substrates. An example is the redox reaction between thiosulphate and Cr (IV) complexes (Edmonds et al, 1970), and also redox reaction between hexacyanoferrate (III) and thiosulphate ions.(Howlett et al, 1976)

Most oxidising agents (including Cl and Br in aqueous solution) slowly oxidise thiosulphate to sulphate but the ion is very rapidly oxidised by iodine to tetrathionate.



This reaction is of immense importance in titrimetric analysis, since nearly all oxidising agent will liberate iodine quantitatively from acidified iodine solution. (Sharpe, 1986).

A different reaction takes place with chlorine in that the thiosulphate acts as reducing agent where it is oxidised to tetrathionate (Wilson and Newali, 1976).



Cold thiosulphate has been reported to have been reduced by action of  $H_2O_2$  to trithionate. The stoichiometry is 2:4.



As part of our continued interest in rosaniline hydrochloride reactions, the oxidation of thiosulphate ions with this dye was investigated.

### 2.4 REDOX REACTIONS OF PERIODATE IONS

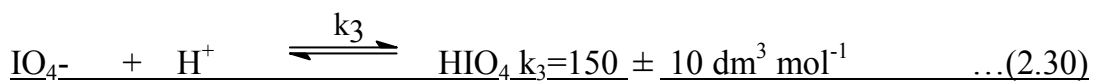
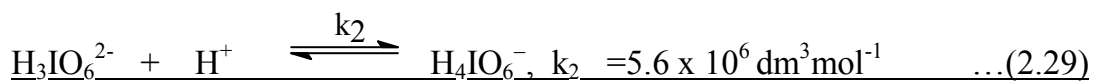
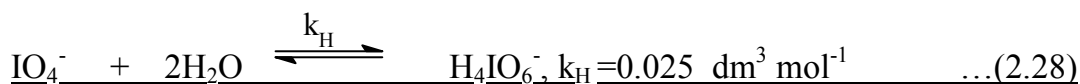
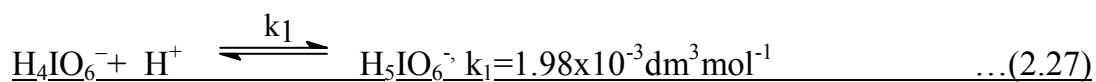
The interest in periodate as the reductant in electron transfer reactions has received a lot of attention (Symons 1955, Sulfab 1976; El-Eziri and Sulfab 1977, Kassim and Sulfab, 1977, Sulfab and Abu-shady 1977). The majority of oxidation reaction of periodate seems to proceed via the inner sphere mechanism (Indelli et al, 1966; Buchacek and Gordon, 1972; Buist, 1972, Sulfab and Kassim ,1981, Sulfab and Abdel – Khalek, 1981).

Symons ,(1955) reported the oxidation of Fe (II) by IO<sub>4</sub><sup>-</sup> to have proceeded via one electron transfer step. The formation of the free radical I<sup>•</sup> from one-electron transfer was confirmed by polymerization of added acrylonitrile.

EI-Eziri and Sulfab, (1977) reported that IO<sub>4</sub><sup>-</sup> has been known to exhibit two –electron oxidant [I (VII)-I (V)] and a concurrent two- electron transfer was equally possible. And Sutin et al (1967) also reported that it is likely for the two electrons to be abstracted from one Fe<sup>II</sup> with the formation of unstable Fe<sup>IV</sup> as with some two –equivalent oxidants or from two Fe<sup>II</sup> (Sutin et al, 1965). The dependence of rate of oxygen exchange and redox reaction on [H<sup>+</sup>] like with oxy-anions has been observed (Birk and Kozub, 1973). In terms of the dependence of k<sub>2</sub> on [H<sup>+</sup>], the commonly observed rate law was given as

$$\underline{-d/dt[IO_4^-] = (k_2+k_H[H^+]) [Fe(CN)_6^{4-}] [IO_4^-] \dots(2.26)}$$

In aqueous medium, periodate ion has been shown to exist in different species.(Benson, 1968). These species include H<sub>5</sub>IO<sub>4</sub><sup>-</sup>, H<sub>4</sub>IO<sub>6</sub><sup>-</sup>, H<sub>3</sub>IO<sub>6</sub><sup>2-</sup> and IO<sub>4</sub><sup>-</sup> which are involved in the following equilibrium;



Where k<sub>1</sub>, k<sub>H</sub>, k<sub>2</sub>, are values at I = 0.1 mol dm<sup>-3</sup> and k<sub>3</sub>..(I=1.0) at T=25°C. At pH=4.2 and I= 0.1 mol dm<sup>-3</sup>, 99.8% of periodate in aqueous solution exist in form of H<sub>4</sub>IO<sub>6</sub><sup>-</sup> and IO<sub>4</sub><sup>-</sup> (Kustin and Lieberman, 1964 ). Thus, the reactive species would be IO<sub>4</sub><sup>-</sup> and H<sub>4</sub>IO<sub>6</sub><sup>-</sup> and this was observed in the reactions of a series of Co(II) complexes with periodate (Wilkin and Yelin,

1970); (Al-Jalla and Sulfab and references there in 1983). However the rate laws for some periodate reductions include the other species (Sulfab and Howlett, 1976), as shown:

$$\text{Rate} = (k_4[\text{IO}_4^-] + k_5[\text{H}_4\text{IO}_6^-] + k_6[\text{H}_3\text{IO}_6^{2-}])[\text{Fe}(\text{CN})_6^{4-}] \quad \dots(2.31)$$

The interest in periodate as an oxidant has been extended to organic compounds, particularly in the oxidation of phenols, (Radhakrishnamurti et al, 1976). For instance the oxidation of 1, 2- diols by  $\text{IO}_4^-$  proceeds by way of a covalent link involving a cyclic intermediate, which corresponds to an inner-sphere pathway (Buist, 1972).

Ige and Amire (1985), investigated the electron transfer reactions between  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{IO}_4^-$  in which both inner sphere and outer sphere mechanism pathways have been proposed to occur simultaneously. The inner sphere pathway occurs by a single step two-electron transfer. This predominant pathway at low acid while the outer-sphere electrons transfer process occurs at high acid.

El-Idris (1991) reported the oxidation of 12- tungstocobalte (II), with periodate .The reaction was catalysed by Cu (II) ions. The reaction was found to be of the outer sphere type with the rate law;

$$d/dt[\text{Co}^{\text{II}}\text{W}] = 2k_3[\text{Co}^{\text{II}}\text{W}] [\text{IO}_4^-] [\text{Cu}^{2+}] \quad \dots(2.32)$$

$$k_2 = a + b [\text{H}^+] \quad \dots(2.33)$$

Reports of the reactions of diaquotetrakis (2,2-bipyridine) -  $\mu$ -oxodiruthenium (III) with  $\text{IO}_4^-$  have also shown lack of evidence for inner sphere mechanism (Lohdip,1989). The rate law for the reaction was proposed as;

$$d/dt[\text{RuORu}^{4+}] = k_3 + Kk_2[\text{H}^+][\text{RuORu}^{4+}][\text{L}^-] \quad \dots(2.34)$$

Where L represents total periodate ( $\text{H}_4\text{IO}_6^-$  and  $\text{IO}_4^-$ ), with

$$k_3 = 7.75 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } Kk_2 = 1.13 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

An outer-sphere mechanism was postulated for this reaction.

The reactions of periodate with organic substrates have been limited to phenols and glycols. This reaction was studied in order to enhance the uses of fuchsin and also collect kinetic data on the reaction of this important oxidant.

## **2.5 REDOX REACTIONS OF 1,3 DIHYDROXYBENZENE**

1,3 dihydroxybenzene (here after referred to as H<sub>2</sub>R) is one of the three isomeric dihydroxybenzene in which the two hydroxyl groups are located in meta position to each other on the ring. Rich in 1982 reported that the dihydroxybenzene compounds and their substituted derivatives along with ascorbic acid are well characterised into two electron reductants which have importance in biological electron transport system.

It has been found that the rate determining step in hydroquinone oxidation is semi-quinone radical (HQ) formation which corresponds to the first electron removal, when one electron oxidising agents are used.

This is a common observation in benzene diol reaction. For example, Yadev and Verma, (1981) reported the oxidation of resorcinol by Cerium (IV) and also, oxidation of 1,3-dihydroxybenzene by trioxiodate in aqueous perchloric acid medium (Iyun and Ukoha, 1999). Here quinone was obtained as one of the products. A second order rate constant with direct acid dependence was reported and the reaction rationalised on the basis of the outersphere electron transfer mechanism.

Oxidation of phenols by metal complexes leading to the production of quinones has recently generated a lot of interest (Davies and Kustin 1985, Iyun et al, 1995, Wells and Kuritsyn, 1970.) Most of these studies focused on the 1,2- and 1,4-dihydroxybenzenes (McAuley et al, 1985). From investigations, these reactions have shown a lot of complexities in terms of acid dependence (Morris and Ritter, 1979). For example, various acid dependence as well as free radical intermediates were reported for the oxidation of 1,2 dihydroxybenzene by tetraoxomanganese(VI) and trioxobromate (V) ions (Iyun, 1990).

Oxidation of 1,3 dihydroxybenzene has not received much attention when compared to the 1,2 and 1,4-isomers. However, (Iyun et al, 1996) reported that its reaction with oxo-bridged ruthenium dimer [(bpy)<sub>2</sub>H<sub>2</sub>ORu]<sub>2</sub>O<sup>4+</sup> gave a 2:1 stoichiometry and inverse acid dependence with increase in ionic strength of the medium with a corresponding increase in rate of reaction. As part of our continuing interest in oxo-bridged reactions, the oxidation of 1,3-dihydroxybenzene with the dimer [Mn<sup>III</sup>O<sub>2</sub>Mn<sup>IV</sup>]<sup>3+</sup> complexes was investigated.

## **2.6 REDOX REACTIONS OF ASCORBIC ACID**



The reducing properties of L-ascorbic acid have made it useful as an antioxidant, stabilizer, flour improving and meat- curing agent (Birch and Parket, 1974)

Creutz, 1981 reported that the oxidation and reduction reactions of L- ascorbic and its redox companion are complicated by the intervention of simultaneous proton transfer reactions. A further factor in this area is the formation of a comparatively stable radical HA<sup>-</sup>, which itself is a strong acid with a pKa of – 0.45. The redox products of ascorbic acid could be protonated ascorbate radical, ascorbate radical, dehydroascorbic acid or dehydroascorbic acid dimer.

Creutz also pointed out that majority of the reduction reactions of metal ions by ascorbic acid were carried out with pH range 2-8 and that under these conditions, ascorbic acid may exist as H<sub>2</sub>A or HA<sup>-</sup>. A one electron oxidation will produce either HA or A<sup>-</sup> and a two electron oxidation will produce dehydroascorbic acid. In all cases, the overall product is assumed to be dehydro ascorbic acid.

### **2.6.1 OXIDATION OF L-ASCORBIC ACID WITH GROUP 5 COMPLEXES**

The kinetics of the oxidation of ascorbic acid by vanadium (V) is one of the older works on the reactions of ascorbic acid. This reaction is similar to that of Iron (III) and unlike most others studied seems to show inner- sphere electron transfer behaviour. A brown colour rapidly appears and then disappears when ascorbic acid is reacted with vanadium (V). (Kusten and Toppen ,1973). They were able to demonstrate that this brown intermediate has an UV spectrum with an absorption maximum at 425nm.

The kinetics showed a first order dependence on ascorbic acid but the rate law at constant ascorbic acid concentration was given by equation (2.35)

$$\frac{k_{\text{obs}}}{1 + K [V^v]} = Kk (V^v) \quad (2.35)$$

The reactions were all carried out at high [H<sup>+</sup>] (0.20 – 1.00M) where H<sub>2</sub>A is the predominant ascorbic acid species and inner sphere mechanism was proposed for the reaction.

### **2.6.2 OXIDATION OF L- ASCORBIC ACID. WITH GROUP 6 COMPLEXES.**

The kinetics of the oxidation of ascorbic acid with chromium (IV) ion indicates that it involves a pre-equilibrium deprotonation with the possibility of other equilibria including the formation of dichromate at higher acid concentration and ascorbate anions at lower  $[H^+]$  as well as the possible formation of  $[HCrO_3]^-$

### **2.6.3 OXIDATION OF ASCORBIC ACID BY GROUP 7 COMPLEXES.**

The reaction of manganese species  $M_{aq}^{3+}$  (Pelizzetti et al, 1975, 1978) at various hydrogen ion concentration also involves the reaction of  $[Mn(OH)_{aq}]^{2+}$  and also as contribution from the reaction of the ascorbic acid with both of these species. They concluded that the acid independent pathway is largely represented by the reaction.



Ascorbic acid reacts with the pertechnate ion in strong acid solution to form a red coloured compound. The kinetics of the formation of this species were studied and was found to be second order in  $[H^+]$  and the ion  $H_3A^+$  is also proposed as an intermediate in the process.

### **2.6.4 OXIDATION OF L-ASCORBIC ACID BY GROUP 8 COMPLEXES.**

A lot of interest has been on reactions of Iron (III) and its complexes with ascorbic. The mechanism originally proposed for the reaction of the Iron (III) aquo ion with ascorbic acid was an inner-sphere process based on formation of an intermediate complex. Lawrence and Ellis, (1972) examined the reaction between 450-650nm and were able to produce a spectrum of this transient complex to which they assigned the formula  $[FeHA]^{2+}$ . Martell also proposed (Davies, 1992) an inner-sphere mechanism for the oxidation of ascorbic acid by Iron (III) modified by complexation with various chelating ligands.

Martinez and co-workers (Davies, 1992) have extensively studied the iron (III) ascorbate system over the years. They isolated a dark blue solid from a mixture of iron (III) chloride and ascorbate at high pH, but they also observed transient species at pH 5.

Martinez in an independent study observed a red- short-line specie in the reaction of tris (oxalato) formate (III) with ascorbic acid. It seems likely that this is a mixed oxalate / ascorbate complex.

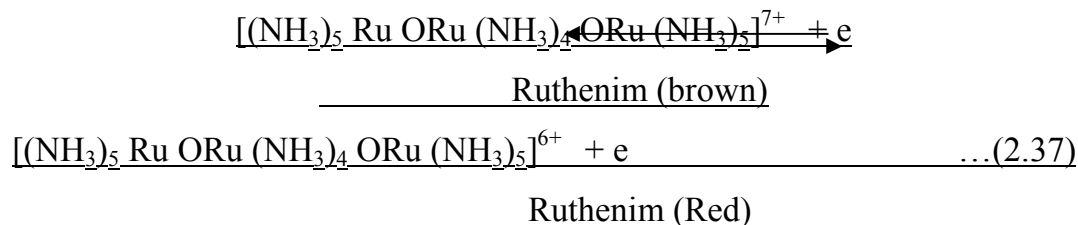
Xu and Jordan (Davies 1992) carried out a careful study and detailed interpretation of the reaction of aqueous iron (III) with ascorbic acid. Unlike other investigations this was carried out under conditions such that there was an excess of iron (III) ( $2 - 7 \times 10^{-3} \text{ mol dm}^{-3}$ ) over ascorbic acid. ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) while following the absorbance change at 560nm.

Under this condition, the results obtained showed that the reaction occurred in two stages which were manifested as a rapid increase in absorbance ( $t_{1/2} = 10 - 20\text{ms}$ ) and a slower decrease ( $t_{1/2} = 200\text{ms}$ ). The first rapid stage of this reaction is attributed to a substitution reaction between ( $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ) and ascorbic acid. The rate of the first reaction is much faster than expected for such a substitution at this substrate.

The question of the unusually high rate of substitution of the ascorbate at ( $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ) is addressed by the authors who suggest that it is due to the unusually large bite distance between oxygen atoms in ascorbic acid which allows the ascorbic acid to approach more easily over an octahedral edge with two oxygen simultaneously moving towards the center of separate octahedral faces, where they have the most favourable interaction with iron (III) in a precursor complex.

These workers have drawn attention to an interesting outcome of their analysis, that the ratio of the rate constants for the reactions of  $[\text{Fe}(\text{HA})]^{2+}$  with  $[\text{Fe}(\text{H}_2\text{O})]^{3+}$  and  $[\text{Fe}(\text{OH})]^{2+}$ , respectively, is  $2.7 \times 10^{-2}$  and hence  $[\text{Fe}(\text{OH})]^{2+}$  is more reactive than is  $[\text{Fe}(\text{H}_2\text{O})]^{3+}$  despite the fact that the latter is a better oxidizing agent than the former.

The reduction of “ruthenium brown” and ruthenium red by the ascorbic acid system has been studied (Banas and Mrizinski, 1982) and the reaction oxidation process is



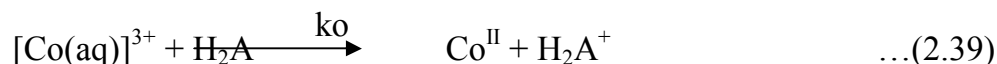
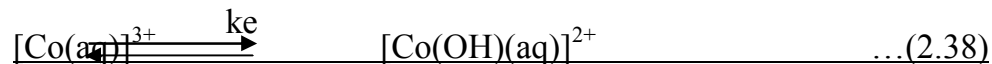
The pattern here is essentially similar to that observed for less complex species and the reaction mechanism resulting in the production of HA<sup>-</sup> is proposed, presumably via – an outer sphere mechanism.

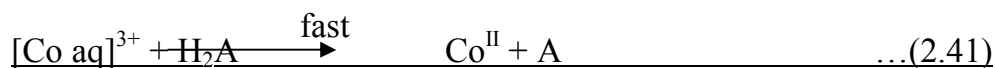
Taqi Khan et al, (1987) have investigated the photochemical oxidation of ascorbic acid using platinum loaded TiO<sub>2</sub> in an aqueous solution of tris (bipyridy)ruthenium (II). The ascorbic acid is present as a sacrificial agent and under the conditions used 130 dm<sup>3</sup>h<sup>-1</sup> of hydrogen were obtained.

### **2.6.5 OXIDATION OF ASCORBIC ACID BY GROUP 9 COMPLEXES**

Redox reactions of kinetically inert cobalt(III) complexes have historically presented important opportunities for the study of both outer sphere and inner sphere reductions of metal ion complexes. In many cases there is little opportunity of forming a bridge and the complexation reaction with ascorbic acid or ascorbate is likely to be slower than the redox reaction. For example the reduction of the hexaaquacobalt (III) ion by ascorbic acid (Rickman et al, 1977)

This was studied at comparatively high hydrogen ion concentration so that H<sub>2</sub>A was the only reductant, while the conditions allowed for the possibility of the reaction of [Co(OH)aq]<sup>2+</sup> as well as [Co(aq)]<sup>3+</sup>. The kinetics of the reaction were readily interpreted in terms of the series of reactions shown below





Even at the fairly high hydrogen ion concentration used in this work, the reaction is fast and has to be followed using stopped flow techniques. There is no evidence for the formation of an intermediate complex and the reaction is assumed to proceed by an outer sphere mechanism.

The reaction of chloropentamminecobalt (III) to (II) ion with L-ascorbic acid in aqueous solution has been studied in the pH range or 8 – 2.0 (Martinez et al, 1988). An outer sphere mechanism was proposed with ascorbic acid radical as the first product, which then rapidly reduces a further mole of complex. The product of the reaction was cited as  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$ , but presumably this labile species quickly decomposes to produce  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

All the reactions of these complexes with ascorbic acid were considered to be outer-sphere, as expected from the known slow exchange rate of  $\text{H}_2\text{O}$  in these complexes.

### **2.6.6 OXIDATION OF ASCORBIC ACID BY GROUP 10 COMPLEXES**

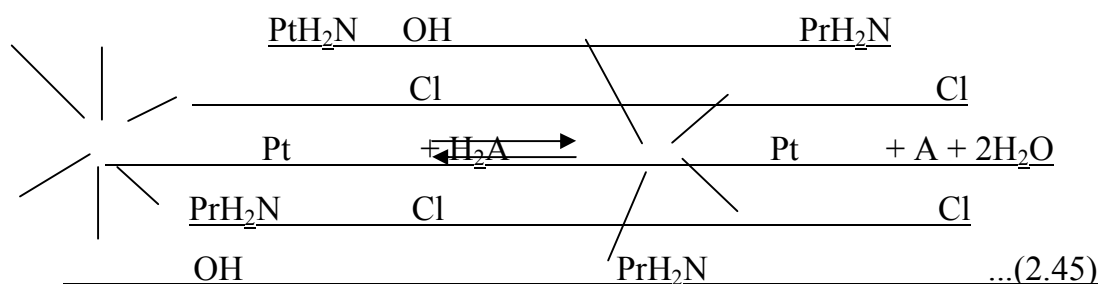
There have been a number of studies of the kinetics and mechanisms of reactions of nickel (IV) complexes with ascorbic acid, like the platinum (IV) complexes discussed below. These are of interest because the nickel (IV) is a two-electron oxidizing agent. It is interesting that McAuley et al (1983) have looked at the oxidation of ascorbic acid by three nickel (III) complexes of the macrocycles. The reactions were first order with respect to complex and ascorbic concentrations and inversely dependent on hydrogen ion concentration. The proposed mechanism includes the possibility of what is called a “proton ambiguity” when reaction with  $\text{HA}^-$  is concerted, since there are two possibilities and the rate equation includes both of these reactions.





The sulphate ion (which is known to form complexes with  $\text{Ni}^{\text{II}}$ ) produced a marked decrease in rate with increasing sulphate ion concentration giving a linear dependence of  $k_{\text{obs}}^{-1}$  vs  $[\text{SO}_4^{2-}]_{\text{T}}$  at constant ascorbic acid concentration.

Evans and Green, (1987) have studied the reaction of ascorbic acid with one of the second generation platinum-containing anti-cancer drugs, cis, -  $\text{Pt}^{\text{IV}}[\text{NH}_2\text{Pr}] \text{Cl}_2(\text{H}_2\text{O})_2$  (CHIP). It is though possible that the effectiveness of this drug is enhanced by the reduction of ascorbic acid in  $v_1v_0$ . The study showed that ascorbic acid reduced the CHIP to the  $\text{Pt}^{\text{II}}$  species cis -  $[\text{Pt}(\text{NH}_2\text{Pr}) \text{Cl}_2]$ . The kinetic measurements were interpreted in terms of the equilibrium as shown below.



#### Equilibrium of CHIP with Ascorbic acid.

### **2.6.7 OXIDATION OF ASCORBIC ACID BY GROUP 11 COMPLEXES.**

Hayakawa et al, (1973) showed that the reduction of copper (II) ions by ascorbate in acetate buffer showed a second order dependence on copper (II) concentration; first order dependence on ascorbic acid concentration and a complex dependence on pH, which was related to the difference in reactivity of  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ , aquacopper (III) ions and acetato copper (II) species. Silver (I) may be titrated directly with Ascorbic acid using variamine blue as an indicator. Davies (1992) concluded that this reaction has a rate determining step reaction between  $\text{HA}^-$  and  $\text{Ag}^+$ . However there is no evidence for or against an outer-sphere or inner-

sphere mechanism. The reaction shows an inverse dependence on  $[H^+]$ , though one would like more data to support this rather their log/log plots.

The reduction of gold (III) by ascorbic acid has been studied over a range of chloride concentrations. The rate was dependent on the inverse sequence of the chloride concentration.

### **2.6.8 OXIDATION OF ASCORBIC ACID BY LANTHANIDES AND ACTINIDES.**

Ascorbic acid has been found to react comparatively slowly with cerium (IV) and the kinetics of the reaction has been studied. Cerium (IV) reactions have the additional interest that like other lanthanide elements cerium forms complex species in aqueous solution with oxo anions such as sulphate ions.

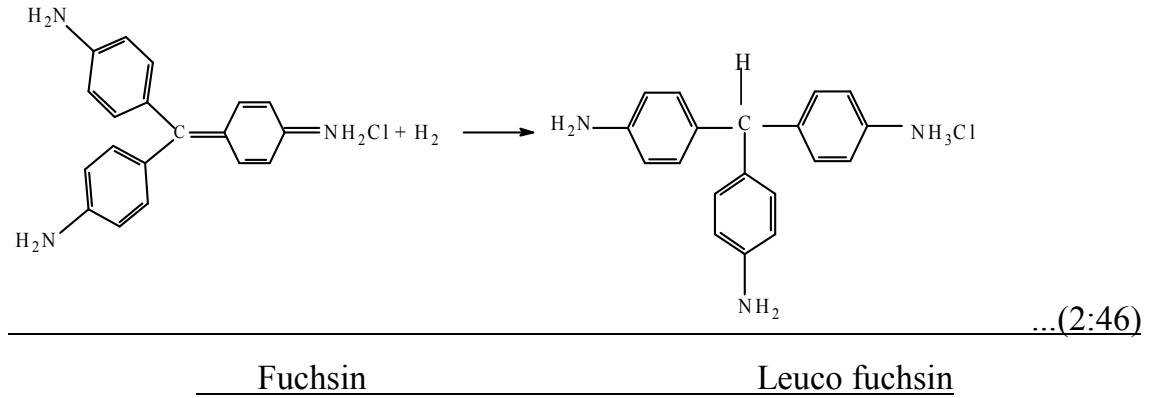
The sulphate and hydrogen ions show considerable inhibition of the reaction due to the formation of complex species such as  $[Ce(SO_4)_3]^{2-}$

The kinetics are interpreted in terms of an inner sphere reaction in which there is a rapidly achieved pre-equilibrium involving the formation of cerium (IV) ascorbic acid complex and the rate determining step is the decomposition of this complex to form  $Ce^{3+}$  and HA.

An inner-sphere mechanism has been proposed for the reaction of mercury (II) acetate by ascorbic acid in acetic acid solution. Of all the reported reactions of ascorbic acid, no report on the reaction of ascorbic acid with  $[Mn^{III}O_2Mn^{IV}]^{3+}$  complexes appeared.

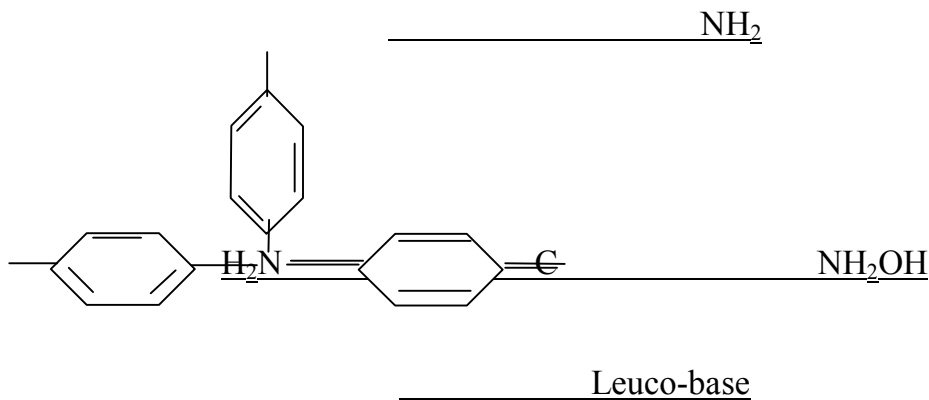
## **2.7 REACTIONS OF BASIC FUCHSIN**

A dye retains its colour only as long as its affinity for hydrogen is not completely satisfied. The colourless compound is known as leuco-fuchsin. In basic fuchsin, the quinoid chromophore has unsatisfied affinity for hydrogen. Therefore, it is easily reducible. The double bonds of the quinoid ring breaks and hydrogen atoms become attached to the valences thus freed. This reduction destroys the chromophore group and as a result the compound loses its colour.



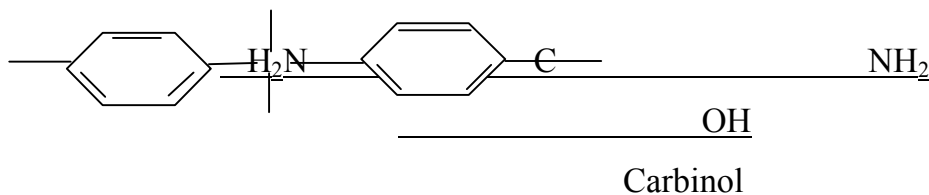
The reaction is reversible under conditions favouring oxidation. It is of special significance to the bacteriologist as dyes can often be used as indicators of reduction.

A leuco-base can also be formed by removal of the acid radical in basic fuchsin the compound becomes colourless. (Conn, 1961)



A re-arrangement of the atoms in the molecule takes place upon neutralization to give carbinol which is without chromophore. Therefore the compound is colourless (Conn, 1961).





Carbinol is of little significance to biologist but it is of much importance to the dye manufacturer as intermediate in the preparation of dyes.

## 2.8 REDUCTION OF DIOXO-BRIDGE MANGANESE COMPLEX

In 1977, Cooper and Calvin gave a comprehensive report on the synthesis and characterization of mixed valence di-oxo-bridged manganese complexes. In that report, they concluded that the electron structure of the complexes  $(L_2Mn^{III}O_2Mn^{IV}L_2)(ClO_4)_3$ , where  $L=2,2^1$ bipyridine or 1,10-Phenanthroline) is compatible with those of photosystem II (Robins and Day, 1967).

Redox reactions between these complexes and various reductants have been reported (Ghosh et al 1994, Chandihur; et al 1995, Lohdip et al, 1998). In all of these systems, a stoichiometry of 2:3 was obtained. The general reaction equation was given as

$$2[Mn^{III}O_2Mn^{IV}]^{3+} + 3R + 2H^+ \longrightarrow 4Mn^{2+} + mX + nH_2O \quad \dots \quad (2.47)$$

Where  $R = NO_2^-$ ,  $m = 3 = X = NO_3$  and  $n=1$

for  $Mn^{III}_2Mn^{IV}/NO_2^-$ , system.

$R = H_2Q, m=3, x = Q$  (benzoquinone) and  $n=4$

for  $Mn^{III}O_2Mn^{IV}$ /hydroquinone system.

$R = H_2C_2O_4, m = 6, x = CO_2$  and  $n = 4$

for Mn<sup>III</sup>O<sub>2</sub>Mn<sup>IV</sup>/H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> system.

All the reactions were found to exhibit first order each in both the reductant and the oxidant concentration giving the rate law as.

$$\frac{-3/2d [\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = k_2 [\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] [\text{reductant}] \dots(2.48)$$

$$k_2 = 1.78 + 0.04 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for NO}_2^- \dots(2.49)$$

$$k_2 = 1.09 + 0.04 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for ascorbate} \dots(2.50)$$

$$k_2 = 2.35 + 0.15 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for H}_2\text{C}_2\text{O}_4 \dots(2.51)$$

$$k_2 = 3.08 \pm 0.25 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for RSCH}_3 \dots(2.52)$$

$$k_2 = 3.44 \pm 0.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for 2-mercaptobenzoic acid} \dots(2.53)$$

$$k_2 = 1.19 \pm 0.05 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for SCN} \dots(2.54)$$

Rate of reduction of [Mn<sup>III</sup>O<sub>2</sub>Mn<sup>IV</sup>] has been shown to increase with increase in the acidity of the reaction medium (Chandhuri et al 1995, Lohdip et al 1998). This acid catalysis has been explained as due to the successive protonation/hydration of the dimer.

Arabel et al, (1997) have also indicated that the dimanganese complex was protonated during the act of electron transfer, even though they observed a decrease in the rate of reaction with increase in the acid concentration.

This decrease was attributed to the high extent of deprotonation or dissociation of the hydroxy acids involved in the reaction. In summary, the results of the systems studied, point to the fact that the solutions of [Mn<sup>III</sup>O<sub>2</sub>Mn<sup>IV</sup>], when stabilized (with buffer pH 4.5) are

reduced rapidly to  $\text{Mn}^{2+}_{\text{aq}}$  through the protein coupled electron transfer pathway, or through outer sphere mechanism.

Most of the authors also concluded that the properties of the high valent oxo manganese complexes are similar to those of Photosystem II and so can serve as active sites for biological redox processes.