# KINETICS AND MECHANISM OF THE SEDUCTION OF DIAQUOTETRAKIS (2, 2-BIPYRIDINE)u OX0DIRUTHENIUM (III) ION BY SOME THIOLS AND RESORCINOL

BY

MUSA, KABIR YUSUF

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## 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 has been acknowledged by means of reference.



K. Y. MUSA

2/11/95

DATE

## CERTIFICATION

This thesis entitled, kinetics and mechanism of reduction of Diaquotetrakis (2,2-bipyridine)-μ-oxodi-ruthenium (III) ion by some thiols and resorcinol by Musa, Kabir Yucuf, meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to scientific and literary presentation.

| | |
|---|---|
| Dr. J.F. Iyun<br>First Supervisor | 30/8/95<br>Date |
| Dr. G.A. Ayoko<br>Second Supervisor | 30/8/95<br>Date |
| External Examiner | 30/8/95<br>Date |
| Professor S.A. Thomas<br>Head of Department | 30/8/95<br>Date |
| Professor D. Muhammad<br>Dean, Postgraduate School | 4/6/97<br>Date |

## DEDICATION

Dedicated to my mother AISHA for her love and prayers

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All praise be to Allah Lord of the worlds Who taught man what he Knew not. Thanks be to Allah By Whose Grace and Guidance, I am able to complete this programme. And May Peace and Blessings of Allah Be upon His Messenger, Muhammad (S.A.W). The sealed of the Messengers.

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## ABSTRACT

The kinetics and mechanism of oxidation-reduction of diaquatetrakis-(2,2-bipyridine)-μ-oxo-diruthenium(III) ion ($RuORu^{4+}$) with some thiols (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) and 1,3-dihydroxybenzene (Resorcinol) have been studied in aqueous perchloric acid ($HClO_4$) solutions at 25.0 ± 0.1°C, I = 1.0M ($NaClO_4$) for thiols and I = 2.0M ($NaClO_4$) for the resorcinol. One mole of the reductant (thiols) is consumed by one mole of the oxidant ($RuORu^{4+}$) and two moles of the oxidant are required for one mole of the resorcinol ($H_2Q$). All the reactions are first-order in both oxidant and reductant, with following rate laws.

$$-\frac{d[RuORu^{4+}]}{dt} = k_a[RuORu^{4+}][RSH]$$

and

$$-\frac{d[RuORu^{4+}]}{dt} = k_b[RuORu^{4+}][H_2Q]$$

Where [RSH] = (L-cysteine, mercarptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol)

$[H_2Q]$ = resorcinol

$k_2$ (L-cysteine) = 2.02 ± 0.2$M^{-1}s^{-1}$ at

$[H^+] = 1.33 \times 10^{-3}M$

$k_2$ (Mercaptoacetic acid) = (8.98 ± 0.09) x $10^{-2}M^{-1}s^{-1}$

at $[H^+] = 1.0 \times 10^{-3}M$

$k_2$ (β-mercaptoethylamine) = (2.28 ± 0.02) x $10^{-1}M^{-1}s^{-1}$

at $[H^+] = 1.0 \times 10^{-3}M$

$k_2$ (2-mercaptoethanol) = 4.54 ± 0.01$M^{-1}s^{-1}$ at

$[H^+] = 1.0 \times 10^{-3}M$

$k_2$ (Resorcinol) = (8.35 ± 0.07) x $10^{-2}M^{-1}s^{-1}$

at $[H^+] = 1.0 \times 10^{-3}M$

The rate of the reactions for both the thiols and resorcinol show an inverse hydrogen ion dependence $[H^+]^{-1}$ and the kinetic data are consistent with the following equations.

$$-\frac{d[RuORu^{4+}]}{dt} = [RuORu^{4+}][RSH][H^+]^{-1}$$

RSH = L-cysteine, mercaptoacetic acid and β-mercaptoethylamine

$$-\frac{d[RuORu^{4+}]}{dt} = [RuORu^{4+}][H_2Q][H^+]^{-1}$$

$H_2Q$ = resorcinol

$$-\frac{d[RuORu^{4+}]}{dt} = (c + b[H^+]^{-1})[RuORu^{4+}][2\text{-mercaptoethanol}]$$

Where c is an intercept for the plot of $k_H$ versus $1/[H^+]^{-1}$ and b the slope for the plot of $k_H$ versus $[H^+]^{-1}$.

The rate, of the. L-cysteine and mercaptoacetic acid systems were enhanced by addition of anions CGI"", NO3" and SOA") and cations <$Na^+$, K-, $Rb^+$ and $Mn^{2+}$). For the |3-mercaptoethylamine, 2-mercaptoethanol and re.sorcinol system, addition of such ions have no effect on the reaction rate. All the thiols reactions show evidence of free radical mechanism, but the re.sorcinol reaction show no evidence, of free radical mechanism. Both the results of spectroscopic investigations and Michaelis-Menten analysis show no evidence of intermediate complex formation of significant stability. Experimental results obtained in all the systems studied are in favour of an outei— sphere, mechanism, and the. mechanism has been proposed for all the systems.

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## ABBREVIATIONS

| ABBREVIATION | NAME |
|---|---|
| aq | Aqueous |
| AnLAR | Anaytical Reagent |
| B.D.H | British Drug House |
| bipy | Bipyridine |
| Calc. | Calculated |
| e.s.r | Electron Spin Resonance |
| G.P.R | General Purpose Reagent |
| $H_2Q$ | Resorcinol |
| I.S | Inner-sphere |
| K | Equilibrium |
| $K_a$ | Acid dissociation constant |
| k | rate constant |
| βMEA | β-mercaptoethylamine |
| MAA | Mercaptoacetic acid |
| 2-METHOH | 2-Mercaptoethanol |
| n.m.r | Nuclear Magnetic resonance |
| Obsd | Observed |
| O.S | Outer-sphere |
| Ox | Oxidant |
| Phen | 1,10-Phenanthroline |
| Red | Redox |
| RSH | Thiol |
| $RuORu^{4+}$ | Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium (III) ion |

# CHAPTER ONE

## 1.0 INTRODUCTION

Oxidation-reduction reactions (redox reactions) have been extensively studied because of the important role they play in chemical, biological and technological processes (Iyun, 1982). Thorough knowledge of this area of chemistry will definitely aid the development and effective control of a wide area of science and technology. The earlier research on this aspect of chemistry has been restricted to stoichiometry and thermodynamic properties. The kinetics of these reactions were overlooked, primarily because the reactions were often very fast and the techniques available could not cope with the rate of reaction.

Recently, quite a large number of kinetic investigation have been carried out on electron-transfer processes (Sutin, 1962; Hunt, 1964; Sykes, 1966; Burgess, 1978). The investigations were made possible by the use of radioisotopes and a wide range of techniques that vary from conventional spectrophotometric methods for slow reaction. ($t_{1/2}$ = Ca 30 seconds) to continuous and stopped-flow methods for fast reactions ($t_{1/2}$ = milliseconds). These methods

have been extensively reviewed (Stranks, 1960; Caldin, 1974; Wilkins, 1974). Below are brief summaries of the methods.

## 1.1 Rate monitoring techniques

### 1.1.1 Conventional methods

These techniques are used in monitoring reaction that have half-lives, of about 30 seconds. These, which include photometric, electrometric, polarimetric, spectrometric methods and isotopic sampling techniques, have been discussed by Stranks, (1962). They involve measuring as a function of time, the concentration of one or more of the reactants or products or even any physical property such as absorbance which is directly related to the concentration (Wilkins, 1974).

Most transition metals ions however, react much faster, hence fast-reaction techniques are required.

### 1.1.2 Fast Reaction Techniques

These techniques are used for reactions with half-lives of about a milliseconds. Fast reaction techniques can be broadly classified into flow, relaxation and resonance methods.

(a) Flow methods: These involved the mixing of separate solutions of two reactants inside the monitoring device, and they permit the observations of the reaction occuring as rapidly as 0.1 milliseconds. (The usual range is 1 - 10 milliseconds) (Espenson, 1981). Different flow methods exist depending on the treatment given to the reaction mixture (Caldin, 1974). Two common flow methods are the continuous and the stopped-flow methods.

(i) Continuous-flow method: In this method, the reaction mixture flow continuously along an observation tube, while conventional monitoring is made either at different points along the observation tube (with the flow maintained at constant rate) or at a fixed point on the tube with varied flow rate. In either cases a series of values for the extent of reaction is obtained at different times. These values constitute the kinetic data required.

(ii) Stopped flow methods: The solutions are forced together through a mixing device and as the mixed solution flow along the tube, it is abruptly stopped so that the solution come to rest within a few milliseconds. The rate of the flow along the

observation tube is such that when the solution is stopped a segment within one centimeter of mixing device has been mixed for only 1-2 milliseconds. Any reaction taking place in this segment of solution is then monitored and the signal relayed to an oscilloscope.

This techniques make it possible to conventionally study reactions with half-lives ranging from a few milliseconds to several seconds. This method is particularly important in the study of the formation of complexes which occurs as intermediate in irreversible reaction.

(b) Relaxation Methods

These methods are applied to reversible reactions with half-lives ($t_{\frac{1}{2}}$) as short as $10^{-9}$ seconds (Eigen et al, 1963). The observed equilibrium is perturbed by rapid variation of physical parameters such as temperature, pressure or electrical field intensity and time taken to readjust to a new equilibrium position is monitored, which is then related to rate constant of foward and backward reaction. The dependence of a particular equilibrium on chosen external physical parameters largely determines the method of pertubation used for such an equilibrium and

hence these methods are referred to as temperature-jump, pressure-jump or electric-jump methods (Wilkins, 1980).

(c) Resonance techniques

Both n.m.r and e.s.r techniques have been used to study complex formation (Pearson and Pulson, 1959; Pearson and Buch, 1962) and aquation of metal ions (Connick and Poulson, 1959) in solution. In nmr techniques, the resonance absorption line is related to the life-time of the nucleus in a given spin state, while in e.s.r it is related to the life-time of paramagnetic species in a given energy state. Any reduction of life-time of these states by chemical interaction results in line broadening. On addition of increasing amount of reagent measurement of the corresponding increase in width of line due to second reagent can be made.

H.n.m.r-line broadening (Pearson and Lanier, 1964) have been extensively used to measure rates of exchange of several mono- and bi-dentate nitrogen and oxygen donor ligands coordinated to $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$ and $Cu^{II}$.

## 1.2 Theoretical Consideration in Electron-transfer Processes

### 1.2.1 Frank-Condon Principle

Electron-transfer process have to satisfy the Frank-Condon principle (restriction). Which states that nuclei motion is so slow ($10^{-13}$s) compared to that of electron ($10^{-5}$s) hence electron transfer occur without appreciable movement of the nuclei (Sutin, 1966). This shows that nuclear position remains essentially unperturbed during the act of electron transfer process (Platzman and Frank, 1954; Sutin, 1966). This leads to two main consequences on electron-transfer processes.

(a) The reactants (oxidant and reductant) must undergo reorganisation before electron-transfer such that their energies in transition state becomes identical in order to minimise the change on electron transfer.

(b) No angular momentum must 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.

### 1.2.2 Electron tunnelling theory

In addition to Frank-Condon principle, the electron tunnelling theory was developed by some workers (Weiss, 1954; Marcus, Zwolinski and Eyring, 1956). It has been noted that electronic energy is not as high in either the 'reactants' or the 'products' activated complex as the classical potential energy barrier to electron migration between these complexes. Therefore, electron migration is viewed as a tunnelling process in which the electron passes through the potential energy barrier rather than over it (Basolo and Pearson, 1967). The result is that the electron can be transferred to a distance much greater than would correspond to the actual collision of reactants. Figure 1.1 illustrates a potential energy barrier leakage.

$u_1$ and $u_2$ refer to ground states of electron in cation 1 and 2 respectively.

d = Width of barrier at height of penetration

V = kinetic energy of the electron

$\Pi_0$ = height of the barrier.

This led some theoreticians to attempt calculations of the electron transmission coefficient (Marcus et al, 1954). Their results were expressed in terms of transition state theory of chemical kinetics and could be written in the form

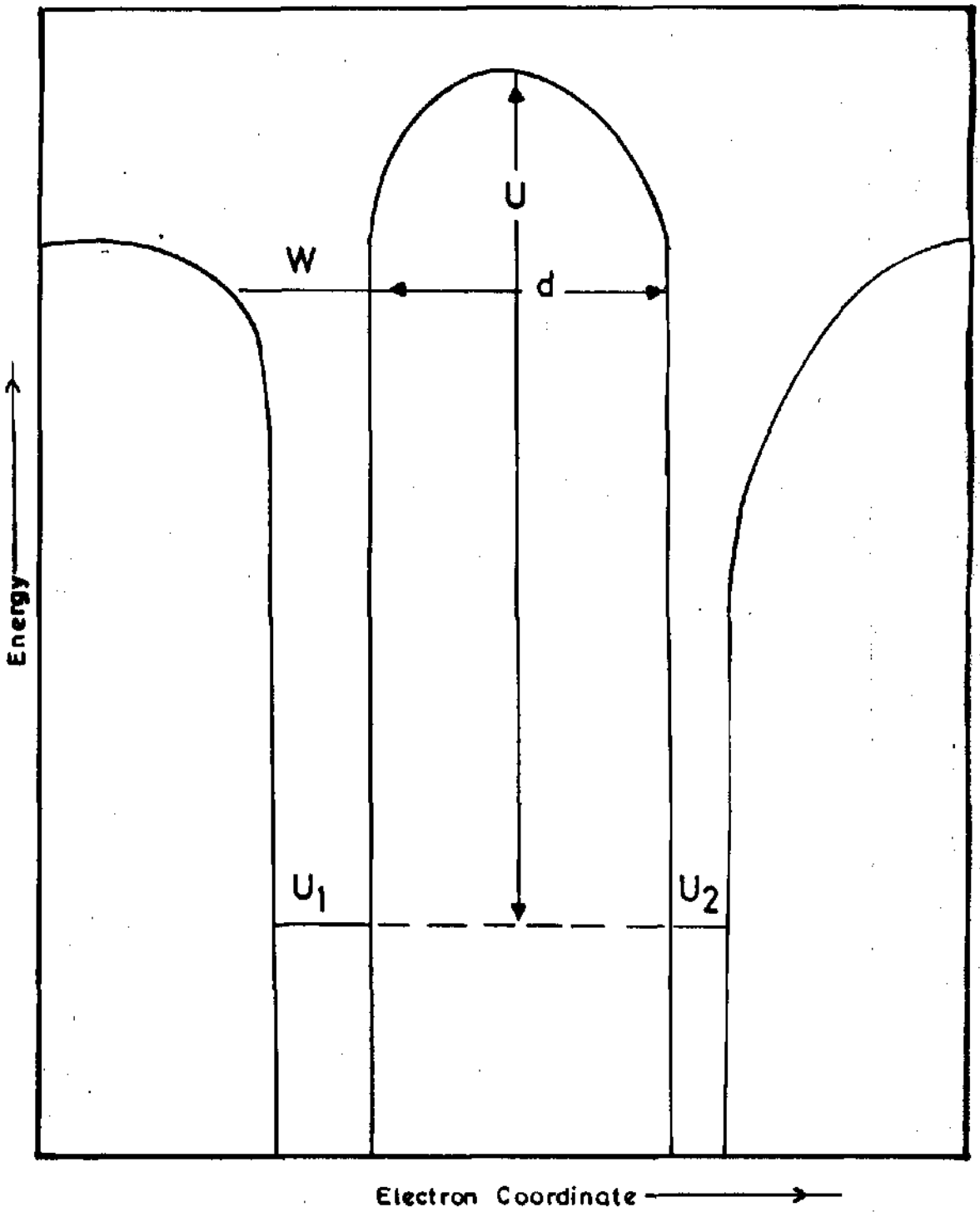



FIG.1.1: ELECTRON TRANSFER BY PENETRATION OF A POTENTIAL ENERGY BARRIER.

$$k = \frac{KT}{h} k' \exp\left(\frac{-\Delta Gr^*}{RT} - \frac{\Delta Ge^*}{RT}\right) \quad \ldots\ldots (1.1)$$

k' = electron transmission coefficient

k = Rate constant

K = Boltzman constant

T = Absolute temperature

Ge' = activation energy

Gr" = hydration energy for inner coordination shell arrangement.

R = Gas constant

The transmission coefficient, which is always less than one, increases (tending to increase the rate constant) as the exchanging partners come close together. As a result of electrostatic repulsion, the energy of activation also increases and this tend to decrease the rate. However, at an optimum distance a maximum exchange rate is obtained. Taube, (1959) and Lewis (1980) all discussed the question of potential energy as a conceptual tool in the study of electron transfer reactions. They all concluded that electron tunnelling is probably involved in most electron-transfer processes, although the tunnelling step might not be the rate determining step in most cases.

## 1.3 Oxidation-Reduction (Redox) Reaction

Redox reaction can be classified into two main types:- Homonuclear (isotopic) exchange reaction and chemical or cross reaction. This classification is on the basis of their thermodynamic parameters.

### 1.3.1 Homonuclear or Isotopic Exchange Reaction

The principle involved here, is that electron transfer takes place between two ions of the same elements, examples

$$Co^{*}(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \longrightarrow Co^{*}(NH_3)_6^{3+} + Co(NH_3)_6^{2+} \quad \ldots\ldots (1.2)$$

$$^{*}Cr^{2+} + CrCl_2^{2+} \longrightarrow Cr^{*}Cl_2^{2+} + Cr^{2+} \quad \ldots\ldots (1.3)$$

(Where (*) is an isotopically labelled species). There is no net chemical change and the rate constant for the forward and backward reaction are equal so $K_{equilibrium} = 1$, $\Delta H = 0$, $\Delta S > 0$, $\Delta G = 0$. The reaction is studied by isotopic labelling.

### 1.3.2 Heteronuclear Electron Exchange or Cross Reaction

The reactants are chemically distinct from the product, the rate can be measured by chemical methods.

$\Delta H \neq 0$, and $\Delta G < 0$ examples

$Fe(CN)_6^{4-} + IrCl_6^{2-} \longrightarrow Fe(CN)_6^{3-} + IrCl_6^{3-}$ .. (1.4)

$Mn(VII) + 4Mn(II) \longrightarrow 5Mn(III)$ .... (1.5)

This class of redox reaction could be complimentry when the oxidant and reductant undergo equal change in oxidation states, example

$Sn(II) + Tl(III) \longrightarrow Sn(IV) + Tl(I)$ .... (1.6)

$Co(en)_3^{3+} + Ru(NH_3)_6^{2+} \longrightarrow Co(en)_3^{2+} + Ru(NH_3)_6^{3+}$

.... (1.7)

In these reactions the stoichiometry is always 1.1. They could be non-complimentry in which case the oxidant and reductant undergo unequal changes in oxidation states. Example

$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$ .... (1.8)

The stoichiometry of these class of reactions is usually not 1.1. These certainly involves the formation of reactive intermediate in which unstable oxidation states of the metal are formed.

## 1.4 Mechanism of Redox Reactions

In studying mechanism of electron transfer process, the following are points of mechanistic interest.

(a) What is the stoichiometry of the reaction and what is the composition of the activated complex?
(b) Is the reaction accompanied by transfer of electrons or atoms. If atoms are transferred which atoms are transferred?
(c) How many electrons are transferred in a single step (for a reaction involving multivalent change)?
(d) How does the rate of electron transfer compared to the rate of substitution?
(e) If the reaction is thermodynamically feasible, what provide the driving force for the reaction?
(f) What is the significance of acid-base catalysis (if any)?
(g) Is it possible to identify or infer the closeness of approach of the reactants in the activated complex prior to electron transfer?
(h) What are the products formed? Can any be isolated and identified?

The answers to these questions led to the two distinct mechanism that have been established for redox reactions. The outer- and the inner-sphere mechanisms first proposed by Taube and his coworkers (Taube, Meyer and Rich, 1953; Taube, 1959).

1.4.1 The Outer-Sphere Mechanism

The electron transfer involves two reactants whose coordination shell remain intact although not completely undisturbed during the act of electron transfer. The outer-sphere occurs when both reactants are inert with respect to substitution or one is relatively inert and does not present site for labile reactant, example.

$$Mo(CN)_6^{3-} + Fe(CN)_6^{4-} \longrightarrow [Mo(CN)_6^{3-}][Fe(CN)_6^{4-}] \longrightarrow Mo(CN)_6^{4-} + Fe(CN)_6^{3-} \quad \ldots (1.9)$$

The mode of activation of outer-sphere mechanism can be illustrated as shown below for the reaction between $Mo(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$

$$Mo(CN)_6^{3-} + Fe(CN)_6^{4-} \longrightarrow Mo(CN)_6^{4-} + Fe(CN)_6^{3-} \quad \ldots\ldots (1.10)$$

The reaction (1.10) which takes place via outer-sphere mechanism is thought to occur in four steps as shown below.

Step 1: Formation of precursor complex.

$$Mo(CN)_6^{3-} + Fe(CN)_6^{4-} \longrightarrow [(CN)_5Mo^{V}CN)(CNFe^{II}(CN)_5)]^{7-} \quad \ldots\ldots (1.11)$$

Step 2: Activation of the precursor complex

$$[(CN)_5Mo^{V}CN)(CNFe^{II}(CN)_5] \longrightarrow [(CN)_5Mo^{V}CN)(CNFe^{II}(CN)_5)]^{*7-} \quad \ldots\ldots (1.12)$$

Step 3: Electron transfer and formation of successor complex

$$[(CN)_5Mo^{V}CN)(CNFe^{II}(CN)_5)]^{4-} \longrightarrow [(CN)_5Mo^{IV}CN)(CNFe^{III}(CN)_5)]^{3-} \quad \ldots\ldots (1.13)$$

Step 4: Decomposition of successor complex to give final products

$$[(CN)_5Mo^{IV}CN)(CNFe^{III}(CN)_5)]^{3-} \longrightarrow Mo(CN)_8^{4-} + Fe(CN)_6^{3-} \quad \ldots(1.14)$$

Step 3 is the rate-determining step.

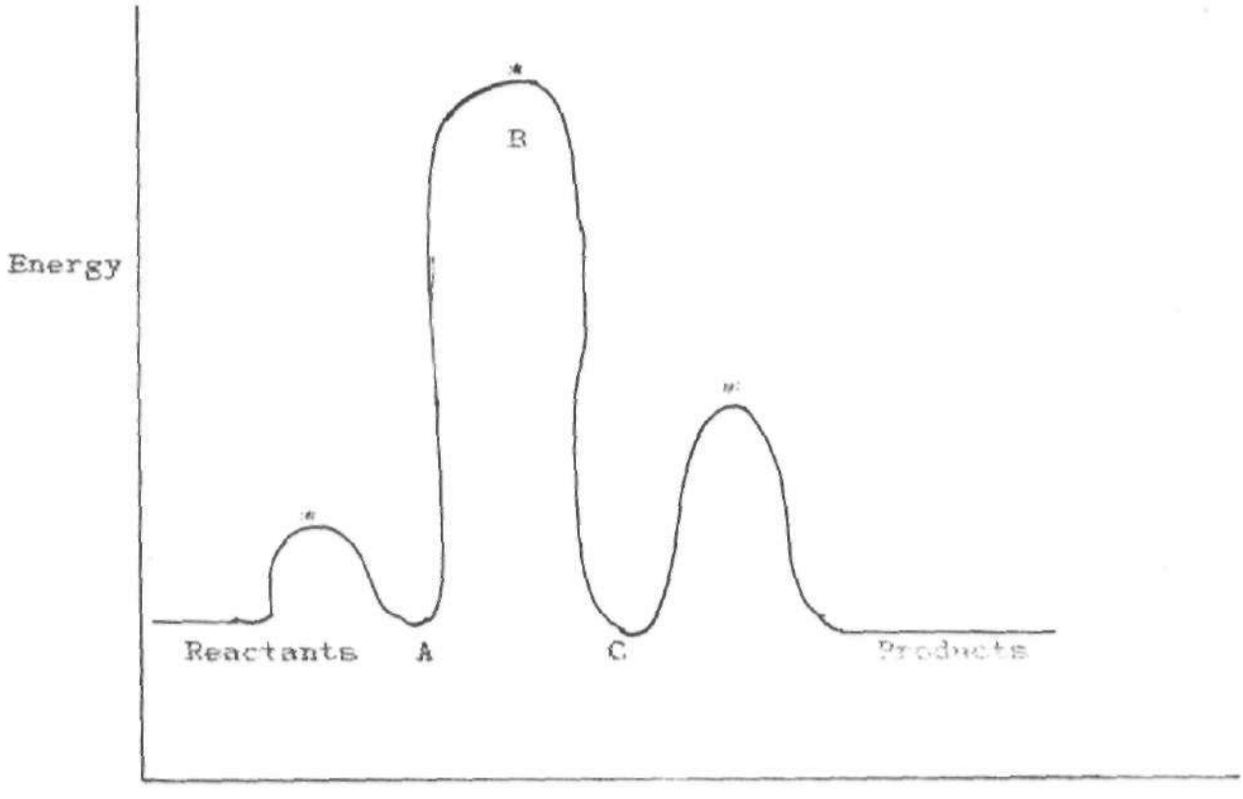



Fig 1.2 Reaction coordinate ----->

Energy profile diagram for a redox reaction which occurs by the outer-sphere mechanism.

In Fig 1.2 A is the formation of precursor complex B is the electron transfer and formation of successor complex, while C is the separation of successor complex to give final products.

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

### 1.4.2 Inner-sphere mechanism

The main characteristic of this mechanism is that substitution occurs at one of the metal centres to give a binuclear ligand-bridged species prior to electron transfer. The two reactants are linked together by at least one bridging ligand common to their coordination shells. Fectron transfer through this ligand which is usually but not always transferred from one reactant to another.

Example

$$Co^{III}(NH_3)_5X^{2+} + Cr^{II}(H_2O)_6^{2+} \longrightarrow Co^{2+} + 5NH^{+}_4 + CrX^{2+} \quad ..(1.15)$$

$$[Co^{III}(NH_3)_5 - X - Cr^{III}(H_2O)_5]^{4+} + H_2O \quad \ldots\ldots (1.16)$$

Binuclear ↓ ligand bridged intermediate

Electron transfer

$$[(NH_3)_5Co^{II} - X - Cr^{III}(H_2O)_5]^{4+} \quad \ldots\ldots (1.17)$$

$$Co^{2+} + 5NH_4^+ + CrX^{2+} \quad \ldots\ldots (1.18)$$

The bridging ligand has been transferred where (X = $F^-$, $Cl^-$, $Br^-$, $I^-$). Taube (1955); (1959); Taube Meyer (1954).

Generally inner-sphere mechanism occurs through the following steps.

Step 1 Formation of encounter or collision complex

$$L_5M^{III}X^{m+} + M^{II}(H_2O)_6^{n+} \longrightarrow [L_5M^{III}-X-M^{II}(H_2O)_5]^{(m+n+)} \quad \ldots\ldots (1.19)$$

Step 2: Formation of a bridged precursor complex

$$[L_5M^{III}-X-M^{II}(H_2O)_5]^{(m+n+)} \rightleftharpoons [L_5M^{III}-X-M^{II}(H_2O)_5]^{(m+n+)} + H_2O \quad \ldots\ldots (1.20)$$

Step 3: Activation of precursor complex

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{(m+\,+\,n+)} \longrightarrow [L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{*(m+\,+\,n+)} \quad \ldots\ldots (1.21)$$

Step 4: Formation of successor complex and electron transfer

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{*(m+\,+\,n+)} \longrightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{*(m+\,+\,n+)} \quad \ldots\ldots\ldots (1.122)$$

Step 5: Deactivation of successor complex

$$[L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{*(m+\,+\,n+)} \longrightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+\,+\,n+)} \quad \ldots\ldots\ldots (1.23)$$

Step 6: Decomposition of the successor complex

$$[L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+\,+\,n+)} \longrightarrow L_5M^{II}(H_2O)^{m+} + M^{III}(H_2O)_5X^{n+} \quad \ldots\ldots (1.24)$$

Any of the reaction scheme could be the rate-determining step, but in principle only 3 special cases have been noted, these are

(a) Formation of successor complex is the rate-determining step, this is found in substitution controlled redox reaction

(b) Electron transfer within the bridged complex is the rate determining step. This is the most commonly observed result in inner-sphere mechanism.

(c) The decomposition of the successor complex is the rate-determining step.

Typical energy profile for a redox reaction which occurs by the inner-sphere mechanism is illustrated in Fig 1.3

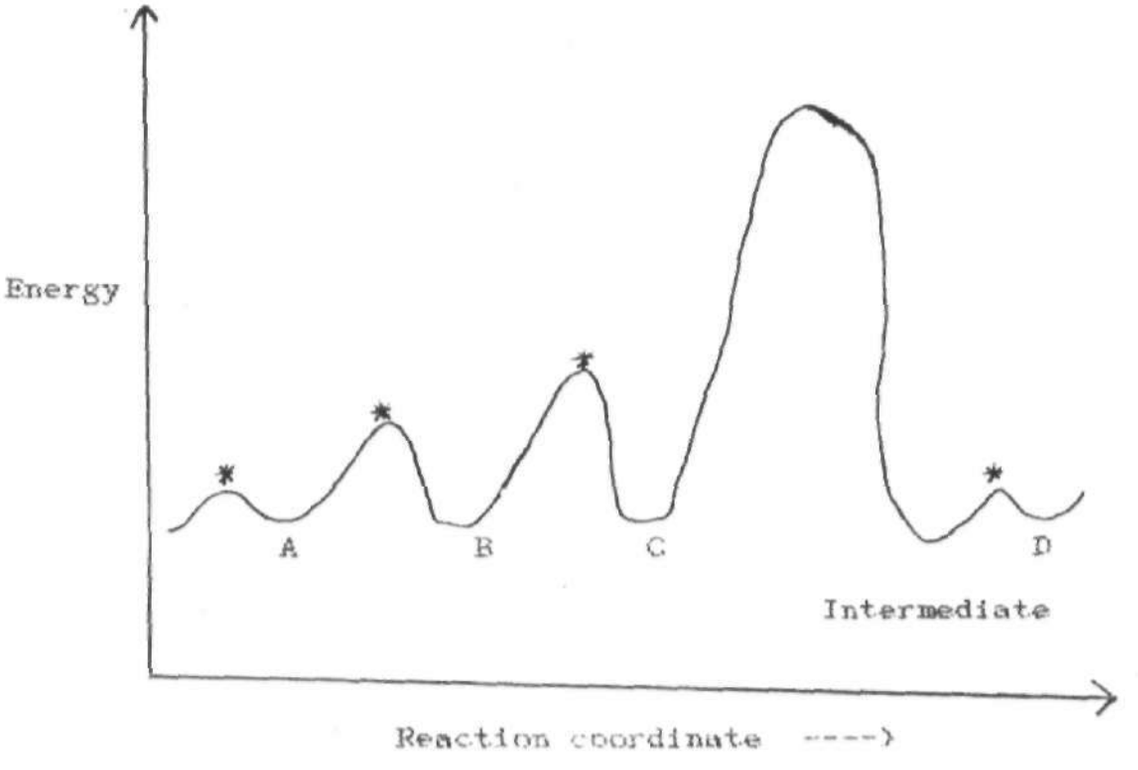



Fig 1.3: Energy profile diagram for a redox reaction which occurs by the inner-sphere mechanism

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

## 1.5 Diagnocis of Redox Reaction Mechanism

The main objectives of the redox kinetics investigations is to distinguish between the two established reaction mechanism, the outer- and inner-sphere in a particular reaction. This task is sometimes obvious but often difficult and sometimes impossible. The following criteria are used in assigning a mechanism for any reaction.

### 1.5.1 $k_{redox}$ ($k_{red}$) Versus $k_{substi}$ ($k_{substi}$)

In an outer-sphere mechanism the rate of redox process is greter than the substitution rate into the coordination shell of the metal. An example of an outer-sphere mechanism is the exchange reaction $Fe^*(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ (Deck and Wahl, 1954). This is shown in the following equation.

$$Fe^*(CN)_6^{4-} + Fe(CN)_6^{3-} \longrightarrow Fe^*(CN)_6^{3-} + Fe(CN)_6^{4-} \quad \ldots\ldots (1.25)$$

With $k_{red} = 10^3 M^{-1}s^{-1}$ while the related $k_{subst} = 2 \times 10^{-7} M^{-1}s^{-1}$ (Rosenheim et al, 1974). Therefore in this case the electron transfer occur much faster than substitution thus, outer-sphere mechanism is favoured. An exceptional situation arises when $k_{red} = k_{subst}$. In this case the reaction is said to be substitution

controlled. But when $k_{subs} >> k_{e-tr}$, substitution occurs prior to electron transfer process, the reaction is said to proceeed via an inner-sphere mechanism. A good example is the reduction of $Co(NH_3)_5Cl^{2+}$ by $Cr^{2+}$ reported by Taube et al (1954).

### 1.5.2 Identification of binuclear intermediate

Presence of an intermediate is an evidence in support of an inner-sphere mechanism. Example is the reaction $VO^{2+}$ with $Cr^{2+}$, an intermediate $VOCr^{2+}$ was characterised (Espenson, 1965). The identification of a binuclear bridged intermediate is not unequivocal evidence that the bridged intermediate is necessary for an inner-sphere mechanism.

### 1.5.3 Product analysis

Inner-sphere mechanism occur by transfer of electron between two metal centres through a bridging ligand common both metal. When the ligand is transferred from one metals centre to another after the act of electron-transfer. This provides an evidence in support of an inner-sphere mechanism, example $Cr^{2+}$ reaction with $Co^{3+}$ (Taube, 1953). The product $CrCl^{2+}$ was isolated, this show that the $Cl^-$ which served as bridging ligand has been transferred from $Co^{2+}$ to $Cr^{3+}$.

Atom transfer is not a strong evidence for the operation of an inner-sphere mechanism because not all inner-sphere mechanism are accompanied by atom transfer. For example, the reaction

$$Co(EDTA)^{2-} + Fe(CN)_6^{3-} \longrightarrow Co(EDTA)^{-} + Fe(CN)_6^{4-} \quad \ldots\ (1.26)$$

is an electron transfer which occurs by inner-sphere mechanism but is not accompanied by ligand transfer (Huchital and Hodges, 1975). The products of some reaction rapidly hydrolyse making detection difficult, example, $Fe^{2+}$ and $Fe^{3+}$.

### 1.5.4 Reactivity Pattern

The reactivity pattern have been used to assign mechanism and comparing this with those for a reagent of a known mechanism. For examples $Cr^{2+}$ in most cases react by an inner-sphere mechanism, while $Ru(NH_3)_6^{2+}$ reacts by the outer-sphere mechanism (from the fact that $k_{o.s} >> k_{i.s}$). Below are some of the reactivity patterns.

(i) Reactivity pattern with wide range of reactants

If a range of similar complexes e.g $Co(NH_3)_5X^{2+}$ (X = $Cl^-$, $F^-$, $Br^-$, or $NO_3^-$) are compared with particular reductant and the rates are found to be similar, the outer-sphere mechanism is said to be operating, since

this mechanism does not depend on the identity of the bridging ligands but when the rates depend on the nature of the bridging group, inner-sphere mechanism is predicted (Sykes, 1967; Shae and Haim, 1973).

(ii) Relative rates of reaction of hydroxo and aquo complexes

The hydroxyl group ($OH^-$) is a better bridging ligand than $H_2O$, so it is expected that the hydroxo complexes react faster via inner-sphere mechanism, thus where $k_{OH^-} << k_{H_2O}$, the outer-sphere mechanism is said to be operating.

### 1.5.5 The effect of added ions

The effect of added anions and cations gives clues to the type of mechanism in a given redox reaction (Pennington and Haim, 1967; Przystas and Sutin, 1973 and Adegite et al, 1977). Anion catalysed reaction are presumed to be operating via an outer-sphere mechanism.

### 1.5.6 Marcus theory

In the outer-sphere mechanism, the weak interaction between the reactants has permitted its theoretical treatments and correlation between knetics

and thermodynamic parameters (Sutin, 1966; Diebler and Sutin, 1964). Probably, the most widely used of these treatments is the Marcus theory. Marcus (1956).

When work terms are small, that is when very little reorganisation is involved prior to electron transfer, the theory predicts that for reaction (1.27).

$$Ox_1 + Red_2 \overset{k_{12}}{\rightleftharpoons} Ox_2 + Red_1 \quad \ldots\ldots (1.27)$$

and related isotopic exchange reactions (1.28) and (1.29).

$$*Ox_1 + Red_1 \overset{k_{11}}{\rightleftharpoons} Ox_1 + *Red_1 \quad \ldots\ldots (1.28)$$

$$*Ox_2 + Red_2 \overset{k_{22}}{\rightleftharpoons} Ox_2 + *Red_2 \quad \ldots\ldots (1.29)$$

The Marcus equation for the cross reaction is

$$\log k_{12} = \tfrac{1}{2}\log k_{11} + \tfrac{1}{2}\log k_{22} + \tfrac{1}{2}\log K_{12} + \log f \quad \ldots (1.30)$$

The value of f is evaluated from the equation (1.31).

$$\log f = \frac{(\log K_{12})^2}{4\log(k_{11}\, k_{22}/Z^2)} \quad \ldots\ldots (1.31)$$

Where $k_{12}$ and $K_{12}$ are the rate and equilibrium constants respectively for the cross reaction, $k_{11}$ and $k_{22}$ are the homonuclear electron exchange rates constants respectively and $Z = 10^{11} M^{-1} s^{-1}$ is the collision frequency for the homogenous reaction. Thus, from Marcus equation, the theoretical rate constants for the electron transfer reaction can be calculated from equation (1.32), by considering the solvent reorganisation occurring outside the inner-coordination shells of each of the reactants.

$$k = X_{exp} - \Delta G^*/RT \quad \ldots\ldots\ldots (1.32)$$

$\Delta G^*$ = the change in free energy of ion-ion and ion-solvent interactions accompanying the formation of activated complex.

$$\Delta G^* = Wr + \Delta G^*in + \Delta G^*out \quad \ldots\ldots (1.33)$$

Where Wr = work needed to bring the two reactants together

$\Delta G^*in$ = inner-sphere reorganisation term

$\Delta G^*out$ = outer-sphere reorganisation term

Using equation (1.30) and (1.31) relation (Marcus and Sutin, 1975) between the kinetics parameters for cross reaction and the components, self-exchange reaction can be derived.

$$\Delta G^*_{12} = 0.5\Delta G^*_{11} + 0.5\Delta G^*_{22} \equiv \Delta G^\circ_{12}(1 + \alpha) \quad \ldots\ (1.34)$$

$$\alpha = \frac{\Delta G^\circ_{12}}{4(\Delta G^*_{11} + \Delta G^*_{12})} \quad \ldots\ (1.35)$$

$\Delta G^*_{12}$ = The free energy of activation

$\Delta G^\circ_{12}$ = The overall free energy in the medium used

$\Delta G^*_{11}$ and $\Delta G^*_{22}$ are free energies of activation for self-exchange reaction. $\alpha$ is usually small when f = 1 thus equation (1.34) becomes

$$\Delta G^*_{12} = 0.5\Delta G^*_{11} + 0.5\Delta G^*_{22} + 0.5\Delta G^\circ_{12} \quad \ldots\ (1.36)$$

The differentiation of equation (1.36) (Marcus and Sutin, 1975) gave related equation for enthalpies and entropies of activation.

$$\Delta H_{12}^* = (0.5\Delta H_{11}^* + 0.5\Delta H_{22}^*)(1 - 4\alpha^2) + 0.5\Delta H_{12}^\circ(1 + 2\alpha) \quad \ldots\ (1.37)$$

and

$$\Delta S_{12}^{*} = (0.5\Delta S_{11}^{*} + 0.5\Delta S_{22}^{*})(1 - 4\alpha^{2})(1-4\alpha^{2}) + 0.5\Delta S_{12}^{o}(1 + 2\alpha) \quad \ldots\ldots (1.38)$$

In a reaction proceeding via outer-sphere mechanism, a linear relationship between the free energy of activation and standard free energy change of the reaction is predicted with a slope of a straight line being 0.50. From Marcus theory $k_{calculated} = k_{observed}$ indicates the outer-sphere mechanism. On the other hand if $k_{obs} >> k_{calc}$, then it can be presumed that inner-sphere mechanism is operating.

It must be noted that, none of the above criteria gives conclusive prove of the mechanism. However, when two or more criteria point to the same conclusion, the mechanism can be assigned with some degree of certainty.

## 1.6 Solvated electron theory

One further possibility of mechanism of electron transfer in solution is that of solvated electron. In this mechanism the reductant eject an electron into solvent which then solvates it and hold it until the oxidant picks it up. The redox process involved is thought to occur as illustrated below.

$$A + S \rightleftharpoons A^{+} + S^{-} \quad \ldots\ (1.39)$$

$$S^{-} + B \rightleftharpoons [S^{-} + B]^{*} \longrightarrow S + B \quad \ldots\ (1.40)$$

Where A = reductant

B = oxidant

S = solvent

Although this process occurs readily in non-aqueous media such as liquid ammonia, it is highly unlikely that a solvated electron with an estimated potential at -2.7V (Latimer, 1952) will exist in water without rapidly reducing water according to this equation.

$$e_{(aq)} + H_2O \longrightarrow \tfrac{1}{2}H_{2(g)} + OH^{-} \quad \ldots\ (1.41)$$

Thus, the possibility that this mechanism operates in aqueous media is remote.

## 1.7 Objectives of the project

The study of redox reaction of biologically important thiols played a vital role in understanding of their role as electron-transfer enzyme (Martin and Spence, 1970). The metal-thiol complex is linked with its effectiveness of the thiol in removing unneeded metal ion (Sugiura, 1972).

The use of thiols in agriculture (Paricha and Levitte, 1967), in tanning, cosmetics and pharmaceutical industries promoted a detail investigation on kinetics of the redox reactions of the thiols.

The interest on the oxo-bridged complex has been largely on its extinction coefficient in the visible region and its relative stability towards photodissociation. The oxo-bridged dimers of ruthenium have complete delocalisation of their excess electrons over the metal centres (Robin and Day, 1967). They are also used as electron conductors in inorganic polymers (Meyer et al., 1981). Recently considerable interests have been focused on the kinetic investigation of the oxo-bridged ruthenium (III) dimer (Iyun et al, 1990, 1992 and 1993). Very little work has been done on the redox reaction of the oxo-bridged ruthenium (III) with thiols.

In this project the oxidation of thiols and resorcinol by the oxo-bridged ruthenium (III) dimer $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ has been investigated, as part of an effort to throw more light on the kinetics and mechanism of the oxo-bridged ruthenium (III) dimer redox reaction with thiols (L-cysteine mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) and a diol (1,3-dihydroxybenzene).

A mechanism consistent with the results obtained is proposed for all the systems studied.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Reaction of Ruthenium (III) Complexes

Many redox reactions of Ruthenium (III) ions have been reported. Reaction of $(NH_3)_5RuCl^{2+}$, $(NH_3)_5RuBr^{2+}$ and $(NH_3)_5Ru.OH_2^{2+}$ with Cr(II), V(III) and Eu(II), studied by (Stritar and Henry Taube, 1969). The reaction of the ruthenium (III) complexes with Cr(II) were found to predominantly occurs by inner-sphere mechanism, but the reaction of V(II) with ruthenium (III) complexes (Stritar and Henry Taube, 1969) are so rapid that they cannot involve substitution by a bridging group into a normal coordination position of the reducing agent. $Ru(NH_3)_5O_2.C.CH_3^{2+}$ reported by (Adegite et al, 1979) and $Ru(NH_3)_5NCS^{2+}$ studied (Lee and Early, 1981) all were found to be of inner-sphere mechanism.

An outer-sphere mechanism was reported for the redox kinetics of $Ru(NH_3^{3+}$, $Ru(NH_3)_5Cl^{3+}$, $Ru(NH_3)_5H_2O^{3+}$, $Ru(NH_3)_5Py^{3+}$ and $Ru(NH_3)_5PyZ^{3+}$ reported by (Davies and Early, 1978). Macartney and Sutin (1983) reported the reaction of $Ru(bipy)_2^{3+}$ with ascorbic acid, these were all found to proceed by the outer-sphere mechanism.

## 2.2 Mixed-Valenced Complexes of Ru(III)

Several mixed-valenced complexes of Ru(III) have been prepared (Krentzen and Taube, 1976; Tom and Taube, 1975) and their properties compared with those of the monomeric analogues. Emphasis placed on their studies are mainly on the nature and extent of metal-metal interaction across the bridging ligands and consequences of such interaction on the physico-chemical properties of such system (Meyer and Miller, 1971; Weaver et al, 1975). It was found that the extent of delocalisation between the two ruthenium sites depend mainly on the oxidation states of ruthenium ions and the effect of bridging and non-bridging group (Tom and Taube, 1975).

Recent studies by (Haim et al, 1988) have shown that metal-metal overlap occurs by the metal-ligand mixing due to the large Ru-Ru distance (6.9A°) for the pyrazine-bridged ruthenium dimer (Haim et al, 1988).

In contrast the study of ruthenium bridged by some heterocycle ligands indicates no metal-metal interaction across the heterocyclic (Sullivan and Meyer, 1979), but transition was observed due to metal-metal charge transfer (Sullivan and Mayer, 1980).

## 2.3 Oxo-bridged complexes of Ruthenium (III)

Oxo-bridged transition metal complexes are strongly oxidising and are often used in synthetic chemistry (Meyer et al, 1981) and some served as a catalyst. For example $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ is used as a catalyst for oxidation of water (Meyer et al, 1981).

The transition metal oxo-bridged complexes play a vital role as redox agents in both chemical and biological systems. They are also used as electron conductors in inorganic polymers. Therefore there is need to establish the factors that govern the nature of their reactivities which help in development of redox catalysis and enhanced their industrial application. High valent oxo-bridged complexes of ruthenium, for example those containing polypyridyl ligand have been used as oxidative catalyst (Chin-Ming et al, 1986) and those derived from trans-$[Ru(bipy)_2(OH_2)]^{2+}$ play an important role in photolytic splitting of water (Taqui et al, 1986).

The properties of the ligand bridged complexes can differ significantly depending on the mode and/or extent of metal-metal interaction (Weaver et al, 1975). There are four main cases in which,

(i) There is strong direct metal-metal bonding

(ii) Strong metal-metal interaction exist but through

a bridging ligand.

(iii) Weak metal-metal interaction exist either through space or through bridging ligand.

(iv) Those in which there is no evidence for metal-electron interaction.

Robin and Day (1967) have shown that the first row transition metal complexes exhibits weak metal-metal interaction and become stronger in case of second and third row transition metals.

Weaver et al (1975) have synthesized and characterised oxo-bridged complexes of type $[(LL)_2XRuORuX(LL)_2]^{n+}$ (LL = bipy. or phen., X = Cl, $NO_2$ or $H_2O$) these fall into Robin and Day class (III) (Robin and Day, 1967). These have been reported to have unsual physico-chemical properties when compared to monomeric analogues (Weaver et al, 1975). These properties have been suggested to arise from chemically significant interaction between the two Ru(III) ions across the oxo-bridged. The RuORu interactions is so strong that the identity of the separate Ru(III) is lost in determining the physical and chemical properties of their own.

The studies of oxo-bridged complexes carried out by Baunann and Meyer (1980) have concluded that the oxo-bridged of Ru(III) dimer can support strong electronic interaction between the metal sites which

lead to extensive reversible redox chemistry. The strong electron-electron coupling can lead to new chemical systems where the physical and chemical properties at the metal sites are significantly modified compared to related monomeric analogues.

The same spectra and chemical properties of RuORu were found in Os-O-Os, but Fe-O-Fe shows different properties (Cotton and Wilkinson, 1980). Metal-metal interaction of Fe(III) is insignificant to effect similar changes in electronic and chemical properties (Khedekar et al, 1977). This is probably due to lesser d-orbital extension of Fe(III) compared to Ru(III) and Os(III).

Most kinetics studies on Ru(III) are those of ammines (Adegite and 1979; Lee and Early, 1981) and the bipyridine complexes (Macartney and Sutin, 1983). Haim and Coworkers (1988) reported the kinetics studies on pyrazine bridged ruthenium dimer (Akhtar and Haim, 1988). The investigation established that the pyrazine bridged ruthenium dimer react by the outer-sphere mechanism based on correlation with Marcus theory.

Iyun and Adegite (1989) reported the reduction of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ by $Eu^{2+}$, $V^{3+}$, $Ru(NH_3)_6^{2+}$

and $TiOH^{2+}$, the rate data obtained were interpreted in terms of an outer-sphere mechanism. The kinetic investigations on the reaction of $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ with sulphite (Iyun, Ayoko and Lohdip, 1992), Iodine (Iyun, Ayoko and Habiba, 1992), Bromate (Iyun, Ayoko and Lohdip, 1992) were all found to proceed by outer-sphere mechanism.

The most recent investigation on the redox reaction of the oxobridged dimer was reported by Iyun, Ayoko and Lawal (1992) with 1,4-dihydroxybenzene. The result obtained was unequivocally interpreted interms of an outer-sphere mechanism.

The kinetics investigation of the oxo-bridged ruthenium dimer was carried out with some thiols (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) and Resorcinol (1,3-dihydroxybenzene), so as to widen the kinetics studies of the oxobridged ruthenium dimer.

## 2.4 Thiols

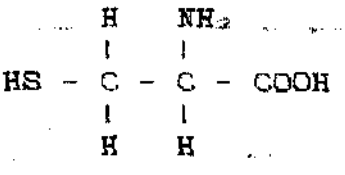
The thiols are basically organic compounds that contains the -SH group. However, the thio-compounds not necessarily having the -SH group are also sometimes loosely referred to as thiols.

Previous oxidation of many thiols by metals or their complexes have been shown to proceed through the formation of an intermediate prior to electron transfer (inner-sphere mechanism).

In aquo-cobaltic oxidation of α-mercaptocarboxylic acid (Hill et al, 1967; Hill and McAuley, 1968) electron transfer was proceeded by the formation of transient species. Similar results were reported in thallium (III) oxidation of thiomalic acid (Amjad et al, 1977), Cr(IV) oxidation of L-cysteine (McCann and McAuley, 1975) and Fe(III) oxidation of mercapto carboxylic acid (Lappin and McAuley, 1975). However, in cerium (IV) oxidation of α-thiols (Hill and McAuley, 1968) and thioureas (Gomwalk et al, 1968) aquo-cobaltic oxidation of thioureas (Shanker et al, 1973) and the reaction of 1,2-tungstocobaltate (III) ion with thioureas (Olatunji, 1975), L-cysteine, mercapto acetic acid and β-mercaptoethylamine (Olatunji and Ayoko, 1983). There was no evidence for intermediate complex formation prior to electron-transfer (outer-sphere mechanism).

### 2.4.1 L-cysteine

L-cysteine is also known as 2-amino-3-mercapto propanoic acid, is an optically active sulphur containing amino acid.



(I)

It is found in fresh milk, Mackerel, beef, pork and wheat flour (Pieniezek, Danuta and Graberek, 1975). L-cysteine crystallised in orthorhombic form (Kerve, Ann and Ashmore, 1975), with four molecules in the unit cell. This was proved by 3-dimentional neutron diffraction studies. It is slightly soluble in water.

It is used in reduction of paracetamol poisoning in male mice (Strubelt and Siegar, 1974). Also addition of 0.1M HCl and 1.0mM cysteine was found to be effective for mineral preservation for about 15 days. Zinc chloride ($ZnCl_2$) remains upto 100% in water containing cysteine. It is therefore used in agricultural studies to maintain mineral concentration in water (Dokiya et al, 1974). Cysteine served as reactivator of fibrin stabilizing factor from an otherwise inactive form in blood clotting (Lorand and Jacobson, 1958). It is also used as a mother substance of taurine a compound which is widely distributed often in remarkably large amount as a

conjugant of bile salt in vertebrete (Earnest Baldwin, 1948).

Redox reaction between cysteine and transition metal or their complexes results in formation of a disulphide products. Cysteine oxidation by molybdenum (Martin and Spence, 1970), chromium reaction with L-cysteine (John and McAuley, 1975), chromic acid oxidation of cysteine (Goswami and Srivastava, 1981), L-cysteine oxidation by 12-tungstocobaltate (III) ion (Olatunji and Ayoko, 1983) and cysteine oxidation by copper-2,9-Dimethyl-1,10-phenanthroline complexes (Gary and Robert, 1984) were all found to produce disulphide product. In most cases the attack was on the sulphur atom as sulphur is more nucleophilic than nitrogen.

L-cysteine oxidation occurs by either inner- or outer-sphere mechanism. Olatunji and Ayoko (1983) investigation on the L-cysteine oxidation by 12-tungstocobaltate (III) ion, indicated no evidence for the formation of an intermediate of significant stability, that occur prior to electron transfer step. But chromium (VI) reduction by L-cysteine reported by (John and McAuley, 1975) presence of an intermediate was observed, thus, the result was interpreted in terms of an inner-sphere mechanism.

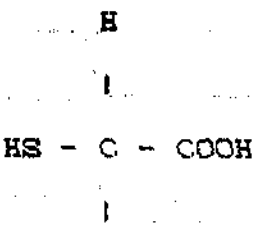
The observed rate constant in L-cysteine redox reaction normally have hydrogen ion dependence. The rates usually decrease with increasing $[H^+]$, this strongly suggests a pre equilibrium step involving the release of a proton, (Ayoko and Olatunji, 1983; Gary and Robert, 1984) reported that the proton is obtained by deprotonation of sulphydryl group (-SH). The emperical rate law was given as

$$-\frac{d[\text{oxidant}]}{dt} = k[\text{oxidant}][\text{L-cyseine}][H^+]^{-1} \quad \ldots\ (2.1)$$

A positive acid dependence was also reported for some redox reactions of cysteine with some transition metals or their complexes (John and McAuley, 1975; Goswami et al, 1981).

In spite of the facts that the reaction of L-cysteine with many transition metals or their complexes have been reported, no reaction of the substrate with the oxo-bridged ruthenium dimer have been reported. Therefore an account of the kinetics investigation on the redox reaction of L-cysteine with the oxobridged dimer is reported in this project.

### 2.4.2 Mercaptoacetic acid



(II)

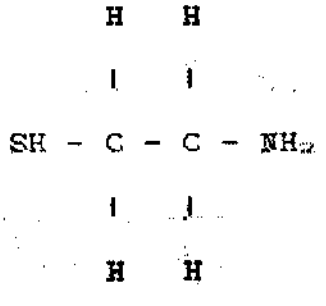
Mercaptoacetic acid (Thioglycolic acid) has wide range of application, it is used in prevention of corrosion of copper (Patel et al, 1975), in cosmetics industry (Tankomato and Yoshihiro, 1979), long-lasting hair conditioning lotion is formulated using mercaptoacetic acid. In pharmaceuticals (Shiffer, 1979) about 75% treatment of acne is achieved by topical application of mercaptoacetic acid.

Earlier reports on the oxidation of many thiols by metals ions have been shown to proceed by an inner-sphere mechanism, oxidation of mercaptocarboxylic acid by aquo cobaltic ion (Hill and McAuley, 1967), α-mercaptocarboxylic acid oxidation by Fe(III) (Lappin and McAuley, 1975), 2-mercaptosuccinic acid oxidation by copper (Lappin and McAuley, 1977) and β-mercaptoethylamine oxidation by 12-tungsto cobaltate (III) ion (Olatunji and Ayoko, 1983) were however found to proceed by outer-sphere mechanism.

Mercaptoacetic acid redox reaction with some metals complexes such as Mo(V) and Mo(VI) (Martin and Spence, 1970) vanadium (V) (Ramakrishna et al, 1977) all were reported to proceed with no formation of an intermediate complexes prior to electron transfer (outer-sphere mechanism).

The observed rate constants in the mercaptoacetic acid redox reactions were found to have both positive acid dependence (Martin and Spence, 1970) and an inverse acid dependence (Olatunji and Ayoko, 1983). The decrease in rate with increasing $[H^+]$ in case of later, strongly suggests a pre-equlibrium step involving the release of a proton (Ellis et al, 1975; Snow et al, 1975 and Olatunji and Ayoko, 1983).

### 2.4.3 β-Mercaptoethylamine



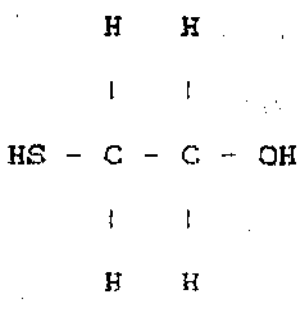
(III)

This compound has been used to impart some protection to animals against the effect of ionising radiation (Kirk-Orthmer, 1969 and it has been a model structure for a considerable volume of U.S Government sponsored research seeking more effective and less toxic antiradiation drug. ß-mercaptoethylamine and other thiols componds such as 3-mercaptovaline (penicillamine) and glutathione in their reactions with metal ions play an important role in understanding of the nature of electron transport enzyme which often incorporate sulphydryl group.

Despite its importance, less redox reaction investigations have been carried out with ß-mercaptoethylamine. Olatunji and Ayoko (1983) reported the reaction of ß-mercaptoethylamine with 12-tungstocobaltate (III) ion, the reaction was found to proceed via free radical intermediate formation, with that formation of a disulphide product. This reaction like most thiols exhibits an inverse acid dependence. Cr(IV) oxidation of L-cysteine (McCann and McAuley, 1975), glutathione and penicillamine (McAuley and Olatunji, 1977), thioureas (McAuley and Olatunji, 1982). All these reactions occur via the formation of intermediate of significant stability and the reaction mechanism were interpreted in terms of inner-sphere mechanism. However, ceric oxidation of

α-thiols (Hill and McAuley, 1968) and thioureas (Gomwalk and McAuley, 1975) and glutathione reaction with diaquotetrakis-(2,2-bipyridine)-μ-oxodiruthenium (III) ion reported by Ayoko, Iyun and Allen (1993), there was no evidence of formation of an intermediate complex prior to the electron-transfer. In all these the outer-sphere mechanism was proposed for the reaction.

### 2.4.4 2-Mercaptoethanol



(IV)

2-mercaptoethanol has been used for the enhancement of draught tolerance by plants (Paricha and Levitt, 1967), it is used as an activator of protinase an enzyme used for hide unhairing (Xia, 1982). 2-Mercaptoethanol acts as free radical scavenger which reduces self decomposition of radio chemical (Baker, 1983).

Like most thiols 2-mercaptoethanol oxidation by metals complexes lead to the formation of

disulphides product, the redox reaction between ferricyanide and 2-mercapto ethanol (Meehan, Kolhoff and Kakiu, 1962) has complicated kinetics. It shows second-order at initial stage of the reaction and become zero-order at later stage of the reaction indicating 1:1 stoichiometry with formation of disulphides product. Amino acid containing the -SH group (RSH) and 2-mercaptoethanol were reported to reduce Se(IV) compound in 0.1M HCl with an RSH to Se in ratio of 4:1 to give disulphide products of the type RSSeR (Sakurai, Tanako and Nakayama, 1985). 2-mercaptoethanol reduces selenium (IV) to elemental state in weakly, acidic, neutral and alkaline media, 2-mercaptoethanol is oxidised to bis (2-hydroxyethyl) disulphide (Resat, Huseyin and Izzet, 1989). The redox reaction between the ligand and selenite can be represented by the following equation

$$H_2SeO_3 + 4HO.CH_2.CH_2SH \longrightarrow Se + 2HO.(CH_2)_2\text{-}SS\text{-}(CH_2)_2OH + H_2O \quad \ldots\ldots (2.3)$$

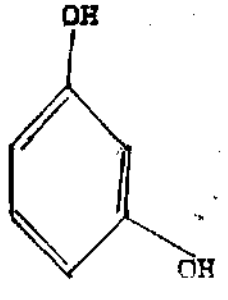
Most of redox reaction of 2-mercaptoethanol with metals go via free radical, Ti(III)-$H_2O_2$ couple and Ce(IV) oxidation of thiols (Gilbert, Lane and Norman, 1975), 2-mercapto-ethanol oxidation by riboflavin

(Holden and Main, 1977), methylene blue (Earl and Tang, 1978).

2-mercaptoethanol redox reactions have shown hydrogen ion dependence. Meehan et al, (1962) reported that the oxidation of 2-mercaptoethanol by ferricyanide, the rate decrease with increasing acidity with no effect on increasing ionic strength. In Se(IV) reduction by 2-mercaptoethanol (Huseyin et al, 1989) the rate is proportional to the square of ligand concentration and inverse square root of hydrogen ion concentration, the over all empirical rate law is given by equation (2.4).

$$-\frac{d[\text{oxidant}]}{dt} = k[\text{2-mercaptoethanol}]^{2}[H^{+}]^{-\frac{1}{2}} \quad \ldots (2.4)$$

### 2.4.5 Resorcinol (1,3-dihydroxyl benzene)




Resorcinol (1,3-dihydroxyl benzene) is one of the three isomeric dihydroxy benzene in which the two

hydroxyl groups are located meta to each other on the ring, that is, 1,3 positions. It is found in Shale oil (Lille et al, 1973) in sugar cane molasses (Takeshi Tohru and Yakiko, 1967). Resorcinol is used in medicine (Shichiro, 1956) as antibacterial agent, in pharmaceutical is used in formulation of compound used for skin disease treatment (Taylory, 1977). The adhesive based on resorcinol are exceptionally water-resistant (Micheal and Dolanko, 1978) and find extensive use in marine plywood and similar applications. The viscosity of brines used for maintanence of petroleum well can be increased by addition of resorcinol (House and Hoover, 1982).

Dihydroxyl benzene compounds and their substituted derivatives along with ascorbic acid are well characterised two electron reductants ($H_2Q$-Q + $2H^+$+2e) that have importance in biologically electron transport systems (Rich, 1982). These compounds have been used in a number of electron-transfer studies involving transition metal oxidant such as $Co(H_2O)_6^{3+}$ (Pelizzetti and Mentasti, 1976) and $[IrCl_6]^{2-}$ (Pelizzetti et al, 1977).

Most redox kinetics of benzenediols proceed via the one-electron oxidation to semiquinone radical ($HQ^{\bullet}$). Catechol and quinol oxidation by Iron (III),

vanadium(III) and Thallium(III) studied by (Pelizzetti, Mentasti, Pramauro Saini, 1974) and benzenediol oxidations by aquapentachloro-diquotetrachloro- and hexabromo-Iridate(IV) studied by (Pelizzetti et al, 1978), cerium(IV) oxidation of resorcinol reported by (Yadav and Verma (1981), ascorbic acid oxidation by tris (2,2-bipyridine) complexes of Osmium(III) Ruthenium(III) and Nikel(III) studied by (Macartney and Sutin, 1983) and same complex redox reaction with $[Ru(CN)_6]^{3-}$ (Macartney and Sutin, 1990) and the most recent kinetics investigation of dihydroxyl benzene (1,4-dihydroxy benzene) with an oxobridged ruthenium dimer (Diaquotetrakis(2,2-bipyridine)-μ-oxodiruthenium (III) ion (Iyun, Ayoko and Lawal, 1992), all these redox reactions were all found to proceed via one electron oxidation to a semiquinone radical which is the rate determining step followed by a second one-eletron oxidation to quinone, by either outer- or inner-sphere mechanism depending on the nature of the oxidant.

Various acid dependence on hydrogen ion concentration is observed for oxidation of dihydroxy benzene compounds with some metals complexes. The kinetics oxidation of 1,2- and 1,4-dihydroxy

benzene by hexacyanoruthanate (III) ion (Macartney and Mark, 1990) shows an inverse first-order $[H^+]^{-1}$ and 1,4-dihydroxy benzene oxidation by diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium (III), ion (Iyun et al, 1992) is acid independent.

In order to enhanced the applicability of resorcinol in industries, there is a need for understanding the kinetics and mechanism of its reactions, thus its reaction with an oxobridged ruthenium (III) ion reported in this thesis.

# CHAPTER THREE

## 3.0 Experimental

### 3.1 Materials and Reagents

All reagents and solvents were used without further purifications. Distilled water was used in preparing the solutions.

#### 3.1.1 Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium (III) perchlorate $[(bipy)_2H_2ORuORuH_2O(bipy)_2]ClO_4$

The oxo-bridged complex $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ ($RuORu^{4+}$) was prepared, purified and characterised as prepared by Weaver et al (1975), as follows.

Cis-Dichlorobis (2,2'-bipyridine) ruthenium (III) (2.0g, 4.13 mmoles) was suspended in 180$cm^3$ of distilled water containing silver nitrate (1.76g, 10.36 mmole). The mixture was heated to reflux for 8 hours then cooled to room temperature and centrifuged. The supernatant liquid was filtered by suction into fine frit to remove silver chloride and silver metal. The filtrate was heated on steam bath and treated with a saturated solution of sodium perchlorate until precipitation began to occur. Slow cooling to 0°C produced desired material which was collected by

suction filtration, washed with small portion of cooled water and air dried. The salt was recrystallised from the hot water containing small amount of $NaClO_4$. The resultant dark microcrystalline solid gave deep green solution in water and acetonitrile.

The yield was about 55% of the theoretical (Theoretical = 2.69g). The concentration of the complex was determined spectrophotometrically using published values (Weaver et al, 1975). The purity was ascertained by comparing the electronic spectral properties of prepared complex with literature values (Weaver et al, 1975) and were found to be similar.

### 3.1.2 L-cysteine solution

0.1M stock solution of L-cysteine 98% (Koch-light) was prepared by dissolving 1.2116g of substrate in 100$cm^3$ distilled water. The desired concentration of L-cysteine solutions for the reaction were made from this solution.

### 3.1.3 Mercaptoacetic acid solution

A 1.0M stock solution of mercaptoacetic acid 96% (B.D.H) was prepared using doubly-distilled water by dissolving 1.82$cm^3$ concentrated solution in 25$cm^3$ of distlled water. The desired concentrations of the substrate for the reaction were made from this solution.

### 3.1.4 β-mercaptoethylamine solution

1.0M stock solution of β-mercaptoethylamine (Koch-light) was prepared by dissolving appropriate volume of the substrate in a distilled water. The required concentrations were made from this solution.

### 3.1.5 2-Mercaptoethanol solution

2.0M stock solution of 99% 2-mercaptoethanol (B.D.H) was prepared by dissolving 14.1cm$^3$ of the substrate in 100cm$^3$ distilled water. The desired concentrations for the reaction were made from this solution.

### 3.1.6 Resorcinol solution

2.0M stock solution of resorcinol (B.D.H) Analar was prepared by dissolving 22.022g of the substrate in 100cm$^3$ distilled water. The required concentrations for the reactions were all prepared from this stock solution.

### 3.1.7 Salts solutions

The solutions of LiCl, NaCl, KCl, RbCl, $MgCl_2$, $MnCl_2$, $NaNO_3$, $Na_2SO_4$ and $CH_3COONa$ were all prepared by dissolving known weights of the respective salts in a known volume of distilled water. All salts were of (B.D.H) L.R.

### 3.1.8 Preparation of standard solution of sodium perchlorate $NaClO_4$

A known weight of $NaClO_4$ (B.D.H, G.P.R) was dissolved in distilled water and standardised by gravimetric method as follows. 2.0$cm^3$ portion of $NaClO_4$ stock solution were taken in preweighed bottle dried at about 100-110°C and cooled in a descicator until constant weights were obtained. The weight obtained after drying 2.0$cm^3$ portion of the salts were used to calculate the actual concentration of the solution.

### 3.1.9 Preparation of standard perchloric acid solution

A stock solution of perchloric acid 2M was made by dilution of a concentrated solution of $HClO_4$ (B.D.H; Analar). The perchloric acid was standardised volumetrically using (Borax) sodium tetraborate decahydrate as a primary standard using methyl red as indicator.

The molarity of $HClO_4$ solution was determined using the equation of the reaction below (Vogel, 1978).

$$B_4O_7^{2-} + 2H^+ + 5H_2O \Longleftrightarrows 4H_3BO_3 \quad \ldots \quad (3.1)$$

## 3.2 Stoichiometric studies

The stoichiometries of the reactions were determined by spectrophotometric titration using the mole ratio method. In all cases the concentration of the oxidant [$RuORu^{4+}$] was kept constant while that of the reductant were varied.

[$RuORu^{4+}$] = (4.2 - 8.0) x $10^{-6}$M, [Reductant] = ($1.6 \times 10^{-5}$ - $2.25 \times 10^{-5}$)M for all the systems at constant ionic strength of 1.0M ($NaClO_4$) for the thiols systems (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) and 2.0M ($NaClO_4$) for the resorcinol system. [$H^+$] = $1.33 \times 10^{-3}$M for L-cysteine system and [$H^+$] = $1.0 \times 10^{-3}$M for the mercaptoacetic acid, β-mercaptoethylamine, 2-mercaptoethanol and resorcinol systems. The reaction was allowed to continue completion at 25.0 ± 0.1°C in all the systems used, the absorbance was measured at λ = 650nm.

## 3.3 Kinetics Measurements

The rate of the reactions were monitored on a corning 253 colorimeter. The rate of reaction of each oxidant with the reductants (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine, 2-mercaptoethanol and resorcinol) was studied by monitoring the decrease in absorbance of the oxidant

at wvelength of $\lambda$ = 650nm. All kinetics measurement were carried out under pseudo-first order condition with respective reductant at least 100 fold in excess over the oxidant concentration at 25.5 ± 0.1°C and 1.0M ($NaClO_4$) ionic strength for the thiols systems and 2.0M ($NaClO_4$) ionic strength for resorcinol system.

## 3.4 Test for intermediate complex

### 3.4.1 Spectrophotometric test

These measurements were done in order to find out whether spectroscopically determinable intermediate complex was formed between oxidant and reductant during the reaction in each case. The electronic spectra of the reaction mixture were run after two minutes in each case over a range of wavelengths. A similar run was made for the oxidant alone in each case.

## 3.5 Test for free radical

5$cm^3$ of acrylamide was added to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion. This was followed by addition of a large excess of

methanol, the acrylamide was also added to solution of the oxidant and reductant separately. This served as control.

### 3.6 Product analysis

The product analysis was carried out in respect of $RuORu^{4+}$-thiols systems. All the reactions studied, the formation of a disulphide product was ascertained by comparing the spectra of the reaction mixture, that had gone to completion, with the spectrum obtained when the reductants (thiols) were treated with hydrogen peroxide which is known to oxidised thiols to disulphide (Zahid et al, 1977).

$$RSH + H_2O_2 \longrightarrow RSSR + 2H_2O \quad \ldots\ldots \quad (3.2)$$

# CHAPTER FOUR

## 4.0 RESULTS

### 4.1 Stoichiometry

The stoichiometry determined for the five systems showed that a mixed-valenced complex $RuORu^{5+}$ is the probable product of the reaction. The titration curves from which the stoichiometries were determined are presented by a typical plot in figure (4.1). The results were consistent with one mole of the diaquo oxobridged dimer being consumed by one mole of L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol. In case of resorcinol, the stoichiometry is, two moles of the oxobridged ($RuORu^{4+}$) are consumed for each one mole of the resorcinol used.

On the basis of the stoichiometries determined, the overall equation for these reactions can be represented by the following equations.

$$2RuORu^{4+} + 2RSH \longrightarrow 2RuORu^{5+} + RSSR + 2H^{+} \quad \ldots \quad (4.1)$$

$$2RuORu^{4+} + H_2Q \longrightarrow 2RuORu^{5+} + Q + 2H^{+} \quad \ldots \quad (4.2)$$

Where $RuORu^{4+}$ = Diaquo oxobridged Ruthenium (III)

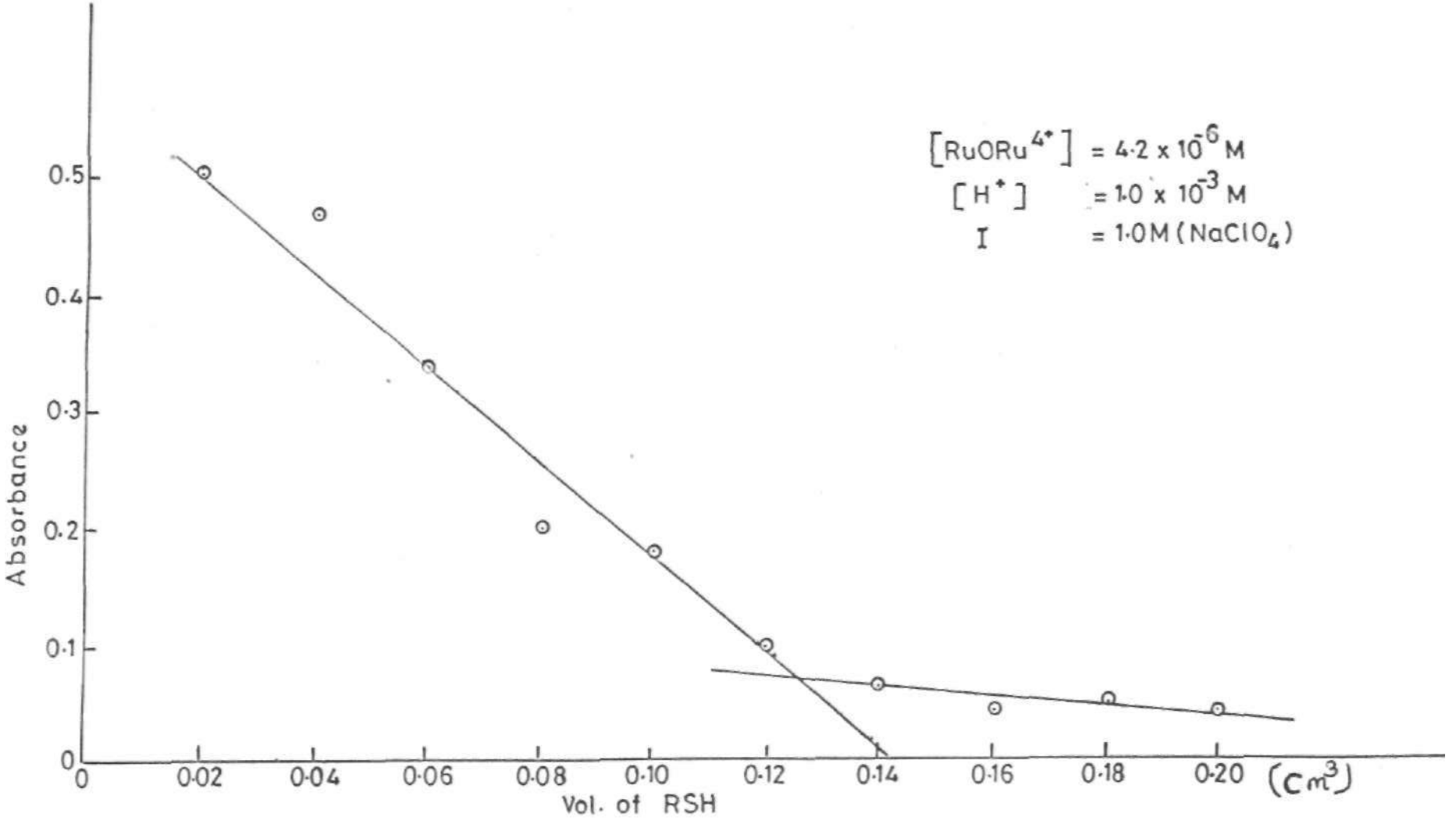



FIG. 4.1: STOICHIOMETRY OF REDOX REACTION BETWEEN $RuORu^{4+}$ AND L-CYSTEINE
CONC. OF RSH = $4.0 \times 10^{-3}$ M .

$RuORu^{5+}$ = Mixed-valenced diaquo oxobridged ruthenium

RSH = L-cysteine, mercaptoethylamine and 2-mercaptoethanol.

$H_2Q$ = Resorcinol

## 4.2 Determination of order with respect to [$RuORu^{4+}$] and [Reductant]

The linearity of the pseudo-first-order plots of log ($A_t$ - $A_\infty$) versus time for these reactions varied from more than 70 to 90% of the reaction. The linearity of these plots indicate that these reaction are first-order with respect to [$RuORu^{4+}$] in each case. ($A_t$ and $A_\infty$ are the absorbances of the complex at time t and the end of the reaction respectively). A typical plot is shown in figure (4.2). From the slopes of such plots the pseudo-first order rates constants ($k_{obsd}$) were obtained.

Plots of log $k_{obsd}$ versus log [R] (R = reductant) gave a slope of 0.92 ± 0.05 (L-cysteine), 0.95 ± 0.02 (mercaptoacetic acid), 0.80 ± 0.06 (β-mercaptoethylamine), 0.96 ± 0.05 (2-mercaptoethanol) and 1.01 ± 0.04 (Resorcinol), showing that the reaction is of first-order in all the substrates. The reactions are therefore second-ordr overall in the

$[RuORu^{4+}] = 4.0 \times 10^{-6}$ M
$[RSH] = 4.0 \times 10^{-4}$ M
$[H^+] = 1.33 \times 10^{-3}$ M
$I = 1.0$M ($NaClO_4$)

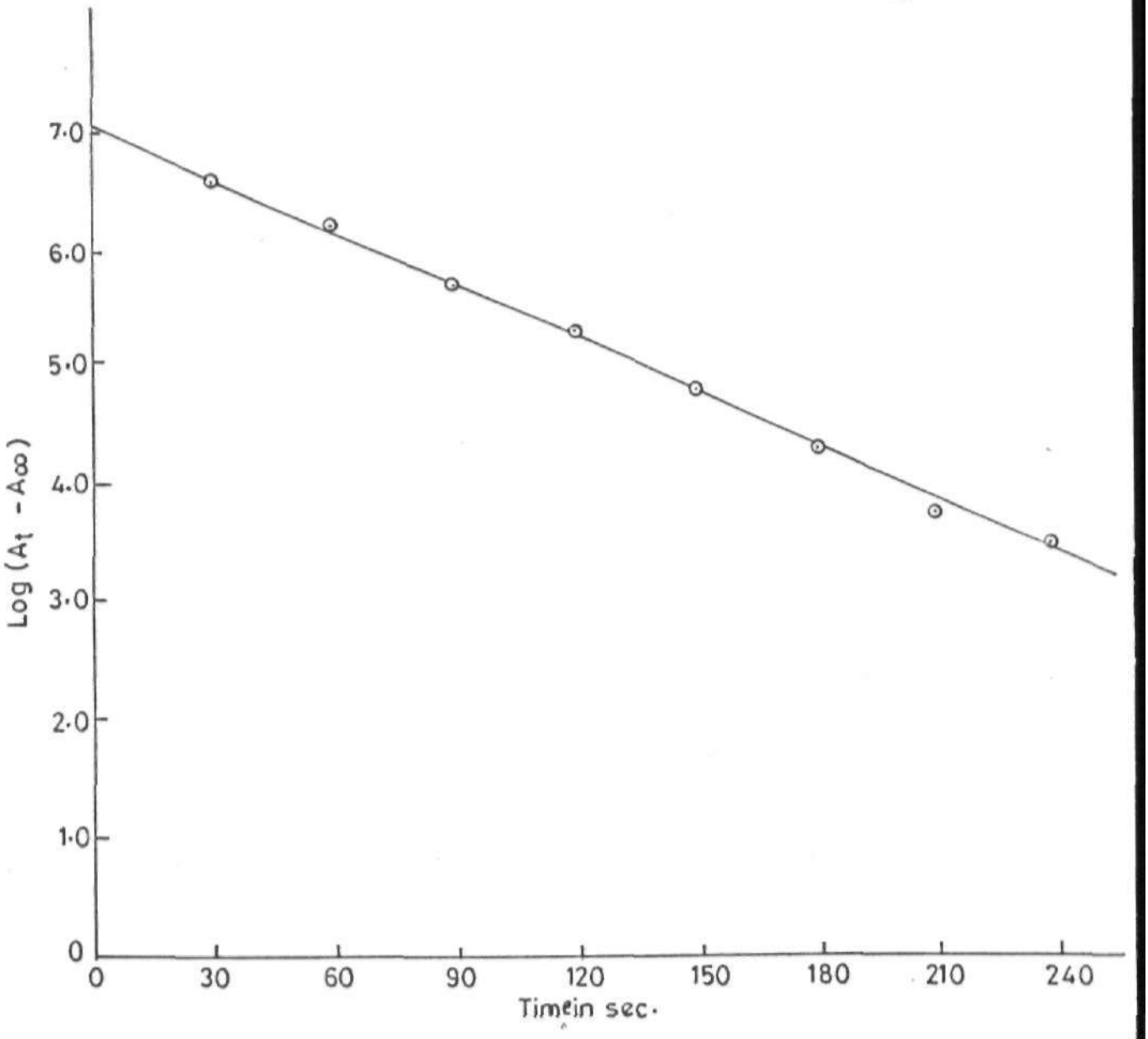



FIG. 4.2: PSEUDO-FIRST-ORDER PLOT FOR THE REDOX REACTION BETWEEN $RuORu^{4+}$ AND L-CYSTEINE.

five systems. The second-order rate constants $k_2$ were determined from the $k_{obsd}$ as $k_{obsd}/[R]$ and are reported in tables (4.1 - 4.5).

Therefore the rate equations for the reaction of the oxidant and the reductants, [R], can be repreesented by the equations (4.3) and (4.4) shown below.

$$-\frac{d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][RSH] \quad .... \quad (4.3)$$

Where RSH = L-cysteine, mercaptoacetic acid,
ß-mercaptoethylamine and mercaptoethanol

$$-\frac{d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][H_2Q] \quad ..... \quad (4.4)$$

Where $H_2Q$ = Resorcinol

The second-order rate constants ($k_2$) calculated from $k_{obsd}/[RSH]$ were fairly constant, further supporting that the reactions are first-order with respect to reductants. Similarly the second-order rate constants obtained by same calculation above for the resorcinol system are fairly constants.

The plots of log $k_{obsd}$ versus log [R] (R = thiol and the resorcinol) were given in figures (4.3 - 4.7).

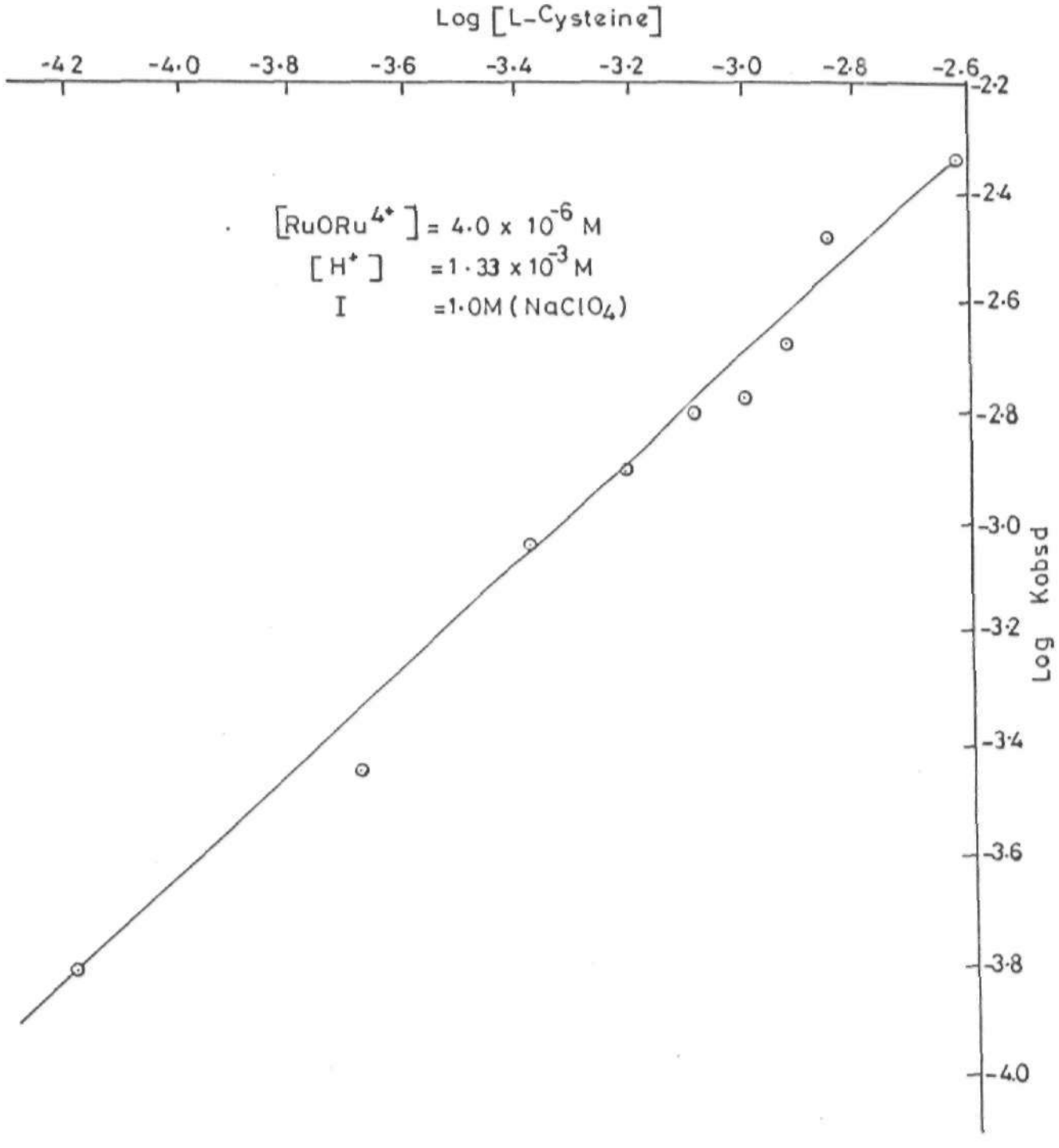



FIG.4.3 : PLOT OF LOG Kobsd VERSUS LOG [L-CYSTEINE]

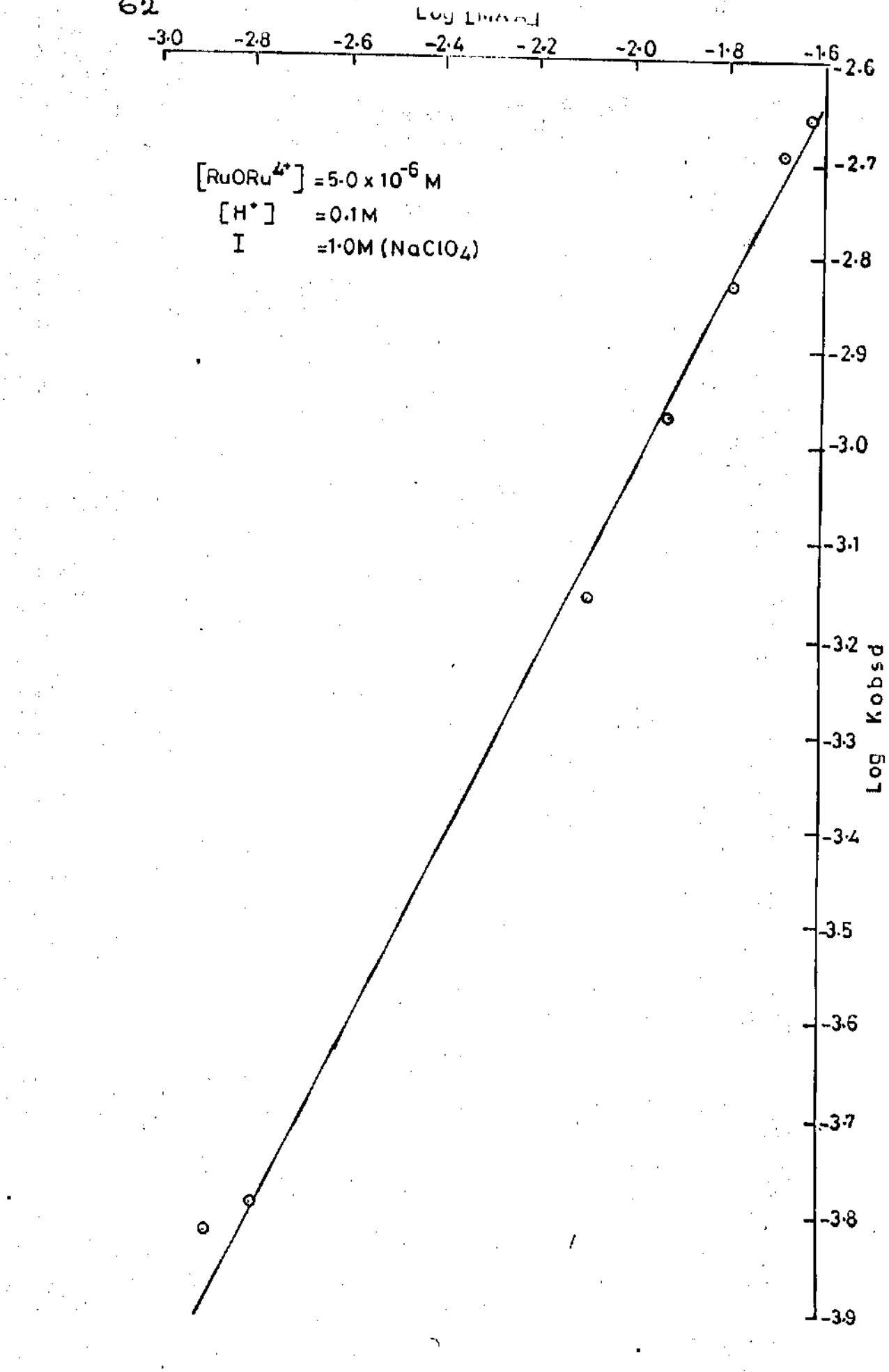



FIG. 4.4: PLOT OF LOG Kobsd VERSUS [MAA].

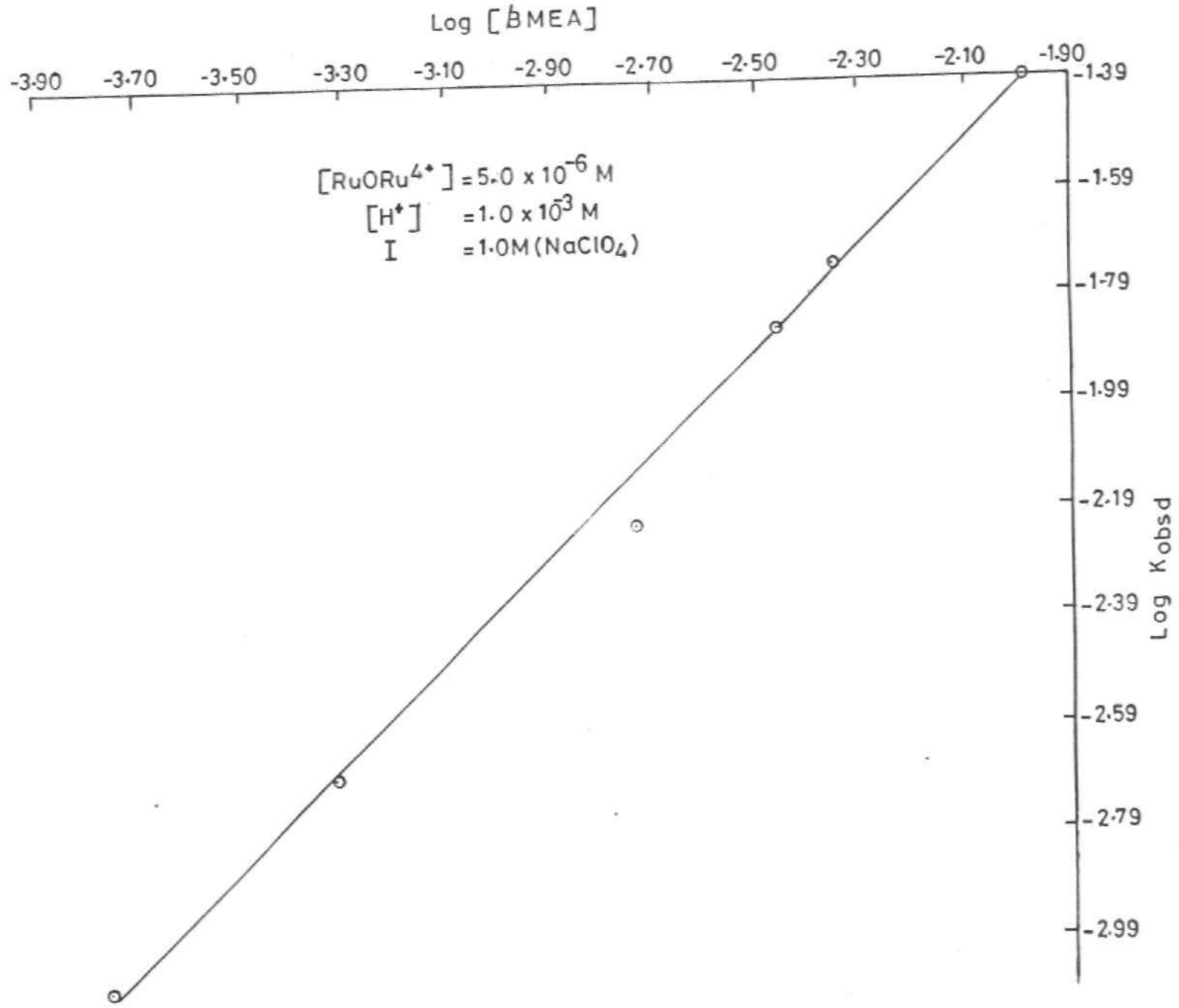



FIG. 4.5: PLOT OF LOG Kobsd VERSUS LOG [BMEA].

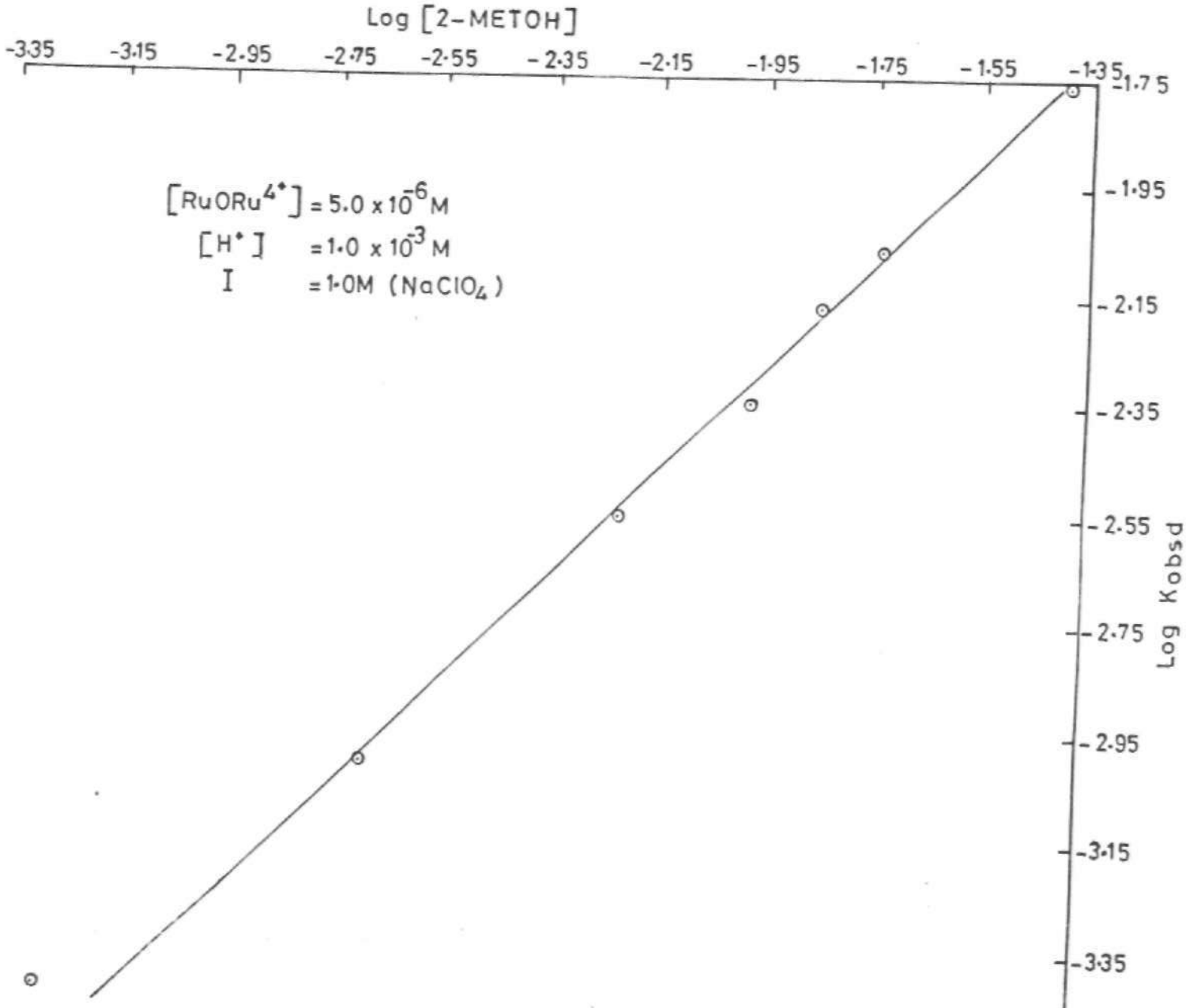
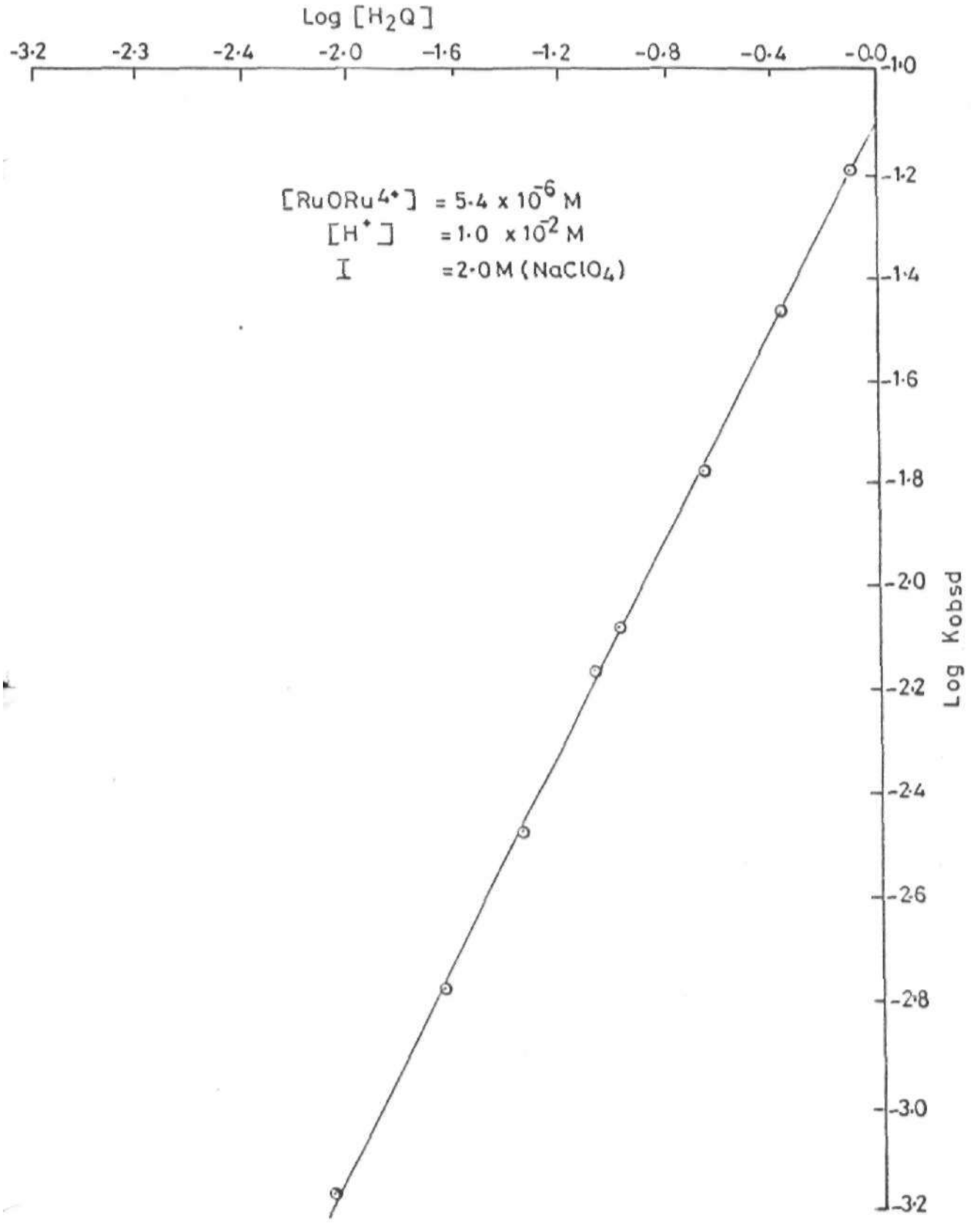



FIG.4.6.: PLOT OF LOG Kobsd VERSUS LOG [2-MET OH]




FIG·4·7: PLOT OF LOG Kobsd VERSUS LOG [$H_2Q$] FOR THE REACTION OF $RuORu^{4+}$ AND RESORCINOL.

For the $RuORu^{4+}$-L-cysteine system

$k_2$ = 2.02 ± 0.02$M^{-1}s^{-1}$ at $[H^+]$ = 1.33 x $10^{-3}$MI = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C

For the $RuORu^{4+}$ - Mercaptoacetic acid system

$k_2$ = (8.98 ± 0.09) x $10^{-2}M^{-1}s^{-1}$ at $[H^+]$ = 1.0 x $10^{-3}$M

I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C

For the $RuORu^{4+}$ - β-mercaptoethylamine system

$k_2$ = (2.28 ± 0.02) x $10^{-1}M^{-1}s^{-1}$ at $[H^+]$ = 1.0 x $10^{-3}$M

I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C

For the $RuORu^{4+}$ - 2-mercaptoethanol system

$k_2$ = 4.45 ± 0.01$M^{-1}s^{-1}$ at $[H^+]$ = 1.0 x $10^{-3}$M

I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C.

For the $RuORu^{4+}$ - Resorcinol system

$k_2$ = (8.35 ± 0.078) x $10^{-2}M^{-1}s^{-1}$ at $[H^+]$ = 1.0 x $10^{-3}$M

I = 2.0M ($NaClO_4$), T = 25.0 ± 0.1°C.

## 4.3 Effect of hydrogen ion on the rates of reaction of [$RuORu^{4+}$] and [Reductant]

The influence of acid on the rate of the reaction were investigated in the acid range 4.0 x $10^{-3}$ - 4.5 x $10^{-2}$M, while the concentration of $RuORu^{4+}$ and the

reductant were kept constant. The reaction was carried out at 25.0 ± 0.1°C and I = 1.0M ($NaClO_4$) except in $RuORu^{4+}$ - Resorcinol system, where the reaction was carried out at ionic strength of 2.0M ($NaClO_4$). All the reactions were inversely influenced by acid. Table (4.1 - 4.5).

Least square plots of $K_{ob}$ versus $[H^+]^{-1}$ pass through the origin (no significant intercept) for L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and resorcinol systems represented by a typical figure (4.8)and plot of $k_{ob}$ versus $[H^+]^{-1}$ was also linear with an intercept for $RuORu^{4+}$ - 2-mercaptoethanol system, figure (4.9).

The rate constant can be represented by equation (4.5) for L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and resorcinol systems and (4.6) for 2-mercaptoethanol system.

$$K_{ob} = a[H^+]^{-1} \quad \ldots\ldots (4.5)$$

$$k_{ob} = b + c[H^+]^{-1} \quad \ldots\ldots (4.6)$$

The overall equation for L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and resorcinol is

Table 4.1

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and L-cysteine

$[RuORu^{4+}] = 4.0 \times 10^{-5}M$, $T = 25.0 \pm 0.1^{o}C$, $\lambda = 650nm$

| $10^{5}[RSH]M$ | $10^{2}[H^{+}]M$ | $I(NaClO_4)M$ | $10^{4}k_{obs}s^{-1}$ | $k_2M^{-1}s^{-1}$ |
|---|---|---|---|---|
| 8 | 1.33 | 1.0 | 1.57 | 1.96 |
| 20 | 1.33 | 1.0 | 3.64 | 1.82 |
| 40 | 1.33 | 1.0 | 9.06 | 2.26 |
| 60 | 1.33 | 1.0 | 12.10 | 2.01 |
| 80 | 1.33 | 1.0 | 15.80 | 1.98 |
| 100 | 1.33 | 1.0 | 16.80 | 1.68 |
| 120 | 1.33 | 1.0 | 21.90 | 1.83 |
| 140 | 1.33 | 1.0 | 31.36 | 2.24 |
| 160 | 1.33 | 1.0 | 33.90 | 2.12 |
| 180 | 1.33 | 1.0 | 40.50 | 2.25 |
| 200 | 1.33 | 1.0 | 44.40 | 2.22 |
| 240 | 1.33 | 1.0 | 45.30 | 1.89 |
| 80 | 0.04 | 1.0 | 39.80 | 4.98 |
| 80 | 0.10 | 1.0 | 34.80 | 4.35 |
| 80 | 0.20 | 1.0 | 25.20 | 3.15 |
| 80 | 0.35 | 1.0 | 11.60 | 1.45 |
| 80 | 0.50 | 1.0 | 3.24 | 0.41 |
| 80 | 0.65 | 1.0 | 2.73 | 0.34 |
| 80 | 0.80 | 1.0 | 2.45 | 0.31 |
| 80 | 1.50 | 1.0 | 2.32 | 0.29 |
| 80 | 3.00 | 1.0 | 2.25 | 0.28 |
| 80 | 4.50 | 1.0 | 1.02 | 0.13 |

Table 4.2

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and Mercaptoacetic acid

$[RuORu^{4+}] = 5.0 \times 10^{-6}M$, $T = 25.0 \pm 0.1^{o}C$, $\lambda = 650nm$

| $10^{4}[RSH]M$ | $10^{2}[H^{+}],M$ | $I = (NaClO_{4})M$ | $10^{4}k_{obsd}s^{-1}$ | $10^{2}k_{2}$ $M^{-1}s^{-1}$ |
|---|---|---|---|---|
| 16 | 10 | 1.0 | 1.51 | 9.40 |
| 20 | 10 | 1.0 | 1.63 | 8.20 |
| 80 | 10 | 1.0 | 6.98 | 8.70 |
| 120 | 10 | 1.0 | 10.78 | 8.90 |
| 160 | 10 | 1.0 | 14.70 | 9.20 |
| 240 | 10 | 1.0 | 22.10 | 9.20 |
| 40 | 2 | 1.0 | 49.0 | 122.00 |
| 40 | 4 | 1.0 | 12.0 | 31.00 |
| 40 | 10 | 1.0 | 5.02 | 12.55 |
| 40 | 14 | 1.0 | 2.39 | 5.90 |
| 40 | 20 | 1.0 | 0.83 | 2.10 |
| 40 | 10 | 0.25 | 2.33 | 5.82 |
| 40 | 10 | 0.50 | 3.25 | 8.12 |
| 40 | 10 | 0.75 | 4.49 | 11.22 |
| 40 | 10 | 1.00 | 5.25 | 13.12 |
| 40 | 10 | 1.25 | 5.72 | 14.30 |
| 40 | 10 | 1.50 | 5.81 | 14.52 |
| 40 | 10 | 1.75 | 5.92 | 14.80 |
| 40 | 10 | 2.00 | 6.35 | 15.86 |

Table 4.3

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and β-mercaptoethylamine [$RuORu^{4+}$] = 5.0 x $10^{-6}$M, T = 25.0 ± 0.1°C, λ = 650nm

| $10^4$[RSH], M | $10^2$[$H^+$]M, | I($NaClO_4$)M | $10^4k_{obsd}$ $s^{-1}$ | $10^2k_2M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 8 | 1.0 | 1.0 | 1.78 | 22.3 |
| 20 | 1.0 | 1.0 | 4.48 | 22.4 |
| 60 | 1.0 | 1.0 | 13.50 | 22.5 |
| 100 | 1.0 | 1.0 | 22.10 | 22.1 |
| 140 | 1.0 | 1.0 | 30.80 | 22.0 |
| 180 | 1.0 | 1.0 | 41.04 | 22.5 |
| 280 | 1.0 | 1.0 | 62.72 | 22.4 |
| 400 | 1.0 | 1.0 | 91.20 | 22.4 |
| 180 | 0.8 | 1.0 | 73.62 | 40.9 |
| 180 | 4.0 | 1.0 | 33.80 | 18.8 |
| 180 | 8.0 | 1.0 | 14.10 | 7.8 |
| 180 | 16.0 | 1.0 | 6.53 | 3.6 |
| 180 | 24.0 | 1.0 | 5.92 | 3.2 |
| 180 | 32.0 | 1.0 | 3.48 | 1.9 |
| 180 | 40.0 | 1.0 | 2.84 | 1.5 |

Table 4.4

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and 2-mercatoethanol

$[RuORu^{4+}] = 5.0 \times 10^{-4}$M, T = 25.0 ± 0.1°C, λ = 650nm

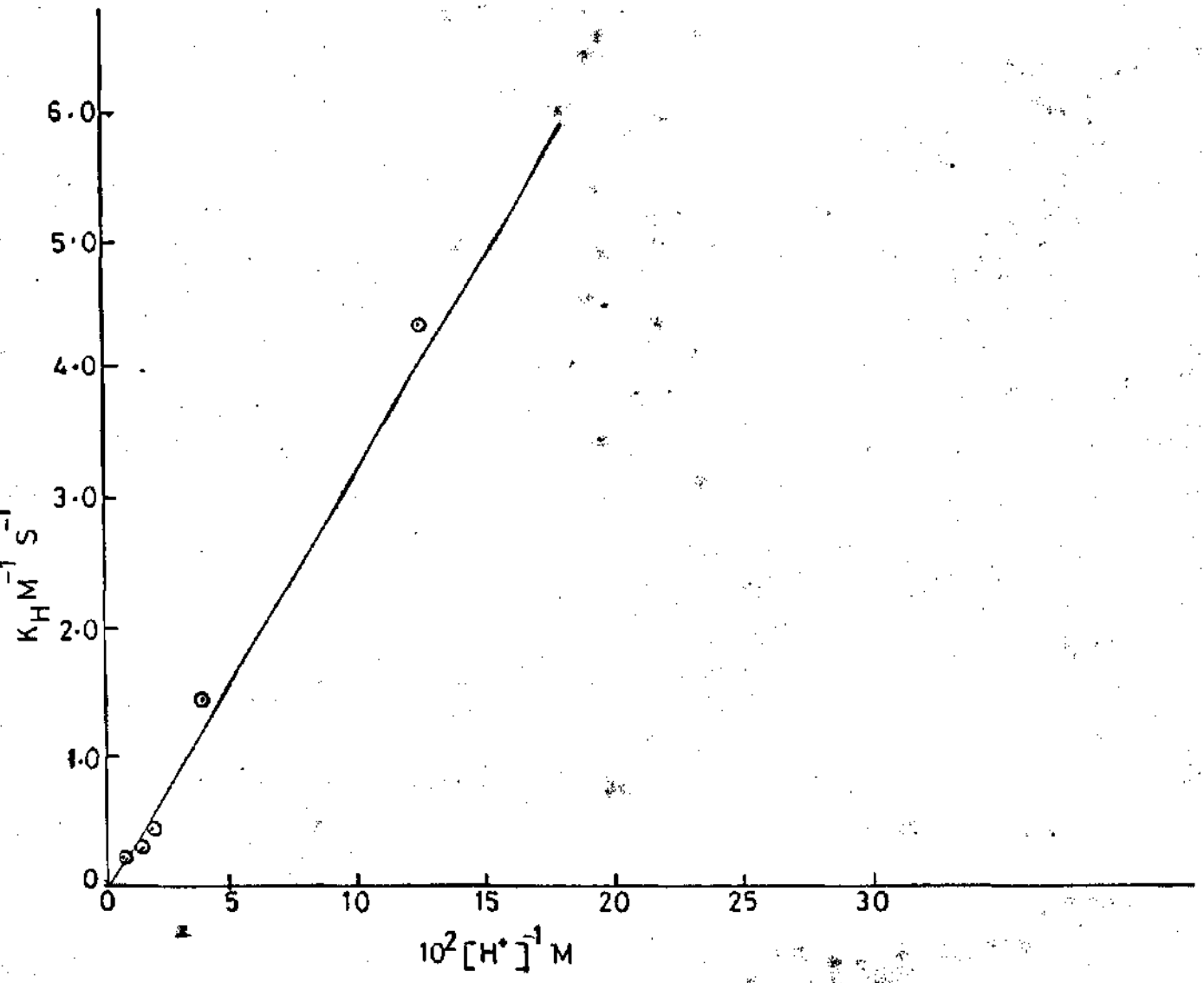
| $10^4$[RSH]M, | $10^2$[$H^+$]M, | I = ($NaClO_4$)M | $10^2 k_{obsd}$ $s^{-1}$ | $k_2 M^{-2}$ $s^{-1}$ |
|---|---|---|---|---|
| 8 | 1.0 | 1.0 | 3.77 | 4.71 |
| 20 | 1.0 | 1.0 | 9.49 | 4.74 |
| 60 | 1.0 | 1.0 | 27.90 | 4.65 |
| 100 | 1.0 | 1.0 | 44.7 | 4.47 |
| 140 | 1.0 | 1.0 | 68.00 | 4.85 |
| 180 | 1.0 | 1.0 | 82.10 | 4.56 |
| 400 | 1.0 | 1.0 | 182.00 | 4.55 |
| 400 | 1.0 | 1.0 | 272.00 | 6.82 |
| 400 | 0.4 | 1.0 | 228.40 | 5.71 |
| 400 | 0.8 | 1.0 | 196.80 | 4.92 |
| 400 | 1.0 | 1.0 | 179.20 | 4.48 |
| 400 | 4.0 | 1.0 | 47.30 | 1.73 |
| 400 | 8.0 | 1.0 | 21.80 | 0.55 |
| 400 | 10.0 | 1.0 | 19.70 | 0.49 |
| 400 | 40.0 | 1.0 | 8.50 | 0.21 |

Table 4.5

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and Resorcinol.

$[RuORu^{4+}] = 5.4 \times 10^{-5}M$, $T = 25.0 \pm 0.1°C$, $\lambda = 650nm$

| $10^3[H_2Q]M$, | $10^3[H^+]M$, | $I(NaClO_4)M$ | $10^3k_{obs}s^{-1}$ | $10^3k_2$ $M^{-1}s^{-1}$ |
|---|---|---|---|---|
| 8 | 10 | 2.0 | 0.67 | 8.45 |
| 20 | 10 | 2.0 | 1.66 | 8.31 |
| 40 | 10 | 2.0 | 3.31 | 8.28 |
| 80 | 10 | 2.0 | 6.77 | 8.46 |
| 100 | 10 | 2.0 | 8.27 | 8.27 |
| 200 | 10 | 2.0 | 16.66 | 8.33 |
| 400 | 10 | 2.0 | 33.64 | 8.41 |
| 800 | 10 | 2.0 | 66.32 | 8.29 |
| 80 | 1 | 2.0 | 8.64 | 10.81 |
| 80 | 4 | 2.0 | 7.37 | 9.21 |
| 80 | 8 | 2.0 | 6.91 | 8.64 |
| 80 | 12 | 2.0 | 6.37 | 7.96 |
| 80 | 20 | 2.0 | 4.66 | 5.85 |
| 80 | 28 | 2.0 | 0.65 | 0.81 |
| 80 | 32 | 2.0 | 0.26 | 0.33 |




FIG·4·8 : PLOT OF $K_H$ VERSUS $[H^+]^{-1}$ FOR THE REDOX REACTION BETWEEN $RuORu^{4+}$ AND L-CYSTEINE.

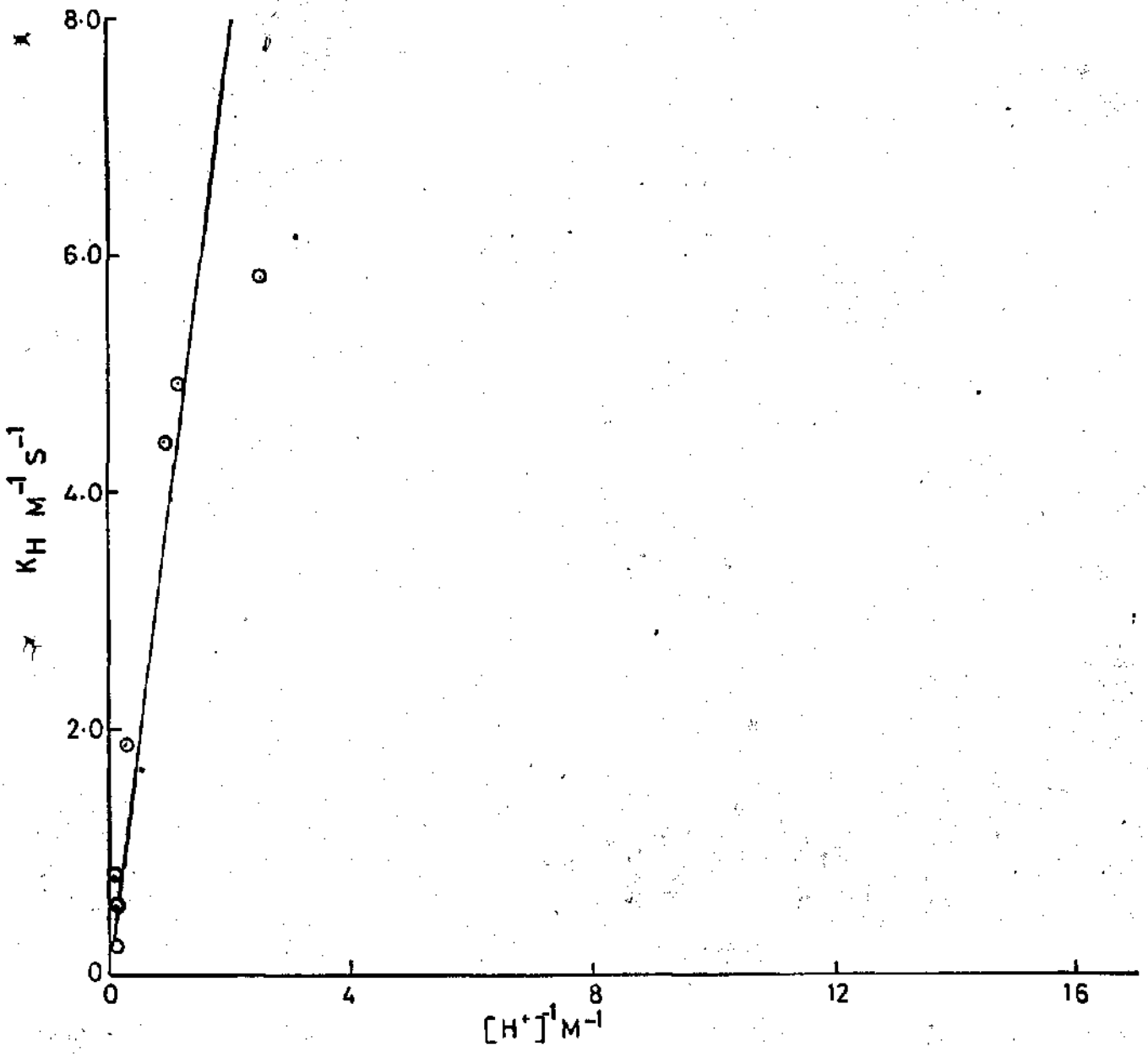



FIG. 4.9 : PLOT OF $K_H$ VERSUS $[H^+]^{-1}$ FOR THE REDOX REACTION BETWEEN $RuORu^{4+}$ AND 2-MERCAPTO ETHANOL.

$$-\frac{d[RuORu^{4+}]}{dt} = a[H^+]^{-1}[RuORu^{4+}][R]$$

Where R = L-cysteine, mercaptoacetic acid, ß-mercapto-ethylamine and resorcinol

and for 2-mercaptoethanol

$$\frac{d[RuORu^{4+}]}{dt} = (b + c[H^+]^{-1})[RuORu^{4+}][2\text{-mercaptoethanol}] \quad \ldots\ldots (4.8)$$

a and c are the slopes for the $[H^+]^{-1}$ in both the (L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and resorcinol) systems and 2-mercaptoethanol reespectively studied at 25.0 ± 0.1°C.

$RuORu^{4+}$ - L-cysteine system

$a = 3.63 \times 10^{-3} M^{-2} s^{-1}$, I = 1.0M ($NaClO_4$)

$[H^+] = (4.0 \times 10^{-4} - 4.5 \times 10^{-2})M$

$RuORu^{4+}$ - mercaptoacetic acid system

$a = 3.95 \times 10^{-2} M^{-2} s^{-1}$, I = 1.0M ($NaClO_4$)

$[H^+] = (0.02 - 0.2)M$

$RuORu^{4+}$ - ß-mercaptoethylamine system

$a = 7.81 \times 10^{-3} M^{-2} s^{-1}$, I = 1.0M ($NaClO_4$)

$[H^+] = (8.0 \times 10^{-4} - 4.0 \times 10^{-2})M$

$RuORu^{4+}$ - 2-mercaptoethanol system

$C = 1.15 \times 10^{-1} M^{-2} s^{-1}$, I = 1.0M ($NaClO_4$)

$[H^+] = (1.0 \times 10^{-4} - 4.0 \times 10^{-2})M$

$RuORu^{4+}$ - Resorcinol system

$a = 2.61 \times 10^{-3} M^{-2} s^{-1}$, I = 2.0M ($NaClO_4$)

$[H^+] = (1.0 \times 10^{-3} - 3.2 \times 10^{-2})M$

**4.4** <u>The effect of added anions</u>

The concentration of all other reactants were kept constant and at ionic strength of 1.0M ($NaClO_4$) for the reaction of the oxobridged ruthenium dimer ($RuORu^{4+}$) with the thiols (L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and 2-mercaptoethanol) and an ionic strength of 2.0M ($NaClO_4$) for the reaction of the oxobridged ruthenium dimer ($RuORu^{4+}$) with resorcinol. The effect of added anions on the rate of the reaction was investigated for $[X] = (1.0 \times 10^{-4} - 5.0 \times 10^{-2})M$ (X = $Cl^-$, $NO_3^-$, $CH_3COO^-$ and $SO_4^{=}$). It was ascertained that the anions did not react with either the oxidant (complex) or the reductants (substrates). The rate of the reaction of $RuORu^{4+}$ - L-cysteine and mercaptoacetic acid systems was found to be influenced by ($Cl^-$, $NO_3^-$ and $SO_4^{=}$) Table (4.6) and (4.7). But the rate of the $RuORu^{4+}$ - ß-mercapto-ethylamine, 2-mercaptoethanol and resorcinol are not affected by the anions ($Cl^-$, $NO_3^-$ and $CH_3COO^-$). The results are illustrated in tables (4.8), (4.9) and (4.10).

Table 4.6

Rate- Data for the effect of anions on the second-order rate constant for $RuORu^{4+}$-L-cysteine reaction. $[RuORu^{4+}] = 4.0 \times 10^{-3}M$, $[H^+] = 4.0 \times 10^{-3}M$ [RSH] = $2.0 \times 10^{-3}M$, I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C, λ = 650nm.

| X | $10^4[X]$, M | $10^4 k_{obs}$, $s^{-1}$ | $k_2$, $M^{-1}s^{-1}$ |
|---|---|---|---|
| $Cl^-$ | 0.4 | 4.67 | 2.34 |
| | 1.6 | 5.49 | 2.75 |
| | 2.4 | 6.21 | 3.10 |
| | 3.2 | 8.20 | 4.10 |
| $NO_3^-$ | 0.4 | 3.64 | 1.82 |
| | 0.8 | 5.02 | 2.51 |
| | 1.6 | 5.83 | 2.91 |
| | 4.0 | 8.50 | 4.25 |
| $SO_4^{2-}$ | 0.8 | 2.49 | 1.24 |
| | 1.2 | 3.28 | 1.64 |
| | 1.6 | 3.38 | 1.69 |
| | 2.0 | 4.60 | 2.30 |

Table 4.7

Rate-Data for the effect of anions and cations on the second-order rate constant for $RuORu^{4+}$ - mercaptoacetic acid reaction.

$[RuORu^{4+}] = 5.0 \times 10^{-6}M$, $[RSH] = 2.0 \times 10^{-3}M$, $[H^+] = 0.2M$, $I = 1.0M$ ($NaClO_4$), $T = 25.0 \pm 0.1^{\circ}C$, $\lambda = 650nm$

| X | $10^4[X]$, M | $10^4 k_{obsd}$, $s^{-1}$ | $10^2 k_2$, $M^{-1}s^{-1}$ |
|---|---|---|---|
| $Na^+$ | 4 | 1.65 | 8.25 |
| | 8 | 2.96 | 14.40 |
| | 12 | 3.19 | 15.95 |
| | 16 | 3.54 | 17.70 |
| | 20 | 3.75 | 18.75 |
| | 24 | 3.89 | 19.45 |
| $K^+$ | 4 | 3.39 | 16.95 |
| | 12 | 3.56 | 17.80 |
| | 16 | 3.74 | 18.70 |
| | 24 | 3.99 | 19.95 |
| $Rb^+$ | 8 | 7.60 | 38.0 |
| | 12 | 7.70 | 38.50 |
| | 16 | 7.80 | 39.50 |
| | 24 | 9.46 | 47.30 |
| $Mn^{2+}$ | 4 | 2.56 | 12.80 |
| | 12 | 2.58 | 12.90 |
| | 16 | 2.63 | 13.15 |
| | 20 | 2.84 | 14.20 |

Table 4.7 continued

| X | $10^4$[X], M | $10^4 k_{obs}$, $s^{-1}$ | $10^2 k_2$, $M^{-1}s^{-1}$ |
|---|---|---|---|
| | 24 | 2.92 | 14.60 |
| $Cl^-$ | 4 | 1.65 | 8.25 |
| | 8 | 2.96 | 14.40 |
| | 12 | 3.19 | 15.95 |
| | 20 | 3.75 | 18.75 |
| | 24 | 3.89 | 19.45 |
| $NO_3^-$ | 4 | 1.35 | 6.75 |
| | 8 | 1.56 | 7.80 |
| | 12 | 1.75 | 8.50 |
| | 28 | 1.83 | 9.55 |
| | 32 | 2.27 | 11.35 |
| $SO_4^-$ | 4 | 1.52 | 5.60 |
| | 8 | 1.75 | 8.75 |
| | 12 | 1.91 | 9.55 |
| | 16 | 1.99 | 9.95 |
| | 20 | 2.64 | 13.20 |
| | 24 | 2.96 | 14.60 |

Table 4.8

Rate data for the effect of anions and cations on the second-order rate constant for the $RuORu^{4+}$ - β-mercaptoethylamine reaction

$[RuORu^{4+}] = 5.0 \times 10^{-6}M$, $[RSH] = 1.8 \times 10^{-3}M$, $[H^+] = 1.0 \times 10^{-3}M$, I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C, λ = 650nm

| X | $10^4[X]$, M | $10^3k_{obsd}s^{-1}$ | $10^2k_2M^{-1}s^{-1}$ |
|---|---|---|---|
| $Cl^-$ | 2 | 4.07 | 22.6 |
| | 6 | 3.98 | 22.1 |
| | 10 | 4.01 | 22.3 |
| | 50 | 4.01 | 22.3 |
| | 100 | 4.01 | 22.4 |
| $CH_3COO^-$ | 2 | 3.98 | 22.2 |
| | 10 | 3.99 | 22.8 |
| | 100 | 4.10 | 22.4 |
| $NO_3^-$ | 2 | 4.01 | 22.4 |
| | 10 | 4.08 | 22.7 |
| | 100 | 4.10 | 22.8 |
| $Li^+$ | 2 | 4.01 | 22.4 |
| | 10 | 4.12 | 22.9 |
| | 100 | 4.01 | 22.3 |
| $Na^+$ | 2 | 4.07 | 22.6 |
| | 10 | 3.98 | 22.1 |
| | 100 | 4.01 | 22.3 |

Table 4.8

| X | $10^4[X]M$ | $10^3k_{obsd}s^{-1}$ | $k_2M^{-1}s^{-1}$ |
|---|---|---|---|
| $K^+$ | 2 | 4.10 | 22.3 |
| | 10 | 4.15 | 22.8 |
| | 100 | 4.09 | 23.1 |
| $Rb^+$ | 2 | 4.05 | 22.7 |
| | 10 | 4.01 | 22.5 |
| | 100 | 4.01 | 22.4 |
| $Mn^{2+}$ | 2 | 4.01 | 22.3 |
| | 10 | 4.05 | 22.5 |
| | 100 | 4.10 | 22.8 |
| $Mg^{2+}$ | 2 | 3.98 | 22.1 |
| | 10 | 4.09 | 22.7 |
| | 100 | 4.01 | 22.4 |

Table 4.9

Rate data for the effect of anions and cations on the second-order rate constants for the $RuORu^{4+}$- 2-mercaptoethanol reaction [$RuORu^{4+}$] = $5.0 \times 10^{-6}$M, [RSH] = $1.0 \times 10^{-2}$M, [$H^+$] = $2.0 \times 10^{-3}$M, I = 1.0M ($NaClO_4$), T = 25.0 ± 0.1°C, λ = 650nm

| X | $10^4$[X]M | $10^3 k_{obs}/s^{-1}$ | $k_2/M^{-1}s^{-1}$ |
|---|---|---|---|
| $Cl^-$ | 2 | 45.1 | 4.51 |
| | 10 | 44.7 | 4.47 |
| | 20 | 45.6 | 4.56 |
| $NO_3^-$ | 2 | 44.8 | 4.48 |
| | 10 | 46.2 | 4.62 |
| | 20 | 47.3 | 4.73 |
| $CH_3COO^-$ | 2 | 52.2 | 5.22 |
| | 10 | 49.3 | 4.93 |
| | 20 | 45.4 | 4.54 |
| $Li^+$ | 2 | 51.1 | 5.11 |
| | 10 | 48.2 | 4.82 |
| | 20 | 44.6 | 4.46 |
| $Na^+$ | 2 | 42.2 | 4.22 |
| | 10 | 43.2 | 4.32 |
| | 20 | 46.1 | 4.61 |
| $K^+$ | 2 | 43.7 | 4.37 |
| | 10 | 45.1 | 4.51 |
| | 20 | 47.1 | 4.71 |

Table 4.9

| X | $10^{3}$[X]M | $10^{3}k_{obs}$ $s^{-1}$ | $k_{2}$ $M^{-1}s^{-1}$ |
|---|---|---|---|
| $Rb^{+}$ | 2 | 45.2 | 4.52 |
| | 10 | 46.3 | 4.63 |
| | 20 | 43.8 | 4.38 |
| $Mg^{2+}$ | 2 | 44.5 | 4.45 |
| | 10 | 45.5 | 4.55 |
| | 20 | 42.9 | 4.29 |
| $Mn^{2+}$ | 2 | 46.2 | 4.62 |
| | 10 | 43.6 | 4.36 |
| | 20 | 44.2 | 4.42 |

Table 4.10

Rate data for the effect of anion and cation on the second-order rate constant for the $RuORu^{4+}$ - Resorcinol reaction

$[RuORu^{4+}] = 5.4 \times 10^{-6}M$, $[H_2Q] = 8.0 \times 10^{-2}M$, $[H^+] = 1.0 \times 10^{-3}M$, I = 2.0M ($NaClO_4$), T = 25.0 ± 0.1°C, λ = 650nm

| X | $10^3[X]M$ | $10^3k_{obsd}S^{-1}$ | $k_2M^{-1}S^{-1}$ |
|---|---|---|---|
| $Cl^-$ | 1 | 6.62 | 8.28 |
| | 20 | 6.62 | 8.28 |
| | 50 | 6.75 | 8.44 |
| $NO_3^-$ | 1 | 6.62 | 8.24 |
| | 20 | 6.32 | 7.90 |
| | 50 | 6.42 | 8.02 |
| $SO_4^-$ | 1 | 6.72 | 8.40 |
| | 20 | 6.42 | 8.02 |
| | 50 | 6.72 | 8.40 |
| $Li^+$ | 1 | 6.53 | 8.16 |
| | 20 | 6.86 | 8.58 |
| | 50 | 6.23 | 7.79 |
| $Na^+$ | 1 | 6.42 | 8.02 |
| | 20 | 6.62 | 8.28 |
| | 50 | 6.75 | 8.44 |
| $Mg^{2+}$ | 1 | 6.53 | 8.16 |
| | 20 | 6.42 | 8.02 |
| | 50 | 6.64 | 8.30 |
| $Mn^{2+}$ | 1 | 6.14 | 7.68 |
| | 20 | 6.52 | 8.15 |
| | 50 | 6.84 | 8.55 |

## 4.5 Effect of added cations

The concentration of all other reactants were kept constant and at ionic strength of 1.0M ($NaClO_4$) for $RuORu^{4+}$ - L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and 2-mercaptoethanol systems and I = 2.0M ($NaClO_4$) for $RuORu^{4+}$ - resorcinol system. The effect of monopositive and dipositive cations on the rate of the reaction were investigated for $[Z^+] = 2.0 \times 10^{-4} - 5.0 \times 10^{-2}$M ($Z^+ = Li^+$, $Na^+$, $K^+$ and $Rb^+$) ($Z^{2+} = Mg^{2+}$ and $Mn^{2+}$). Both the mono- and dipositive cations were found not to affect the reaction in all the systems studied.

## 4.6 Test for intermediate complex

### 4.6.1 Spectrophotometric tests

These tests were carried out on all the systems in order to find out whether spectroscopically determinable intermediate complex was formed between the oxobridged dimer and each of the reductants during the reaction. The electronic spectra of the reacting mixture were run after two minutes of the commencement of the reaction, over a range of wavelength (550 - 690)nm. A similar run was made for the complex alone. From the spectral there was no clear shift from 660nm, the $\lambda max$ for the oxobridged ruthenium in all the tests carried out for the systems. The extinction coefficient (E) was not also enhanced. All these do

not completely ruled out the formation of an intermediate complex, even if any occur it must have a very small formation.

4.6.2 Michaelis-Menten plots

Least square analysis of the plot of $1/k_{obsd}$ versus 1/[R] where (R = L-cysteine, mercaptoacetic acid, β-mercaptoethylamine, 2-mercaptoethanol and resorcinol) gave a straight lines passing through the origin. Typical plot is presented in figure (4.10).

The Michaelis-Menten model of enzyme action lead to a rate law of form

$$-\frac{d[Product]}{dt} = k_{obsd}[E^o] \quad \ldots\ldots (4.10)$$

With $k_{obsd} = k_1[S]/(K_m + [S]$ $\ldots\ldots (4.11)$

The expression for the $k_{obsd}$ in equation (4.11) can rearranged into

$$1/k_{obsd} = 1/k_1 + (K_m/k_1)[S]^{-1} \quad \ldots\ldots (4.12)$$

Where $k_{obsd}$ = rate constant for the overall reaction

$[E]_o$ = total enzyme concentration

$K_m$ = Micaelis-Menten rate constant.

$k_1$ = rate constant for the break-up of an active intermediate into products.

s = substrate (S = reductant in the reaction studied)

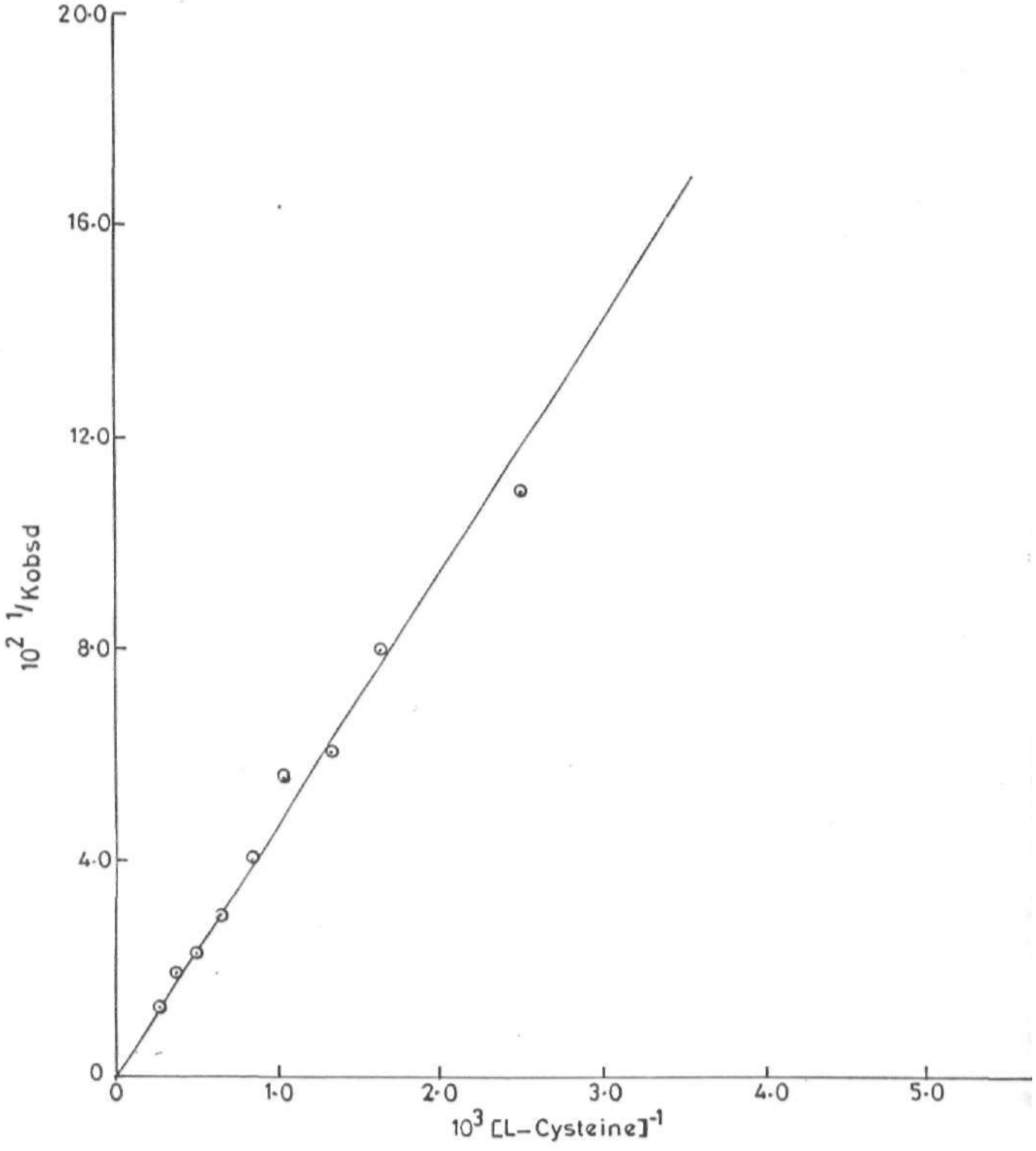



FIG. 4·10: MICHAELIS-MENTEN'S PLOT FOR THE REACTION OF $RuORu^{4+}$ AND L-CYSTEINE.

From the equation (4.12) plot of $1/k_{obs}$ versus 1/[S] will give $1/k_1$ as an intercept. Therefore in Michaelis-Menten plots the straight line passing through the origin show that $1/k_1$ is zero and this suggests that the absences of an intermediate complex formation in the reaction studied.

## 4.7 Free radical test

Acrylamide was polymerized when it was added with excess of methanol to partially oxidised reaction mixture in $RuORu^{4+}$ - L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol systems, but no such gel formation was observed in respect of the resorcinol reaction. Acrylamide did not polymerise in presence of either of the reactant alone. This suggests that free radicals were formed in thiols reactions but were not detected in resorcinol reactions probably their formation and destruction may be so fast that it is not detected.

## 4.8 The effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range of I = 0.25 - 2.5M ($NaClO_4$) for mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol reactions and

I = 0.50 - 2.5M ($NaClO_4$) for L-cysteine and resorcinol reactions. In all the reactions the concentration of other reactants were kept constants at 25.0 ± 0.1°C. The rate constants were found to increase with increasing ionic strength for $RuORu^{4+}$ - mercaptoacetic acid and resorcinol systems, Tables (4.2) and (4.14), while the decrease in rate with increasing ionic strength was observed for $RuORu^{4+}$ - L-cysteine, ß-mercaptoethylamine and 2-mercaptoethanol systems Tables (4.11), (4.12) and (4.13).

The effects of ions on the rate constant of the reaction involving two reactants with charges $Z_A$ and $Z_B$ are related by the following equation (Bronsted, 1922).

$$\log k = \log k_\infty + 2\alpha Z_A Z_B I^{1/2} \quad \ldots\ldots (4.12)$$

k = The rate constant of the reaction

$k_\infty$ = hypothetical rate constant in medium of infinite dielectric constant

I = ionic strength

α = 0.50 at 25°C.

This equation has been used to correlate salt effect with rate constant for reaction involving ions thus plots of log k vs $I^{1/2}$ should be linear with slope $Z_A Z_B$ (at 25°C) and intercept values of log $k_\infty$ (Bronsted, 1922). The equation predict a positive

Table 4.11

Effect of ionic strength and medium dielectric constant on the reaction of $RuORu^{4+}$ and L-cysteine

$[RuORu^{4+}] = 4.0 \times 10^{-5}M$, $T = 25.0 \pm 0.1^{\circ}C$, $\lambda = 650nm$

| I,M | $10^4$[RSH],M | $10^2$[$H^+$],M | % Acetone | D* | $10^4 k_{obs}$ $s^{-1}$ |
|---|---|---|---|---|---|
| 0.50 | 4 | 1 | - | - | 4.51 |
| 0.75 | 4 | 1 | - | - | 4.28 |
| 1.00 | 4 | 1 | - | - | 2.52 |
| 1.25 | 4 | 1 | - | - | 0.96 |
| 1.50 | 4 | 1 | - | - | 0.71 |
| 1 | 4 | 1 | 0.5 | 78.24 | 2.63 |
| 1 | 4 | 1 | 1.0 | 77.94 | 23.90 |
| 1 | 4 | 1 | 1.5 | 77.63 | 24.52 |
| 1 | 4 | 1 | 2.0 | 77.33 | 28.90 |
| 1 | 4 | 1 | 2.5 | 77.04 | 31.30 |
| 1 | 4 | 1 | 3.0 | 76.75 | 44.40 |
| 1 | 4 | 1 | 3.5 | 76.45 | 47.90 |
| 1 | 4 | 1 | 4.0 | 76.16 | 55.00 |
| 1 | 4 | 1 | 4.5 | 75.87 | 55.60 |
| 1 | 4 | 1 | 5.0 | 75.59 | 73.60 |

*Where D is Dielectric constant of the medium

Table 4.12

Effect of ionic strength and medium dielectric constant on the reaction of $RuORu^{4+}$ and β-mercaptoethylamine

$[RuORu^{4+}] = 5.0 \times 10^{-5}M$, $T = 25.0 \pm 0.1^{o}C$, $\lambda = 650nm$

| I.M | $10^{3}$[RSH].M | $10^{4}$[$H^{+}$]M | % Ethanol | D | $10^{3}k_{obs}s^{-1}$ |
|---|---|---|---|---|---|
| 0.25 | 18 | 10 | - | - | 5.35 |
| 0.50 | 18 | 10 | - | - | 4.55 |
| 0.75 | 18 | 10 | - | - | 4.12 |
| 1.00 | 18 | 10 | - | - | 3.85 |
| 1.25 | 18 | 10 | - | - | 3.73 |
| 1.50 | 18 | 10 | - | - | 2.92 |
| 1 | 18 | 10 | 1.0 | 77.94 | 4.04 |
| 1 | 18 | 10 | 1.5 | 77.63 | 4.34 |
| 1 | 18 | 10 | 2.0 | 77.33 | 4.49 |
| 1 | 18 | 10 | 2.5 | 77.04 | 5.01 |
| 1 | 18 | 10 | 3.0 | 76.75 | 5.54 |
| 1 | 18 | 10 | 3.5 | 76.45 | 5.64 |
| 1 | 18 | 10 | 4.0 | 76.16 | 5.71 |
| 1 | 18 | 10 | 4.5 | 75.87 | 5.84 |
| 1 | 18 | 10 | 5.0 | 75.59 | 5.92 |

Where D is the dielectric constant of the medium

Table 4.13

Effect of ionic strength and medium dielectric constant on the reaction of $RuORu^{4+}$ and 2-mercapto ethanol

$[RuORu^{4+}] = 5.0 \times 10^{-6}M$, T = 25.0 ± 0.1°C, λ = 650nm

| I,M | $10^{3}[RSH]$,M | $10^{4}[H^{+}]$,M | % Ethanol | D* | $10^{3}k_{obs}s^{-1}$ |
|---|---|---|---|---|---|
| 0.25 | 10 | 20 | - | - | 49.8 |
| 0.50 | 10 | 20 | - | - | 49.4 |
| 1.00 | 10 | 20 | - | - | 45.5 |
| 1.50 | 10 | 20 | - | - | 32.0 |
| 2.00 | 10 | 20 | - | - | 31.5 |
| 2.50 | 10 | 20 | - | - | 23.5 |
| 1 | 10 | 20 | 10 | 73.09 | 2.70 |
| 1 | 10 | 20 | 20 | 67.65 | 2.97 |
| 1 | 10 | 20 | 30 | 62.26 | 3.05 |
| 1 | 10 | 20 | 40 | 56.85 | 3.85 |
| 1 | 10 | 20 | 50 | 51.41 | 4.13 |
| 1 | 10 | 20 | 60 | 45.97 | 4.28 |

* D is the Dielectric constant of the medium

Table 4.14

Effect of ionic strength and medium dielectric constant on the reaction of $RuORu^{4+}$ and Resorcinol

$[RuORu^{4+}] = 5.4 \times 10^{-6}M$, T = 25.0 ± 0.1°C, λ = 650nm

| I.M | $10^3[H_2Q]M$ | $10^4[H^+]M$ | % Ethanol | *D | $10^3k_{obs}s^{-1}$ |
|---|---|---|---|---|---|
| 0.50 | 80 | 10 | - | - | 0.93 |
| 1.00 | 80 | 10 | - | - | 4.38 |
| 1.50 | 80 | 10 | - | - | 5.90 |
| 2.00 | 80 | 10 | - | - | 9.05 |
| 2.50 | 80 | 10 | - | - | 16.10 |
| 2 | 80 | 10 | 10 | 73.09 | 6.92 |
| 2 | 80 | 10 | 20 | 67.66 | 6.67 |
| 2 | 80 | 10 | 30 | 62.27 | 6.57 |
| 2 | 80 | 10 | 40 | 56.55 | 6.46 |
| 2 | 80 | 10 | 50 | 51.41 | 6.34 |
| 2 | 80 | 10 | 60 | 45.98 | 6.13 |

* Where D is dielectric constant of the medium

salt effect (i.e an increasing rate constant with increasing salt concentration) when reactant are of the same sign and negative salt effect when charges are of opposite sign (Bronsted, 1992). In this work linear plots were observed for log $k_{obsd}$ versus $I^{1/2}$, figures (4.11) and (4.12).

## 4.9 Effect of the dielectric constant of the medium on the rate of reaction [RuORu$^{4+}$] and [Reductant]

For reaction between two ions of charges $Z_A$ and $Z_B$ the rate constant is given by

$$\ln k = \ln k_o - \frac{e^2}{2DKT}\left[\frac{Z_A+Z_B}{r_*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \quad .... \quad (4.14)$$

Where k is the hypothetical rate constant, D is the dielectric constant, and $r_A$, $r_B$ and $r_*$ are the radii of the reactant ions A and B and the activated complex respectively.

In a reaction between anion $Z_A$ and a polar molecule ($Z_B$ = 0) equation (4.14) becomes

$$Ink = Ink_o + \frac{Z_A^2e^2}{2DKT}\left[\frac{1}{r_A} - \frac{1}{r_*}\right] \quad ..... \quad (4.15)$$

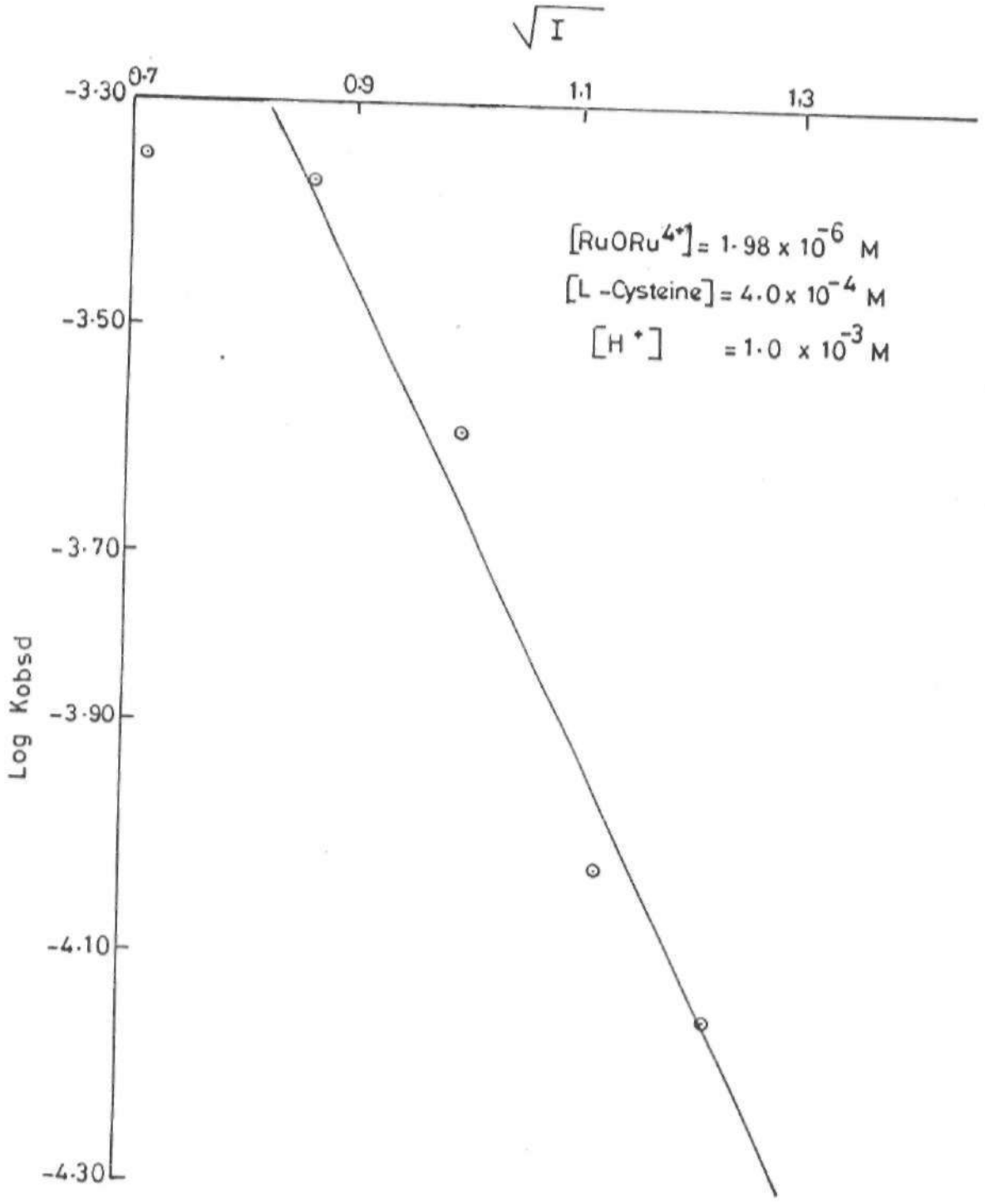



FIG. 4.11 : PLOT OF LOG Kobsd VERSUS $\sqrt{I}$ FOR THE REACTION OF $RuORu^{4+}$ AND L-CYSTEINE.

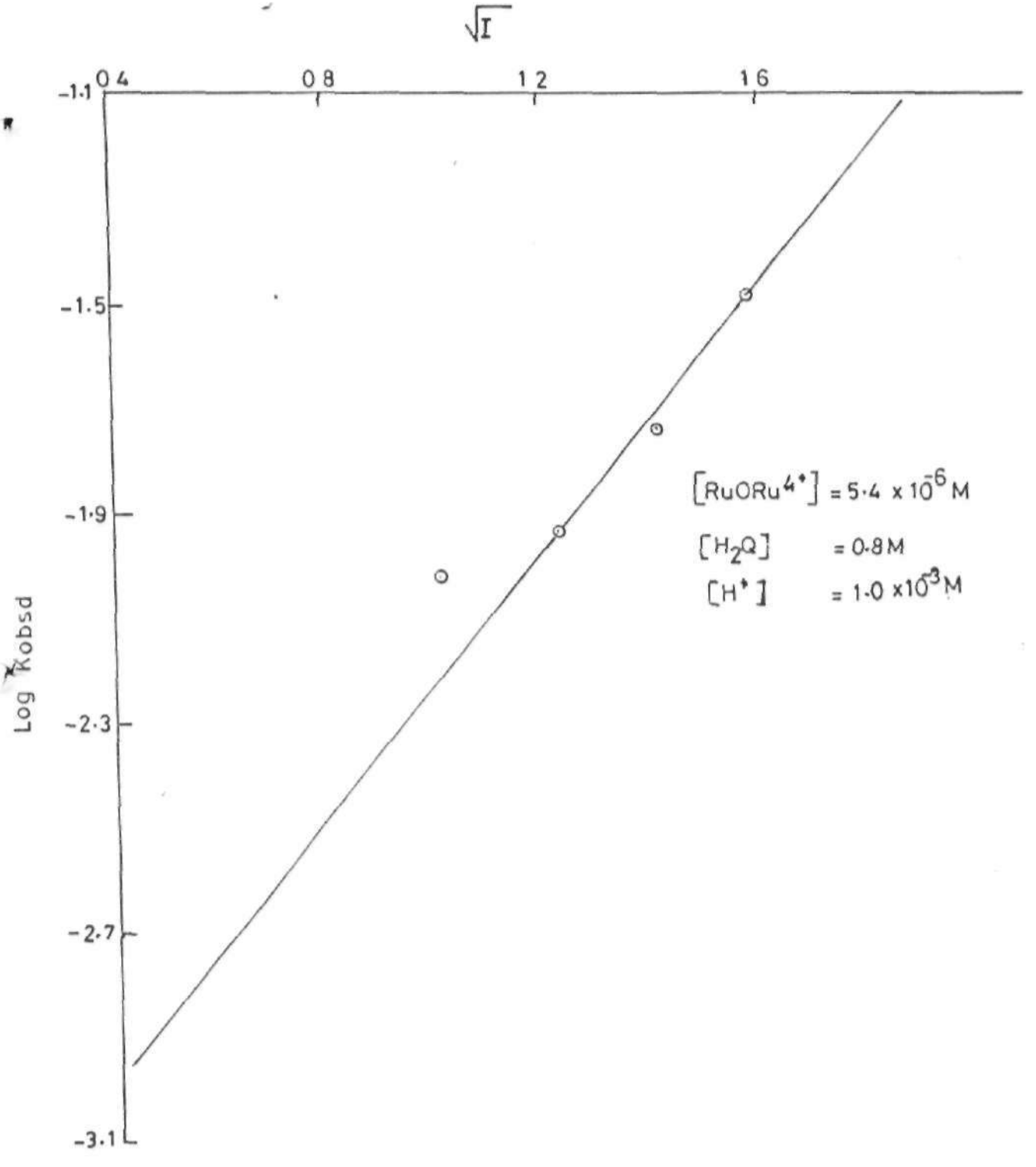



FIG. 4.12 PLOT OF LOG $K_{obsd}$ VERSUS $\sqrt{I}$ FOR THE REDOX REACTION BETWEEN $RuORu^{4+}$ AND RESORCINOL.

The equation (4.15) predicts a linear plot of log k versus 1/D with a negative slope if the charges of the ions are of the same sign and with a positive slope if the ions are oppositely charged (Wilkins, 1974). The effect of medium dielectric constant on the rate constant for the reaction of $RuORu^{4+}$ and reductants was investigated using 10-60% v/v ethanol for 2-mercaptoethanol and resorcinol system and 0.5 - 5.0% v/v acetone for L-cysteine and β-mercaptoethylamine systems. The values for the rate constant are presented in tables (4.11) - (4.14). Typical plots of $k_{obsd}$ versus 1/D (where D = Dielectric constant) is shown in figure (4.13).

## 4.10 Activation parameters

The rate of the reaction between $RuORu^{4+}$ and L-cysteine was determined in temperature range 25.0°C - 35.0°C. And plot of log $k_2$ versus 1/T is shown in figure (4.15). ($\log k_2$ is obtained as the slopes of plot of $k_{obsd}$ versus $[H^+]^{-1}$ at each temperature) figure (4.14). From the slope of the curve an activation energy for the reaction was determined. Knowing the activation energy for the reaction, $\Delta H^*$ for the reaction is calculated from the equation (4.16) below

$$Ea = \Delta H^{*} + RT \quad \ldots\ldots \quad (4.16)$$

(Wilkins, 1974)

Where R = Gas constant

T = Temperature at (25°C) 298K

and $\Delta S^{*}$ can be obtained from the equation (4.17) below

$$\Delta S^{*} = 4.6(\log A - 13.2)\ cal mol^{-1} deg^{-1} \quad \ldots. \quad (4.17)$$

(Wilkins, 1974)

Where log A = intercept on Arrhenius plot fig (4.15)

Table (4.15) displays the values of the rate constants at different temperatures and associated activation parameters.

## 4.11 Product analysis

The uv and visible spectra of the reacted mixture of the reactants (for the thiols) were measured and these were found to correspond with the spectra of the reactions between the thiols (L-cysteine, mercapto acetic acid, 2-mercaptoethanol and β-mercaptoethyl-amine) with hydrogen peroxide ($H_2O_2$), $\lambda$ = 290nm, Figure (4.16). This correspond with the report of Zahid (1977) in which $TlOH^{2+}$ was found to oxidised thiols to disuphide. Thus, the result obtained in this research unquivocally confirmed that disulphide is one of the product.

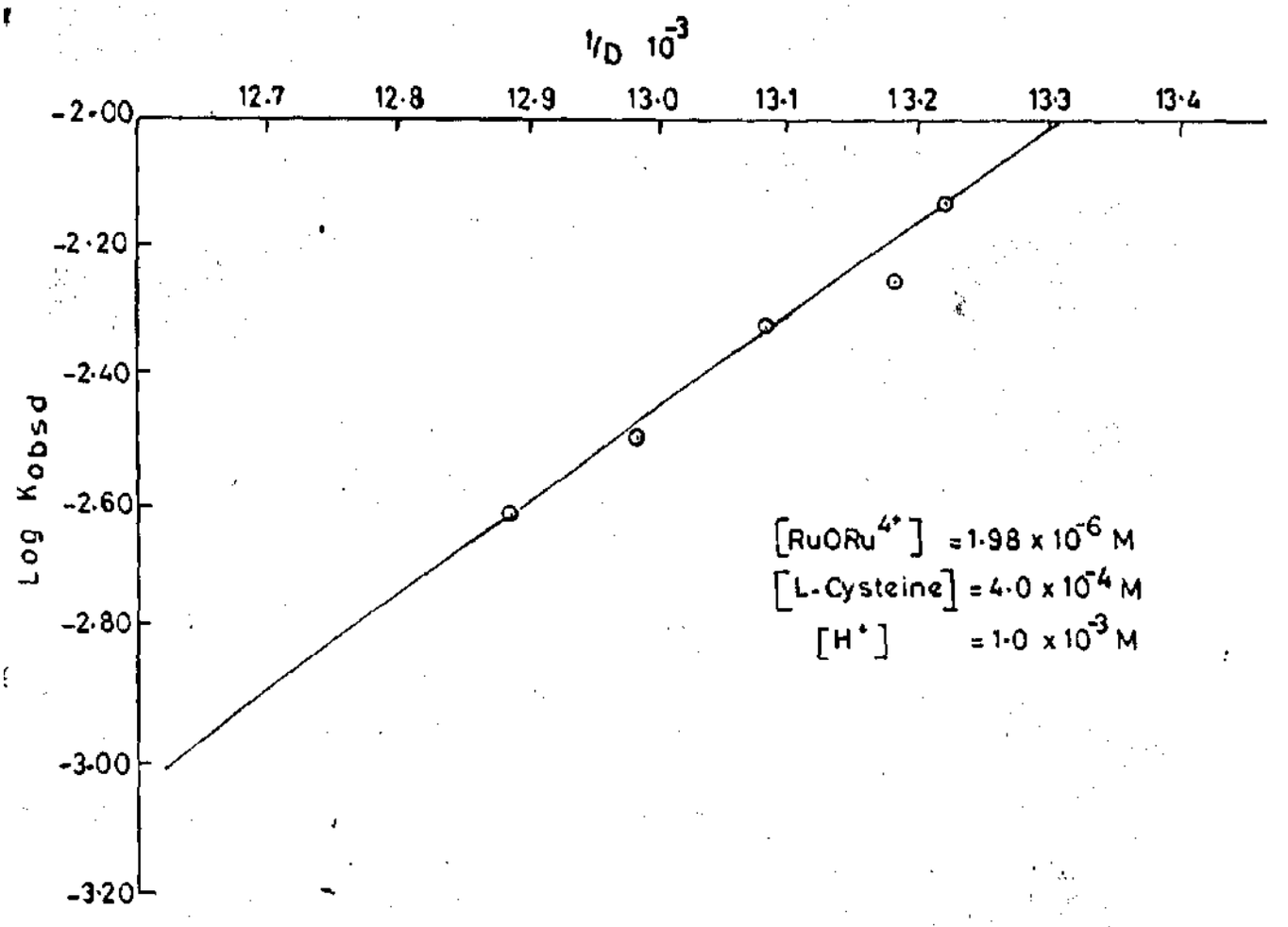



FIG.4.13 PLOT OF LOG Kobsd VERSUS $^{1}/_{D}$ FOR THE REACTION OF $RuORu^{4+}$ AND L-CYSTEINE.

Table 4.15

Effect of acid and temperature on the reaction of $RuORu^{4+}$ and L-cysteine

$[RuORu^{4+}] = 2.0 \times 10^{-6}M$, $\lambda = 650nm$

| T°C | $10^4[H^+]M$ | $10^4[RSH]M$ | $I(NaClO_4)M$ | $10^4k_{obs}$ $s^{-1}$ | $k_2M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|---|
| 25.5 | 2 | 8 | 1.0 | 61.20 | 7.62 |
| 25.5 | 4 | 8 | 1.0 | 45.40 | 5.63 |
| 25.5 | 8 | 8 | 1.0 | 38.90 | 4.86 |
| 25.5 | 20 | 8 | 1.0 | 7.11 | 0.89 |
| 25.5 | 80 | 8 | 1.0 | 1.48 | 0.19 |
| 30.0 | 2 | 8 | 1.0 | 78.30 | 9.79 |
| 30.0 | 4 | 8 | 1.0 | 52.20 | 6.53 |
| 30.0 | 8 | 8 | 1.0 | 39.80 | 4.98 |
| 30.0 | 20 | 8 | 1.0 | 18.10 | 2.26 |
| 30.0 | 80 | 8 | 1.0 | 3.53 | 0.44 |
| 35.0 | 2 | 8 | 1.0 | 146.00 | 18.25 |
| 35.0 | 4 | 8 | 1.0 | 112.00 | 14.00 |
| 35.0 | 8 | 8 | 1.0 | 86.20 | 10.78 |
| 35.0 | 20 | 8 | 1.0 | 56.30 | 7.04 |
| 35.0 | 80 | 8 | 1.0 | 9.80 | 1.23 |
| 35.0 | 200 | 8 | 1.0 | 4.10 | 0.50 |

Activation parameters for the reaction at constant $[H^+]$

$RuORu^{4+}$ - L-cysteine system

$Ea = 69.27\ KJmol^{-1}$

$\Delta H^{\neq} = 22.01\ KJmol^{-1}$

$\Delta S^{\neq} = -310.64\ KJmol^{-1}$

$\Delta G^{\neq} = 106.81\ KJmol^{-1}$

The spectra of the reaction mixtures for all the five systems were taken over a range of wavelength (400-700nm) after about an hour of the commencement of the reaction. It was found that the absorption occurs maximally at about 482nm this compared to $\lambda max$ of 485nm reported by (Iyun et al. 1992) for the reduction of the same oxidant $RuORu^{4+}$ which is probably the mixed-valenced complex $Ru^{III}ORu^{IV}(RuORu^{5+})$ figure (4.17).

$[RuORu^{4+}] = 2.0 \times 10^{-6} M$

$[L\text{-Cysteine}] = 8.0 \times 10^{-4} M$

$I \quad = 1.0 M\ (NaClO_4)$

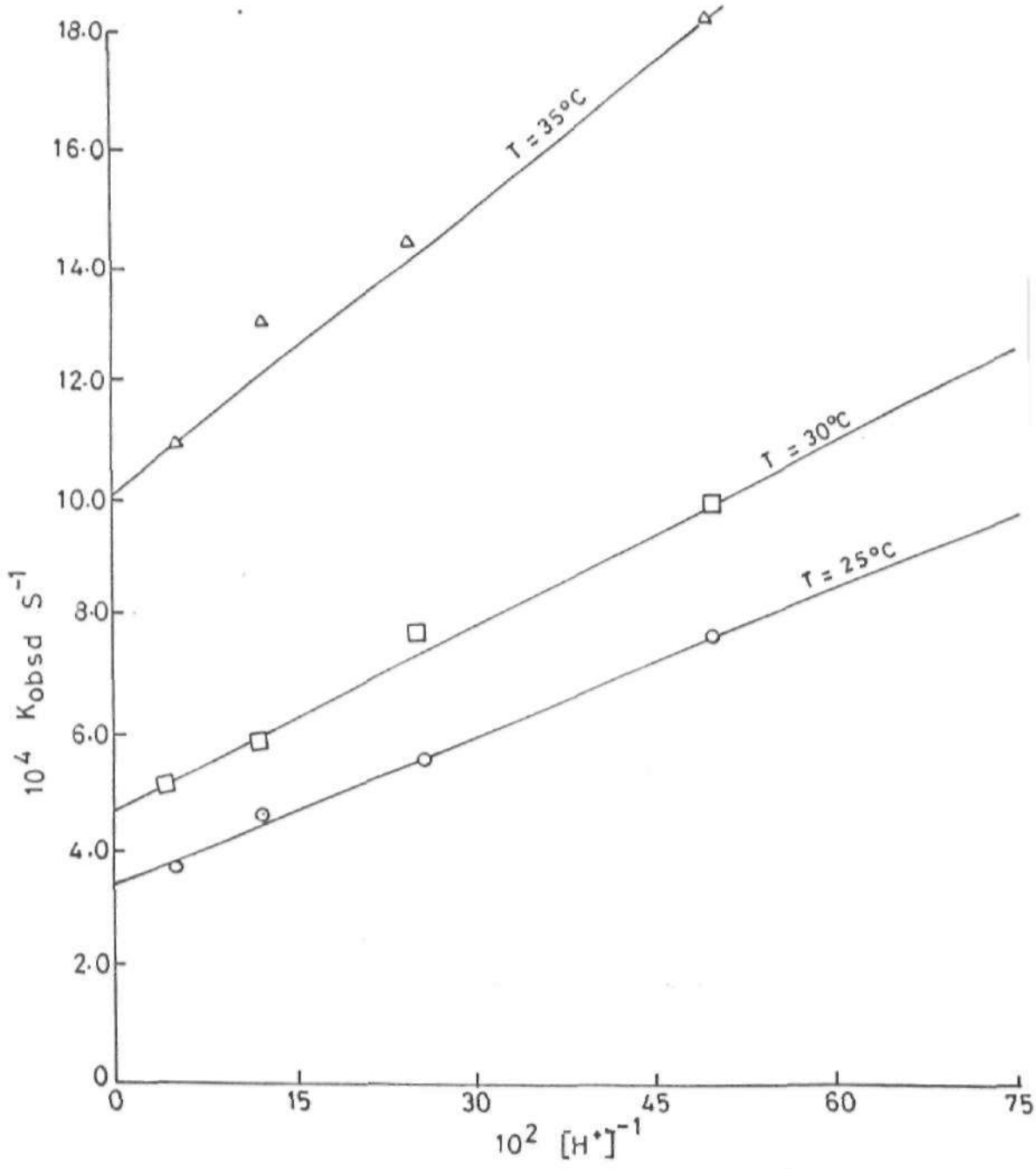



FIG. 4.14. TYPICAL PLOT OF $K_{obsd}$ VERSUS $[H^+]^{-1}$ FOR REDOX REACTIONS OF $RuORu^{4+}$ AND L – CYSTEINE.

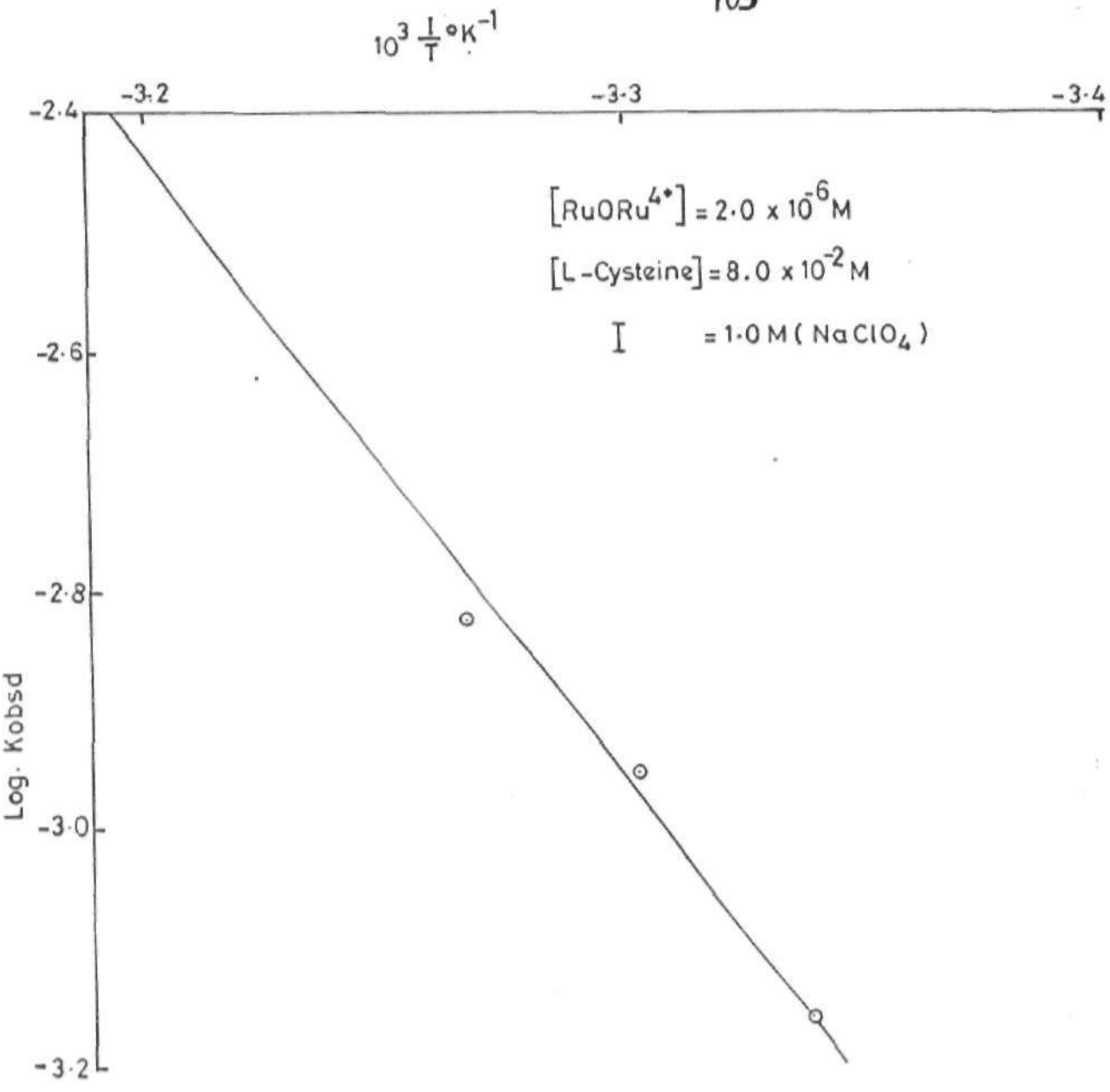



FIG. 4.15 TYPICAL ARRHENIUS PLOT FOR THE REDOX REACTIONS OF $RuORu^{4+}$ AND L-CYSTEINE

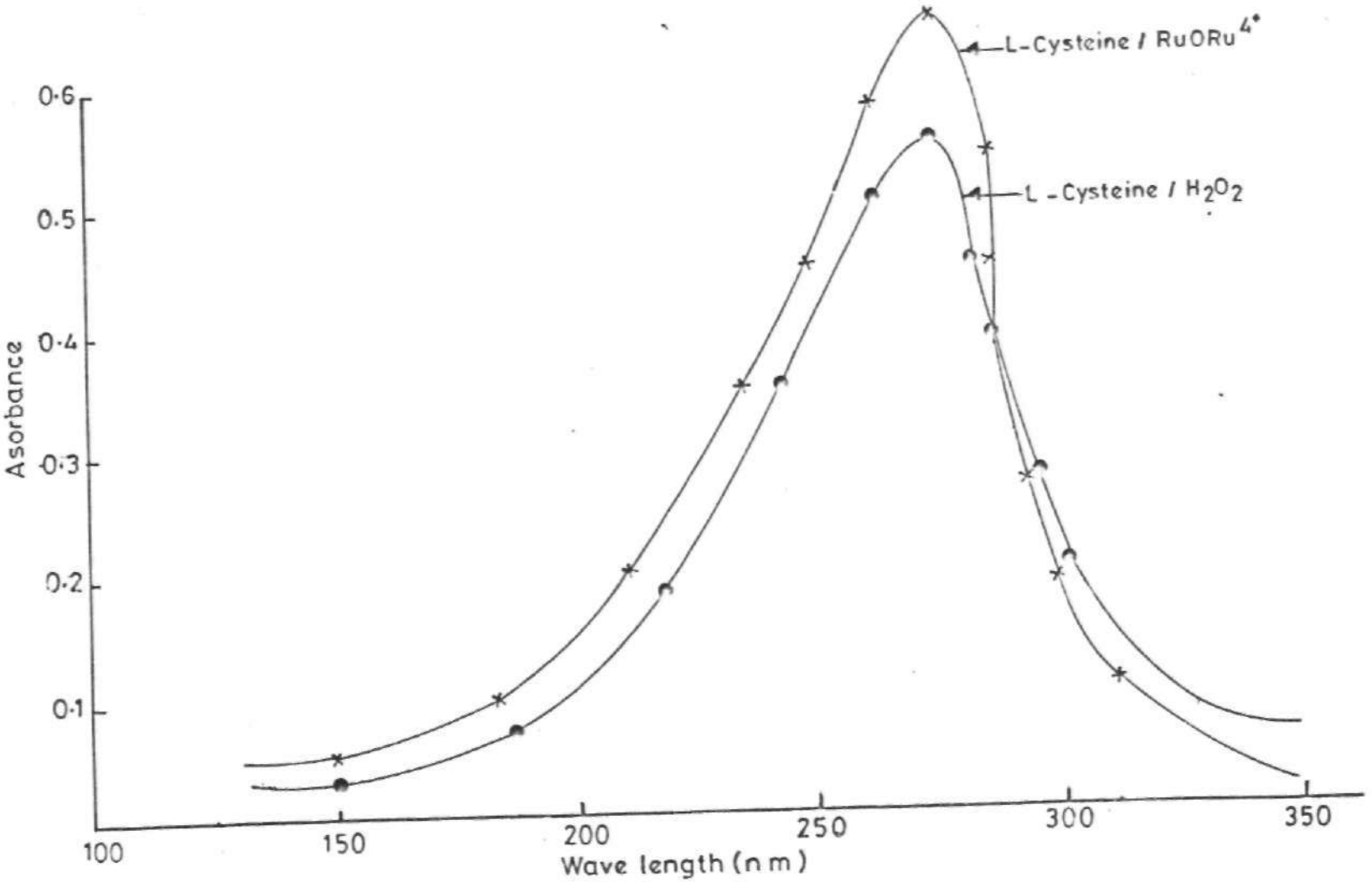



FIG. 4.16 ; Uv / VISIBLE SPECTRA OF PRODUCTS OF THIOL (L-CYSTEINE) OXIDATION BY $RuORu^{4+}$ AND $H_2O_2$ AFTER 18 HOURS.

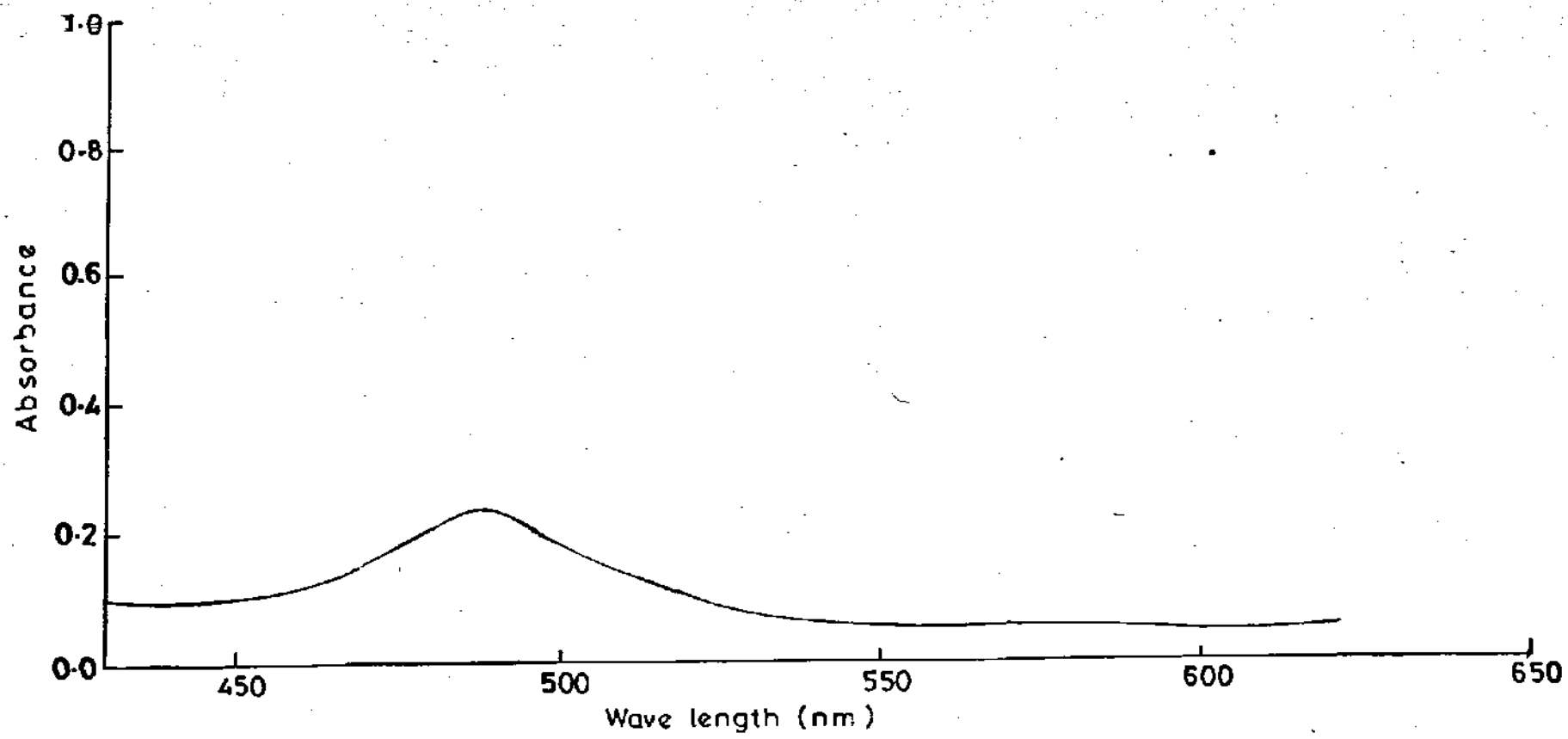



FIG. 4.17 SPECTRUM OF THE PRODUCTS OF THE REDOX REACTION (FOR THE FIVE SYSTEMS)

# CHAPTER FIVE

## 5.0 DISCUSSION

### 5.1 $RuORu^{4+}$-Thiols Systems

The stoichiometries for the reactions indicated that one mole of the reductants (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) is consumed by one mole of the oxidant ($RuORu^{4+}$), (equation 4.1). This result is consistent with reaction of L-cysteine with chromium (VI) (McCann and McAuley, 1975) 12-tungstocobaltate (III) (Ayoko and Olatunji, 1983), Cu(II)-2,9-Dimethyl-1,10-phenanthroline (Gary and Robert, 1984). Mercaptoacetic acid and β-mercaptoethylamine were reported to undergo 1:1 stoichiometric reaction in redox reaction with 12-tungestocobaltate(III) ion reported by Olatunji and Ayoko (1983). Other stoichiometric ratios were reported for the redox reaction of thiols L-cysteine, reaction with Mo (VI) and peroxide - Bound chromium(IV) (Martin and Spence, 1970; Gould and Gosh, 1989) indicated a 1:2 and 1:5 stoichiometry reductant: oxidant respectively and 2-mercaptoethanol reaction with Se(IV) a 1:4 stoichiometry was observed (Resat *et al*, 1989). The oxidant ($RuORu^{4+}$) redox reactions with

various substrates were reported to shown varying stoichiometric ratios. The oxobridged ruthenium dimer reaction with $I^-$, $SO_3^{2-}$, $Fe(H_2O)_6^{2+}$ and glutathione (Iyun et al, 1992; and 1993) a 1:1 stoichiometry was observed. And 5:1 and 2:1 stoichiometry in its reaction with $BrO_3^-$ (Iyun et al, 1992) and hydroquinone (Iyun, Ayoko and Lawal, 1992) respectively.

Kinetics studies of the thiols (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol (RSH) with the oxobridged ruthenium dimer ($RuORu^{4+}$) have shown that the reaction is first-order in both the oxidant and reductants concentration as illustrated in equation (5.1).

$$-\frac{d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][RSH] \quad \ldots\ldots (5.1)$$

Under the experimental conditions used for these reaction $k_2$ was evaluated as $k_2 = 2.02 \pm 0.2 M^{-1}s^{-1}$ (L-cysteine); $(8.93 \pm 0.06) \times 10^{-2} M^{-1}s^{-1}$ (mercaptoacetic acid); $(2.24 \pm 0.02) \times 10^{-2} M^{-1}s^{-1}$ (β-mercaptoethylamine) and $(4.54 \pm 0.01) M^{-1}s^{-1}$ 2-mercaptoethanol. All the reactions were carried out at ionic strength I = 1.0M ($NaClO_4$) and T = 25.0 ± 0.1°C.

The acid dependence observed for the reaction of thiols with the oxidant in this investigations suggest the release of proton in pre-equilibrium step, that is, the deprotonation of sulphydryl group (-SH) of the thiols or this could also arised by the depronotation of potentially acidic aqualigand of the oxobridged ruthenium dimer. The later possibility is ruled out by the stability of the oxobridged dimer in acidic and anionic media reported by (Iyun, Ayoko and Lohdip, 1992). This suggests that it may be relatively inert. The inverse hydrogen ion concentration dependence for the thiols oxidation were earlier reported for the reaction of L-cysteine, mercaptoacetic acid and ß-mercaptoethylamine with 12-tungestocobaltate(III) ion (Olatunji and Ayoko, 1983) thiols oxidation of the metals (Kuyundzic and Everse, 1979). Similar result were reported for the oxidation of 2-mercaptoethanol by ferricyanide (Meehan et al, 1962). Se(IV) (Resat et al, 1989) reduction by 2-mercaptoethanol, the rate is proportional to inverse square root of hydrogen ion concentration. However, cysteine oxidation by Goswami et al, (1981) reported an increased in rate with increasing hydrogen concentration. But cysteine, cysteine methyl ester and penicillamine (2-mercaptovaline) oxidation by copper (II)-2,9-Dimethyl-

1,10-phenonthroline (Gary and Robert, 1981) and L-cysteine and mercaptoacetic acid oxidation by peroxide-Bound-chromium (IV) (Gould and Gosh, 1989) were all reported to show an acid independent path within the pH range used for the kinetic investigation.

In the redox reaction of ($RuORu^{4+}$) with various substrates, various types of acid dependencies of the reaction rates were observed. In the oxidant reaction with $SO_5^{=}$ and glutathione (Iyun et al, 1992; 1993) an inverse acid $[H^+]^{-1}$ was reported. With hydroquinone and $BrO_3^-$ (Iyun et al, 1992) an acid-independent and an $[H^+]^2$ term were observed respectively. The oxidation of $I^-$ and $Fe(H_2O)_6^{2+}$ and reduction of $IO_4^-$ (Iyun et al, 1992) by the oxobridged ruthenium dimer were all $[H^+]$ dependent.

The rate law for the reaction of the thiols (RSH) and the oxobridged ruthenium dimer ($RuORU^{4+}$) can thus be represented by equation (5.2) and (5.3)

$$-\frac{d[RuORu^{4+}]}{dt} = a[H^+]^{-1}[RuORu^{4+}][RSH] \quad \ldots (5.2)$$

Where RSH = L-cysteine, mercaptoacetic acid, and
ß-mercaptoethylamine

$$- d[RuORu^{4+}] = (C + b[H^+]^{-1})[RuORu^{4+}][RSH] \quad \ldots \quad (5.3)$$

RSH = 2-mercaptoethanol.

Possible mechanisms consistent with the result obtained for the reaction of the oxobridged ruthenium dimer with thiols (L-cysteine, mercaptoacetic acid, ß-mercaptoethylamine and 2-mercaptoethanol) are given below.

<u>L-Cysteine-$RuORu^{4+}$ reactions</u>

Mechanism I

$$RSH \overset{K_a}{\Longleftrightarrow} RS^- + H^+ \qquad \ldots\ldots \quad (5.4)$$

$$RSH + RuORu^{4+} \xrightarrow{k_1} RS^{\cdot} + RuORu^{3+} + H^+ \qquad \ldots \quad (5.5)$$

$$RS^- + RuORu^{4+} \xrightarrow{k_2} RuORu^{3+} + RS^{\cdot} \qquad \ldots \quad (5.6)$$

$$2RS^{\cdot} \xrightarrow{\text{fast}} RSSR \qquad \ldots\ldots \quad (5.7)$$

$K_a$ = The acid dissociation constant for the sulphydryl group (-SH) in L-cysteine.

From the above reaction schemes, the rate of the reaction could be derived as follows.

$$-\frac{d[RuORu^{4+}]}{dt} = k_1[RSH][RuORu^{4+}] + k_2[RS^-][RuORu^{4+}] \quad \ldots\ldots (5.8)$$

If $k_2 >> k_1$ equation (5.8) becomes

$$-\frac{d[RuORu^{4+}]}{dt} = k_2[RS^-][RuORu^{4+}] \quad \ldots\ldots (5.9)$$

substituting for $RS^-$ from equation (5.4) gives

$$-\frac{d[RuORu^{4+}]}{dt} = k_2K_a[RuORu^{4+}][RSH][H^+]^{-1} \quad \ldots\ldots (5.10)$$

This equation is similar to equation (5.2) with

$$a = k_2K_a$$

Hence the proposed mechanism correspond to the result obtained.

<u>Mercaptoacetic acid-$RuORu^{4+}$ reaction</u>

Mechanism II

$$RSH \overset{K_a}{\rightleftharpoons} RS^- + H^+ \quad \ldots\ldots (5.11)$$

$$RuORu^{4+} + RS^- \overset{K_{com}}{\rightleftharpoons} [RuORu^{4+}], RS^- \quad \ldots\ldots (5.12)$$

$$[RuORu^{4+}], RS^- + RSH \xrightarrow{k_2} RuORu^{2+} + RSSRH \quad \ldots\ldots (5.13)$$

$$RuORu^{4+} + RSSRH \overset{\text{fast}}{\rightleftharpoons} RuORu^{3+} + RSSR + H^{+} \quad \ldots\ (5.14)$$

Applying steady state approximation to the concentration of $RuORu^{4+}$ complex, the following rate law is arrived at.

$$-\frac{d[RuORu^{4+}]}{dt} = \frac{k_b K_{a_1} K_w [RSH][RuORu^{4+}]}{[H^+] + K_{a_1} K_w [H^+][RSH]} \quad \ldots\ (5.15)$$

If $[H^+] \gg K_{a_1} K_w [H^+][RSH]$

$$-\frac{d[RuORu^{4+}]}{dt} = \frac{k_b K_{a_1} K_w [RSH][RuORu^{4+}]}{[H^+]} \quad \ldots\ (5.16)$$

The equation is identical with the rate expression in equation (5.2) with $a = k_b K_{a_1} K_w$. Thus the proposed meachinsm is in line with the result obtained.

<u>β-mercaptoethylamine-$RuORu^{4+}$ reaction</u>

The $pK_w$ corresponding to the loss of a proton from -SH and $NH_3^+$ groups is greater than 8 (Wilson and Martin, 1971; Morris, 1974). If the rate of protonation of RSH is diffusion controlled, the rate of dissociation of such a protonated species may be estimated from the dissociation constant of thiol group (McCann and McAuley, 1975; McAuley and Olatunji, 1977).

Thus,

$$RSH \overset{K_a}{\Longleftrightarrow} RS^- + H^+ \quad \ldots\ldots \quad (5.17)$$

$$K_a = K_a/k_{-a} \quad \ldots\ldots\ldots \quad (5.18)$$

$$\text{or } K_a = 10^{10}K_a \quad \ldots\ldots\ldots \quad (5.19)$$

Since the value of $K_a$ is approximately $10^{-7} - 10^{-9}$ the value of $K_a$ can be obtained in equation (5.19) is of order $10^2 - 10^3 s^{-1}$, the value is much higher than the observed rate constant for this electron transfer reaction. It is therefore reasonable to assume that the dissociation of -SH preceed electron transfer. The following mechanism is therefore proposed for the reaction of $RuORu^{4+}$ and β-mercaptoethylamine.

Mechanism III

$$2RSH \overset{k_a}{\Longleftrightarrow} 2RS^- + 2H^+ \quad \ldots\ldots \quad (5.20)$$

$$[RuORu]^{4+} + RS^- \overset{K_{os}}{\Longleftrightarrow} [RuORu]^{4+},RS \quad \ldots\ldots \quad (5.21)$$

$$[RuORu]^{4+},RS^- + RS^- \overset{k_A}{\longrightarrow} [RuORu]^{3+} + RSSR^- \quad \ldots \quad (5.22)$$

$$[RuORu]^{4+} + RSSR^- \overset{fast}{\longrightarrow} [RuORu]^{3+} + RSSR \quad \ldots \quad (5.23)$$

$K_{os}$ is the outer-shere equilibrium constant.

Based on the reaction scheme the rate of loss of $RuORu^{4+}$ is given by equation (5.24).

$$-\frac{d[RuORu^{4+}]}{dt} = \frac{k_a K_{os} K_a [RSH]^2 [RuORu^{4+}]}{[H^+]^2 + K_{os} K_a^{1/2} [RSH][H^+]} \quad \ldots (5.24)$$

if $[H^+]^2 << K_{os} K_a^{1/2} [RSH][H^+]$, then

$$K_{obs} = \frac{K_a K_{os} k_a [RSH]^2 [RuORu^{4+}]}{K_{os} K_a^{1/2} [RSH][H^+]} \quad \ldots . (5.25)$$

$$= \frac{K_a k_a^{1/2} [RSH][RuORu^{4+}]}{[H^+]} \quad \ldots . . (5.26)$$

The equation (5.26) is in agreement with equation (5.2) with $a = k_a k_a^{1/2}$

Another mechanism which is also consistent with the observed experimental data is given below.

Mechanism IV

$$[RuORu]^{4+} + RSH \overset{k_{os}}{\Longleftrightarrow} [RuORu]^{4+}, RS^- + H^+ \quad \ldots (5.27)$$

$$[RuORu]^{4+}, RS^- \overset{k_s}{\longrightarrow} [RuORu]^{3+} + RS \quad \ldots . (5.28)$$

$$2RS \cdot \overset{fast}{\longrightarrow} RSSR \quad \ldots . . (5.29)$$

This mechanism is in agreement with the rate law,

$$-\frac{d[RuORu^{4+}]}{dt} = K_s K_{os} [RuORu^{4+}][RSH][H^+]^{-1} \quad \ldots (5.30)$$

This mechanism agrees with the experimental rate law in equation (5.2) with a = $K_a K_{cm}$.

2-mercaptoethanol - $RuORu^{4+}$ reaction

The following mechanism is proposed based on the experimental results obtained for the reaction.

Mechanism V

$$RSH \overset{K_a}{\rightleftharpoons} RS^- + H^+ \quad \ldots\ldots (5.31)$$

$$[RuORu]^{4+} + RS^- \overset{K_{1,2}}{\rightleftharpoons} [RuORu]^{4+},RS^- \quad \ldots\ldots (5.32)$$

$$[RuORu]^{4+} + RSH \xrightarrow{k_a} [RuORu]^{3+} + RS + H^+ \quad \ldots (5.33)$$

$$[RuORu]^{4+},RS^- \xrightarrow{k_2} [RuORu]^{3+} + RS \cdot \quad \ldots\ldots (5.34)$$

$$2RS \cdot \xrightarrow{\text{fast}} RSSR \quad \ldots\ldots\ldots (5.35)$$

With equations (5.33) and (5.34) as the rate determining steps the rate equation can be written as

$$-\frac{d[RuORu^{4+}]}{dt} = K_a[RuORu^{4+}][RSH] + k_2[RuORu^{4+},RS^-] \quad \ldots\ldots (5.36)$$

Substituting for $[RuORu^{4+},RS^-]$ from equation (5.32) gives

$$-\frac{d[RuORu^{4+}]}{dt} = k_a[RuORu^{4+}][RSH] + k_2K_{1,2}[RuORu^{4+}][RS^-] \quad \ldots\ldots (5.37)$$

Substituting for $RS^-$ from eaquition (5.31) gives

$$-\frac{d[RuORu^{4+}]}{dt} = k_6[RuORu^{4+}][RSH] + \frac{k_7K_1K_a[RuORu^{4+}][RSH]}{[H^+]} \quad \ldots(5.38)$$

$$-\frac{d[RuORu^{4+}]}{dt} = [RuORu^{4+}][RSH]\left(k_6 + \frac{K_aK_1k_7}{[H^+]}\right) \quad \ldots\ldots (5.39)$$

This equation is in agreement with the experimentally obtained rate law (5.3) with $c = k_6$ and $b = k_1K_ak_7$. Thus the proposed mechanism is consistent with the experimental result obtained.

The negative salt effect observed in the reaction of L-cysteine, B-mercaptoethylamine and 2-mercapto-ethanol with the oxobridged dimer indicated that unlike charges are interacting in the activated complex (Wilkins, 1977). This agrees with equations (5.6), (5.21) and (5.32) in the proposed reaction schemes. And the positive salt effect observed for the reaction of mercaptoacetic acid with the oxobridged dimer also agrees with the equation (5.13) in the proposed reaction scheme in which like charges are interacting or a charge reactant with a neutral molecule (Wilkins, 1977).

The presence of gel formation resulting from polymerisation, when acrylamide was introduced into the reaction mixture observed in all the substrate (L-

cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) oxidation by the oxobridged ruthenium dimer, suggests the presence of free-radical as the possible intermediate in these reactions. Free radical intermediate formation has been previously reported for varieties of thiols reactions (Karmann et al, 1968). Ayoko and Olatunji, (1985), also reported the presence of free radical intermediate in various thiols reaction. Ayoko and Olatunji (1983) reported the oxidation of L-cysteine, mercaptoacetic acid and β-mercaptoethylamine by 12-tungstocobaltate (III) ion proceed via a free-radical formation mechanism. Similar observation was reported for L-cysteine and mercaptoacetic acid oxidation by [illegible]-Bound-chromium (IV) (Gould and Gosh, 1989) and 2-mercaptoethanol reaction with Se(IV) (Resat et al, 1989) and most recently the report of Iyun, Ayoko and Ekubo (1993) on the glutathione oxidation by diaquotetrakis (2,2-bipyridine)-μ-oxo-diruthenium (III) ion, the reaction proceed via free radical formation mechanism. Therefore the observed free radical intermediate formation for the reaction of thiols with the oxobridged dimer reported in this work agrees with a literature observation that thiols compounds react in the s-deprotonated form to give

thiyl radicals ($RS\cdot$) i.e, the intermediate for disulphide formation (Grachev and Soroka, 1981).

The observed anions ($Cl^-$, $NO_3$, $CH_3COO^-$ and $SO_4^{=}$) catalysis on the reaction rate for the reaction of L-cysteine and mercaptoacetic acid with oxobridged dimer and the cation ($Na^+$, $K^+$, $Rb^+$ and $Mn^{2+}$) acceleration of the rate for the reaction of mercaptoacetic acid with the oxobridged dimer suggest that the reaction occurs by outer-sphere mechanism. Ions catalysis of the reaction rate were ealier reported as characteristic of an outer-sphere reactione (Pennington and Haim, 1967; Przystas and Sutin, 1973; Adegite et al; 1977). Although cation and anion catalysis was not observed in the reaction of ß-mercaptoethylamine and 2-mercaptoethanol with the oxobridged dimer, this does not rule out the possibility of the outer-sphere mechanism for these reactions, since the rate-determining steps for these equations (5.22) and (5.35) are the dissociation of the ion-pair. Therefore the anions and cations are excluded in the activated complex formation, hence the expected catalysis by the ions cannot be observed. Outer-sphere redoxx reaction accompanied by anion catalysis was reported for the redox reaction of the oxidant ($RuORu^{4+}$) with $BrO_3^-$, $SO_3^{=}$ and 1,4-benzene diol (Iyun et al, 1992).

Further support for outer-sphere mechanism for these reactions (thiols/$RuORu^{4+}$) systems is observed by lack of intermediate complex formation in these reactions. This was proved by absence of any shift in $\lambda max$ nor an enhancement of absorbance when the spectra of the reaction mixtures for the individual thiols and the oxidant were run two minutes after the initiation of the reaction (in each case). The result indicated that there was no spectroscopic evidence for intermediate complex formation prior to the electron transfer step. To buttressed this evidence, Michaelis-Menten plots of $1/k_{obsd}$ versus $1/[RSH]$ (RSH = L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) (fig 4.10) were carried out, and all these were found to be linear passing through the origin with no intercept, this further suggests absence of any detectable intermediate of significance stability. Therefore the reactions of all the thiols with the oxobridged dimer occurs by the outer-sphere mechanism. In this respect the mechanism is similar to the one proposed for the reaction of L-cysteine, mercaptoacetic acid and β-mercaptoethylamine with 12-tungestocobaltate (III) ion (Olatunji and Ayoko, 1983) and glutathione oxidation by the oxobridged ruthenium dimer (Iyun et al, 1993),

oxobridged ruthenium dimer reaction with some oxyanions ($BrO_3^-$, $SO_3^{2-}$) (Iyun et al, 1992), all were found to proceed via outer-sphere mechanism.

Unfortunately, the absence of requisite data could not allow the Marcus theory (Marcus, 1963) to be tested for these reactions. However from the observed data, it is possible to assume that the reaction of $RuORu^{4+}$ with the thiols (L-cysteine, mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) all proceed by outer-sphere mechanism.

## 5.2 $RuORu^{4+}$ - Resorcinol system

The stoichiometric studies for the reaction indicated one mole of the reductant per two moles of the oxidant in excess of $RuORu^{4+}$ (equation 4.2). This value is consistent with that reported for 1,4-benzene diol reaction with the oxobridged ruthenium dimer ($RuORu^{4+}$) (Iyun et al, 1992), resorcinol oxidation by vanadium (Mittal and Mehrotta, 1965) and cerium (Yadav and Verma, 1981).

First-order dependence on each of the reactants is commonly encountered in the reaction of dihydroxybenzenes (Verma and Yadav, 1981; Iyun et al, 1992). This is illustrated by equation (5.40)

$$-\frac{d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][H_2Q] \quad \ldots\ldots \quad (5.40)$$

An inverse first-order hydrogen ion dependence has been featured in the reaction of dihydroxybenzenes with metal complexes, outer-sphere oxidation of hydroquinone by $Cu(dmp)_2^{2+}$ (Clemmer et al, 1979), 1,4- and 1,2-dihydroxybenzene oxidation by $[Ru(CN)_6]^{2-}$ (Macartney et al, 1990), 1,4-dihydroxybenzene oxidation by the oxobridged ruthenium dimer (Iyun et al, 1992). Similarly, an inverse first-order hydrogen ion dependence has been observed in resorcinol - $RuORu^{4+}$ reaction. This conforms to the equation;

$$k_2 = a[H^+]^{-1} \quad \ldots\ldots \quad (5.41)$$

The overall rate law for the reaction can be written as in equation (5.42).

$$-\frac{d[RuORu^{4+}]}{dt} = a[H^+]^{-1}[RuORu^{4+}][H_2Q] \quad \ldots\ldots \quad (5.42)$$

The observed acid dependence could be due to the thermodynamic stability of the phenolate ion (Clemmer et al, 1979). From the data obtained the following reaction schemes can be proposed for the reaction of the oxobridged dimer with resorcinol.

$$H_2Q \xrightleftharpoons{K_1} HQ^- + H^+ \quad \ldots\ldots (5.43)$$

$$[RuORu^{4+}] + HQ^- \xrightleftharpoons{K_{1,c}} [RuORu]^{4+}, HQ^- \quad \ldots\ldots (5.44)$$

$$[RuORu^{4+}], HQ^- \xrightarrow{K_a} RuORu^{3+} + HQ \quad \ldots\ldots 5.45$$

$$[RuORu]^{4+} + HQ \xrightarrow{fast} RuORu^{3+} + H^+ + Q$$

$$\ldots (5.46)$$

With equation (5.45) as the rate-determining step, the rate equation can be written as

$$-\frac{d[RuORu^{4+}]}{dt} = K_a[RuORu^{4+}, HQ^-] \quad \ldots\ldots (5.47)$$

Applying steady state approximation to the concentration of $[RuORu^{4+}, HQ^-]$ substituting for $[RuORu^{4+}, HQ]$ from equation (5.44) gives

$$-\frac{d[RuORu^{4+}]}{dt} = K_a K_{1,c}[RuORu^{4+}][HQ^-] \quad \ldots\ldots (5.48)$$

Substituting for $[HQ^-]$ from equation (5.43) in equation (5.48) gives

$$-\frac{d[RuORu^{4+}]}{dt} = \frac{K_a k_a k_{1,2}[RuORu^{4+}][H_2Q]}{[H^+]} \quad \ldots\ldots (5.49)$$

This equation is identical with experimental rate equation (5.42) with $a = k_a K_{1,2} k_a$.

The positive salt effect (Bronsted, 1922) observed in this redox reaction is in line with the proposed reaction scheme (5.45) . Free radical test was found to be negative, but this does not completely negate the formation of radical in the reaction. Report on the hydroquinone reaction with $[Ru(CN)_6]^{3-}$ (Macartney et al, 1990) the rate determining is one-electron oxidation of $H_2Q$ or $HQ^-$ which are rapidly followed by second one-electron oxidation of the semiquinone radical $HQ\cdot$. Baxendale and Hardy (1951) reported that the semiquinone free radical is so reactive that on most systems it cannot be observed experimentally, accounting probably for the lack of free radical trapping experiment. Free radicals are commonly observed in most of the reaction of dihydroxybenzene (Rykova et al, 1978).

Addition of cations ($Li^+$, $Na^+$, $K^+$, $Pb^+$, $Mg^{2+}$ and $Mn^{2+}$) and anions ($Cl^-$, $NO_3^-$ and $SO_4^{2-}$) were found to have no effect on the reaction rates. A characteristic

of an inner-sphere reaction mechanism (Przstas and Sutin, 1973; Adegite et al, 1977). Lack of ions catalysis observed in the reaction of resorcinol with $RuORu^{4+}$ may be due to electron transfer in the rate-determining step (equation 5.45) occurs within an ion pair complex, therefore the ion catalysis can not be observed.

Michaelis-Menten plot of $1/k_{obsd}$ versus $1/[H_2Q]$ pass through the origin, fig (4.10) indicating the absence of complex formation. The spectrum of the reaction mixture was run one minute after the initiation of the reaction and the spectrum was compared to that of oxobridged dimer, no any shift observed in the λmax 658nm, characteristic of the oxobridged dimer. This suggest that an intermediate complex is most likely not formed between the reactants. This observation suggests resorcinol - $RuORu^{4+}$ reactions occur via outer-sphere mechanism. Based on the observed results an outer-sphere mechanism can safely be proposed for the reaction of the oxobridged dimer with resorcinol.

## Summary and Conclusion

The redox reactions of diaquotetrakis 2,2-bipyridine)-μ-oxo-diruthenium(III) ion was studied with thiols (L-cysteine mercaptoacetic acid, β-mercaptoethylamine and 2-mercaptoethanol) and resorcinol in acid medium. The rates of all the reactions showed inverse hydrogen ion dependence. This shows deprotonation of the reductant.

The stoichiometries were 1:1 for the $RuORu^{4+}$ thiols reactions, while 2:1 oxidant: reductant was observed for the $RuORu^{4+}$-resorcinol reaction. The thiols reaction gave a disulphide product.

The rate of reaction of the oxidant with cysteine was found to be catalysed by added anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$) while that of mercaptoacetic acid was catalysed by both the anions and cations ($Li^+$, $Na^+$, $K^+$, $Rb^+$, $Mn^{2+}$). But the rate of reaction of β-mercaptoethylamine, 2-mercaptoethanol and resorcinol with the oxidant were found to be independent of the added ions. Free radical intermediate formation was observed for all the thiols - oxidant ($RuORu^{4+}$) reactions but it was not observed in case of resorcinol - oxidant-reaction. The product for all the systems was found to observed at about 485nm.

This probably correspond to the absorption band of a mixed-valenced complex $RuORu^{5+}$.

The following rate constants for the reactions of the oxidants and the reductants were observed.

$k_{obs}$ (L-cysteine) = $2.02M^{-1}s^{-1}$, $k_{obs}$ (mercapto acetic acid = $8.98 \times 10^{-2}M^{-1}s^{-1}$, $k_{obs}$ (β-mercaptoethylamine) = $2.28 \times 10^{-1}s^{-1}$, $k_{obs}$ (2-mercaptoethanol) = $4.54M^{-1}s^{-1}$, $k_{obs}$ (resorcinol) = $8.35 \times 10^{-2}M^{-1}s^{-1}$.

On the basis of the results of these investigations, the absence of both spectroscopic and kinetic evidence of complex formation prior to electron-transfer and non-conformity of the results with Michaelis-Menten equation, it is suggested that all the reactions of the $RuORu^{4+}$ with the reductants studied in this project, probably proceed by outer-sphere mechanisms and the mechanism is proposed for all the systems.

## REFERENCES

Adegite, A., Iyun J.F and Ojo, J.F (1977). Kinetics and mechanism of Electron-Transfer Reaction Between Uranium(III) and some Ruthenium(III) Ammines Complexes J. Chem. Soc. Dalton Trans. 115.

Adegite, A. and Iyun J.F (1979). Kinetics and Mechanism of Oxidation of $Ti(H_2O)_6^{3+}$ and Ti(EDTA) by Aqueous solution of Iodine Inorg. chem 18: 3602.

Akhtar, M.J. and Haim, A. (1988). Kinetics and Mechanism of the reaction of mononuclear and Binuclear Ruthenium (III) ammines complexes with Ascorbic acid Inorg. Chem. 27: 1608.

Ayoko, G.A. and Olatunji M.A. (1983). Oxidation of L-cysteine, Mercaptoacetic acid and β-mercaptoethylamine by 12-tungstocobaltate (III) ion Polyhedron 2,7: 577.

Baker Bryun, W. (1983) Self-Decomposition of Radio chemicals. Chem. abstr. 98. 212480c.

Basolo, F. and Pearson, R.G (1967). Mechanism of inorganic reaction, A study of metal complexes in solution. Wiley and Sons Inc. New York. 454-525.

Baumann, J.A. and Meyer, T.J. (1980). Oxo-bridged ion $[(NH_3)_4RuORu(NH_3)_4]^{n+}$ (n = 4, 5) Inorg Chem. 19: 345.

Baxendale, J.H. and Handy, H.R. (1951). Kinetic and equilibria in solution containing Ferrous ion, ferric ion hydroquinone and quinone Trans. Faraday Soc. 47 963.

Beatle, J.K and Haigh Jnr. P.G. (1972). Chromium (IV) oxidation of inorganic substances Prog. Inorg. Chem 17:93.

Brigart, G.L., Fuller, M.W. and Wilson I.R (1973). J. Chem. Soc. A 1274.

Bronsted, J.N. (1922). Kinetic of aquotization Z. Phys. Chem 102:160.

Burgess J. (1988). Metal ions in solutions. Wiley, New York. Chapter 3.

Caldin, E.F (1974). Fast Reaction in solutions. Backwell Oxford.

Chaffee E. and Edward J.O. (1970). Inorganic Reaction Mechanism Wiley, New York pg 216.

chi-Ming, C; Kwak, Y.N; Wai-Ho.1 and Chung-Kwong, P (1986). A high-valent Dioxoruthenium (III) complex of 2,2-bipyridine (bpy-preparation and characterisation of trans-[Ru(bipy)$_2$(H$_2$O)]$^{2+}$. Inorg. Chem 25: 345.

Clemmer, J.D; Hogaboom, G.K and Holwerda R.A (1979). Reduction of the bis (2,9-dimethyl-1,10-phenonthroline) Copper (II) ion by substituted hydroquinones. Inorg. Chem. 18: 2567.

Cotton, F.A. and Wilkinson, G. (1980). Advanced inorganic chemistry Fourth edn. Wiley Inter. New York. Lodon, Sydney and Toronto. pg. 154.

Davies, K.M. and Early J.E (1978). Linear free energy relationship for outer-sphere Reduction of ruthenium (III) ammines complexes of Titanium (III) Inorg. Chem. 17: 3350.

Diebler H. and Sutin. N. (1964). The kinetic of some oxidation-reduction reaction involving Manganese (III) J. Phys. Chem. 68: 174.

Dokiya, Y; Ashikawo, H; Yamataki, S. and Fuwa, K. (1974). Loss of trace element from natural water during storage Spectroscop Lett. 7: (11) 551-556.

Early, E.J. (1970). Non-bridging ligand in electron-transefer reaction. Prog. Inorg. Chem 13: 243.

Eigen, M. and Meyer, L.D (1963). Techniques of organic chemistry. Ed. S.L. Friess E.S Lewes and A. Weissberger, 2nd edn Interscience, New York Vol. 8 pg 895.

Erneat Baldwin (1948). "Dynamic Aspect of Biochemistry" University Press Cambridged, pg 233.

Espenson, J.H. (1965). Kinetics and Mechanism of reaction of Fe(III) and acidopenta ammines Co(III) ion Inorg. Chem 4:121.

Espenson J.H. (1981). Chemical Kinetics and reaction mechanism McGraw-Hill, series in advanced chemistry.

Gary, D.S. and Robert, A.H. (1984). Oxidation of cysteine, cysteine methyl esters and penicillamine by copper (II)-2,9-Dimethyl-1,10-phenanthroline comple-xes. Inorg. Chem. 23: 2777-2780.

Gilbert Bruce A.; Lane, Hugh; Norman, A.H., Richard, O.C. and Sealy, R.C. (1975). electron spin resonance studies XLVI oxidation of thiols to disulphides in aqueous solution, formation of thinyl, sulphinyl and

sulphony radicals anions and carbon radicals. J. Chem. Soc. Perkin Trans. 2 9: 892-900.

Gomwalk, U.D. and McAuley, A. (1968). Metal ion oxidation in solutions part V cerium (IV) oxidation of thiourea and its N-substituted Deriatives J. Chem. Soc. A 2948.

Goswami, K.B; Chandr G. and Srivastava, S.N (1981). Kinetics of chromic acid oxidation of serine, methione and cysteine J. Ind. Chem. Soc LVIII: 252-258.

Gould, E.S. and Gosh, S.K. (1989). Electron Transfer. Iron-catalysed Reduction of peroxide-Bound-chromium(IV) with mercaptoacids Inorg. Chem. 28: 3651-3655.

Grachev, S.A. and Soroka, N.V. (1981). Preparation of thinyl radicals and the study of their reaction with oxygen and 2-sulphoethyl thiosulphate Izv. Akad. Nauk SSSR 8: 1756 (Chem. abstr. 1981: 95, 186357m).

Haque, D.N (1972). Fast reactions Wiley Interscience

Hill, J. McAuley, A. and Pickering, W.F (1967). Spectra evidence for intermediate in oxidation of α-mercaptans. Chem. Comm. 573-574.

Hill, J. and McAuley, A. (1968). Metal-ion oxidation in solution (II) oxidation of malic acid by cobaltic ions J. Chem. Soc A 1169.

Hill. J. and McAuley, A (1968). Metal-ion oxidation in solution (IV) oxidation of thiomalic acid by cobaltic ion J. Chem. Soc. A 2405.

Holden J.W. and Main Lyndsay (1977). Kinetics and mechanism of oxidation of mercaptoethanol by Riboflavin Aust. J. Chem. 30(6) 1387-1391.

Huchital, D.H. and Hodgee, R.T. (1971). Interaction of multidentate Cobalt(II)-chelate complexes with Ferricyanate Ion: $Co^{II}$EDTA and CoCYDTA. Inorg. Chem. 998.

Hunti J.P. (1963) Metal ions in Aqueous solution Benjamin, New York.

House, Roy, Francis; Hoover, L.D (1982). Composition for improving viscosity of brines for well maintanance fluids (NL industries) Inc. (1982). Chem. Abstr 98: 110298g

Hyser, E.S; Tang-H. Sia O - Nein (1978). Kinetics analysis of Methylene Blue oxidation of thiols Sym. Ser. 69: 258-274.

Iyun, J.F. (1982). Kinetics and Mechanism of oxidation-reduction and substitution reactions of some metal ions complexes in acid solution Ph.D Thesis, Ahmadu Bello University, Zaria Nigeria

Iyun, J.F. and Adegite, A. (1989). The role of orbital symmetry in electron-transfer reaction the reduction of $[(bipy)_2ClRuORuCl(piby)_2]^{2+}$ by some aquometals ions J. Chem. Soc. Nig 14:11.

Iyun, J.F; Ayoko, G.A. and Lohdip, Y.N. (1992). The oxidation of sulphite by Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium(III) ions in perchloric acid Bull. Chem. Soc. Ethiop. 6(1), 1-9.

Iyun, J.F; Ayoko, G.A. and Lawal, H.M. (1992). Kinetics and mechanism of the oxidation of iodine diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium (III) ions in acid medium. Trans. Met. Chem. 17: 63-65.

Iyun, J.F; Ayoko, G.A. and Lohdip N.Y. (1992). The kinetics and mechanism of the oxidation of Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium (III) ion by Bromate in aqueous perchloric acid Polyhedron II:(18) 2389-2394.

Iyun, J.F; Ayoko, G.A. and Lawal H.M. (1992). The stoichiometry and kinetics of oxidation of 1,4-benzene diol by diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium(III) cation in perchlorate medium. Ind. J. Chem 31ᴬ: 943-946.

Iyun, J.F; Ayoko, G.A. and Ekubo, T.A. (1993). Oxidation of glutathione by Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium(III) ion in aqueous acidic solutions. Trans. Met. Chem. 18: 6-8.

Jocobsen A. and Lorand, L. (1952). Biogenesis of proteine fibres. The clotting of Blood plasma. J. Biol. Chem 230:421.

Karmann, W. Granzow, A; Meissner G, and Henylein, A. Internat. J. Radiation phys. Chem. (1968).

Kerv. K.A; Ashmore J.P; Koetzle T.F. (1975). Neutron differaction study of L-cysteine Acta crystallogr Sec. B 13 (8) 2022-2026.

Kirk-Orthmer (1969). Encyclopedia of Chemical Technology: 20: 2nd Ed. Interscience Publishers New York. pg 215.

Krentzien, K. and Taube, H. (1976). Binuclear mixed-valence Ruthenium ammines complexes with Tert-Butylmalonitrile Bridging ligand. J. amer. Chem. Soc. 98: 6378.

Kujundzic, N. and Everse, J. (1978). Reduction of horse heart ferricytochrome by Glutathine: Evidence for two different conformational forms of ferricytochrone in neutral and slightly alkaline solutions. J. Biochem. Biophys. Res. Commun. 82, 1211.

Lappin, A.G. and McAuley, A. (1975). Metal-ion in solution: Formation of intermediate in reaction of Fe(III) with 2-mercapto carboxylic acid J. Chem. Soc. Dalton Trans. 16: 1560-1564.

Lappin A.G. and McAuley A. (1977). Reaction between copper (II) and 2-mercaptosuccinic acid in aqueous perchlorate acid solution J. Chem. Soc. Dalton Trans 7:1606.

Lee, R.A. and Early, J.E. (1981). Thiocynate as bridging ligand in reduction of Ruthenium (III) by Titanium (III) and (N-hydroxy ethylene diammine triacetate) Titanium (III) Inorg. Chem 201:1739.

Lewis, N.A. (1980). Potential Energy Diagrams. A conceptual Tool in study of Electron-Transfer Reaction. J. Chem. Educ. 478.

Lille, W and Purre, T. (1973). Composition of distillates obtained by delayed cooking of Baltic shale. Tom. Keem Geol. 12: 196-201.

Lohdip, Y.N. (1989). Kinetic and mechanism of oxidation-reduction reaction of Diaquotetrakis (2,2-bipyridine)-μ-oxodiruthenium(III) cation in acid medium M.Sc thesis, Ahmadu Bello University, Zaria Nigeria.

Macartney, D.H. and Sutin, N. (1983). The oxidation of Ascorbic acid by Tris (2,2-bipyridine) complexes of Os(III), Ru(III) and Ni(III). Inorg. Chim acta 74:221.

Macartney, D.H; Mark, J. and Hoddenbagh, A. (1990). Kinetics of the oxidation of Ascorbic acid and substituted 1,2- and 1,4-dihydroxybenzenes by Hexacyanoruthenate (III) ion in acidic perchlorate media J. Chem. Soc. Dalton trans 615-520.

Marcus, R.A. (1956). On the theory of oxidation reduction reactions involving electron-transfer J. Phys. Chem. 24:966.

Marcus R.A. (1966). Theory of Electron Transfer reaction rates of solvated electrons J. Phys. Chem 43(10) 3477.

Marcus R.A. and Sutin, N (1975). Electron-transfer reaction with unsual activation parameters treatment of reaction accompanied by large entropy decrease Inorg. Chem. 14:213.

Martin J.F. and Spence J.T. (1970). The oxidation of thioglycolic acid by molybdenum (IV) and molybdenum (V). J. Phys. Chem 74:(20) 3589.

Martin, J.F. and Spence J.T. (1970). The oxidation of cysteine and Glutathione by Molybdenum(VI) J. Phys. Chem 74: (15) 2863-2867.

MacCann J.P. and McAuley, A. (1975). Metal ion oxidation in solution part XIII: The reaction of chromium (VI) with L-cysteine in perchlorate media. J. Chem. Soc A 783.

Meehan, E.J., Kolthoff J.M and Kakill. Chi H (1962). Reaction between ferrocynide and 2-mercaptoethanol. J. Phys. Chem 66 1238-1241.

Meyer, T.J; Sipe K.B. and Moyer, B.A. (1981). Oxygen transfer in oxidation of triphenyl-phosphine by $[(bipy)_2PyRuO]^{2+}$ Inorg. Chem. 20: 1475.

Meyer T.J; John, A.C; Drake S.E; Wyatt R.M. Jr; Daniel, A.G; Susan W.C. and Derek J.H. (1985). Structure and redox properties of water oxidation catalyst. $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$. J. Amer. Chem. Soc. 107:3855-3864.

Michael, R and Dolenko, A (1978). Methylated Craft-ligand polymer resin Chem. Abstr. 90:56689g.

Miller, J.F. and Meyer, I.J. (1971). Reaction between Azide ion and $[Ru(bipy)_2NOCl]^{2+}$. J. Amer. Chem. Soc. 93: 1294.

Mittal R.K. and Mehrotta R.C. (1965). Oxidation of some phenolic compounds. Z. Anal. Chem. 209: 337-339.

Olatunji, M.A. and McAuley, A (1975). Metalion Oxidation in solution part XII: Oxidation of thiourea and N-N-Ethylene thiourea by chromium(VI) in perchlorate media. J. Chem. Soc. Dalton Trans 682.

Paricha, P.C. and Levitt, J. (1967). Enhancement of draught tolerance by applied thiols. Physiol. Plant. 20(1) 83-89.

Patel, N.K; Patel L.N. and Patel K.C. (1975). Effect of thioglycolic acid on corrosion of copper in acid media J. Inst. Chem. Calcutta

Pelizzetti, Ezio; Mentasti, Edoardo; Pramauro Edomando and Saini, Giido (1974). Kinetics of reaction of catechol (o-dihydroxybenzene) and quinol (p-dihydroxy-benzene) with oxidising metal ion present in excess; Reaction with Irion (III) Vanadium (III) and Thallium (III). J. Chem. Soc. Dalton Trans 18: 1940-1944.

Pelizzetti, E. and Mentasti, E. (1976). Reaction between iron (III) and catechol I. Equilibrium and Kinetic of Complex formation in queous acid solution J. Chem. Soc. Dalton Trans 2222.

Pelizzetti E; Mentasti, E. and Baocchi, C. (1977). Kinetic and mechanism of oxidation of quinols by hexachloroiridate (IV) in aqueous acidic perchlorate media J. Chem. Soc. Dalton Trans 132.

Pelizzetti, E. Mentasti, E. and Pramauro, E (1978). Electron-Transfer between benzene diol and aquo-chloro-diquotetrachloro- and hexabromoiridate (IV). J. Chem. Soc. Perkin Trans 2: 620-623.

Pennington: D.E. and Haim, A (1967). Kinetics and mechanism of chromium (II) catalysed-substitution of Iodine ion in Iodo-pentaaquo chromium (III) ion by water, fuoride, chloride and Bromate ion Inorg. Chem. 6: 2138.

Pearson R.G. and Lanier R.D. (1964). Rates of rapid ligand exchange reaction of nuclear magnetic resonance line-broadening studies. J. Amer. Chem. Soc. 86:765.

Pickering, W.F. and McAuley, A. (1968). Oxidation of 2-mercaptosuccinic acid by Vanadium J. Chem. Soc. (A). 5: 1173-1176.

Pieniazak D and Graberek, Z (1975). Quantitative determination of the content of avaliable methionine and L-cysteine in food protein. Nutr. Metab 18(1) 16-22.

Platzman, R.L. and Frank, J. (1954). Hydration configuration in electron processes involving ions in aqueos solution. Chem. Abstr. 48: 13364g.

Przystas, T.J and Sutin, N. (1973). Kinetic studies of anion assisted outer-sphere electron-transfer reaction. J. Amer. Chem. Soc. 95: 5545-5555.

Ramakrishna, R.S and Williams, M (1977). Vanadium (V) as oxidant to thiol compounds Talanta 24: 639-641.

Reset, A; Izzet T. and Huseyin, A (1989). Reduction of selenium (IV) and complexation of selenium (O) with 2-mercaptoethanol Analyst 14: 1315-1318.

Rich, P.R (1982). A Mechanism for the reduction of cytochromes by quinols in solution and its relevance to biological electron transfer reactions. Faraday Disc. Chem. Soc. 74: 349.

Robin, M.B. and Day, P. (1967). Mixed-valenced chemistry a survey and classification. Adv. Inorg. Radiochem. 10:247.

Rosseinsky, R. (1972). Aqueous Electron-transfer Reactions of Vanadium (IV) as reductant compared with iron (II) Chem. Rev. 72:215.

Rykova, L.A. Kiprianova, L.A. Levit, A.F. and Siragerova, I.P. (1978). The study of the mechanism of the chain reaction of phenyldiazonium tetrafluorobo-rate with Esters in presence of Hydroquinone. Teor. Chem. Acta 137: 139-143.

Sakurai, H. Tanaka and Nakayamna, M (1985). Chem. abstr 103: 81092b.

Shanker, R. and McAuley, A. (1973)

Ibid. 232.

Shea, H. and Haim, A. (1973). Adjacent attack in redox reaction between pentaammine coboltate (IV) Inorg. Chem. 12:3013.

Shichiro, A. (1956). Synthetic compounds active against samonella-dyeentry. Japan. J. Exptl. Med 26: 91-112.

Shiffer Aron, L. (1978). Topical application of thioglycolic acid in treatment of acne Chem. abstra. 90:43831.

Snow, Y.T. Finley, J.W. and Friedman, M. (1975). Oxidation of Sulphydryl groups to disulphides by sulphoxides. Biochem. Biophys. Res. Commun 64, 441-7.

Stranks, D.R. (1960). Mechanism of some Electron Exchange Reactions. Disc Faraday Soc. 31: 270.

Stranks D.R. (1960). Modern Coordination Chemistry Ed. Lewis J. and Wilkins, R.G. Interscience, New York pg 78.

Striar J.A. and Taube, H. (1969). Electron-Transfer Reaction of Ruthenium (III) pentaammine with chromium (II), vanadium (II) and Europium (II). J. Amer. Chem. Soc. 8(11) 2281.

Strubelt, O; Siegers, C.P; Schueft, A. (1974). Curative effect of Cysteine, Cysteammine in experimental paracetamol poisoning. arch. Toxicol. 33 55-64.

Sugiura, Y.H, and Yasushi, T. Hasashi (1972). Sulphur-containing chelating agent XXXIII interaction of penicillamine and its related compounds with chromium ion and Hemoglobin bound chromium. Pharm. Chem. Bull. 20 1362-1367.

Sukaeki, H. (1968) $K_{\alpha 2}$ radiation monochromated by a new filler and its topographical and other application used in x-ray crystallography. Jap. J. App. Phy. (7)(1) 1-6.

Sulivan, B.P and Meyer, T.J. (1980). Intermolecular outer-sphere electron transfer in mixed-nvalence ion $[(bipy)_2ClRu(Ph_2PCH_2P.PPh_2)RuCl(bipy)_2]^{3+}$ Inorg. Chem. 20: 1475.

Sutin, N. (1962). Mechanism of oxidation reduction reaction in solution Annn. Rev. Nucl. Sci 12: 285.

Sutin, N. (1966). Electron-Exchange reaction in solution. At. Energy. Common BNL - 91715 Chem. abstr. 64: 5803, Chem. Abstr. 62: 14165g).

Sykes, R.G. (1967). Further Advances in the study of mechanism of redox reaction. In Emelems H.T. and Sharpe, A.G. Ed Adv. Inorg. Radiochem 10: 153.

Takeshi H.Z; Tohru, Y. and Yakiko S. (1967). Constituent of Cane molasses II separation and identification of phenolic compound. Agr. Biol. Chem. 31(3) 324-329.

Taube, H., Meyer, H. and Rich, R.L. (1953). Observation on the mechanism of electron-transfer in solution J. Amer. Chem. Soc. 75: 4118.

Taube, H. (1955). Anion as bridging and non-bridging ligand in reaction of Co(III) compounds with $Cr^{2+}$ J. Amer. Chem. Soc. 77: 4481.

Taube, H. (1959). Bridging and non-bridging ligand effect on redox reaction of metal ions Can. J. Chem. 37: 129.

Taube, H. (1968). Mechanism of oxidation reduction reaction J. Chem. Educ. 45: 452.

Tankomota, A. and Asebu, Y. (1979). Hair conditioner. Jap. Kokai 77: (105) 226.

Tom, G.M. and Taube H. (1975). Mixed-valenced state based on μ-cyanogen-bis (penta ammine-ruthenium) J. Amer. Chem. Soc. 97: 5310.

Tayloy, J. (1975). Compound for skin treatment Chem. abstr. 85: 149147r.

Taqui-Khan, M.M. Ramachandraiah, G. and Prakas Rao, A. (1986). Ruthenium(III) Chloride in aqueous solution: Electrochemical and Spectra studies.

Vogel, A.I. (1978). A Text book of Quantitative inorganic analysis including elementary instrumental analysis ELBS Longman.

Weaver, T.R. Meyer, T.J. Adeyemi, S.A., Brown G.M., Eckbergy, R.F; Halfield, W.E. Johnson, E.C. Murry R.V. and Utereker D. (1975). Chemically significant interaction between Ruthenium ions in oxo-bridged complexes of Ruthenium. J. Amer. Chem. Soc. 97: 3039-3048.

Weiss (1954). Isotopic exchanges between metal ions of different valency. Proc. Roy. Chem. Soc. (London) A22:126.

Wilkins, G.R. (1974) The study of kinetics and mechanism of reaction of transition metal complexes Allyn and Bacon. Inc. Boston. Pg 111.

Wilkins F. (1980). Chemical kinetics and reaction mechanism. Van Nastrand Reinnold. Pg 66-94.

Xia Yaulian (1982). Factors affecting enzymatic depilation by pineaple. Pige Keii 5: 8-12.

Yadav, R.L. and Verma. R.G. (1981). Ceric-Cerium oxidation of Resorcinol Univ. Indore. Res. J. Sci. 7 (1) 500-100

Zahid, A. Chambers, G. and McAulely, A. (1977). Metal ions in solution, The mechanism of reaction of Tl(III) with 2-mercaptosuccinic acid in perchlorate media. Can. J. Chem. 55: 3575.