KINETICS AND MECHANISM OF THE OXIDATION-REDUCTION REACTIONS OF DIAQUOTETRAKIS(2,2'-BIPYRIDINE-μ-OXO-DIRUTHENIUM (III) ION IN ACID MEDIUM.

By

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B.Sc. (HOIS) APPLIED CHEIISTRY

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OCTOBER, 1989.

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 references.

.....
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CERTIFICATION

This thesis entitled "Kinetics and Mechanisms of the Oxidation-Reduction Reactions of Diaquotetrakis (2,2'-bipyridine)-μ-oxo-diruthenium (III) Ion in Acid medium" by Lohdip Yilkur Nandul, meets the regulations governing the award of the degree of Master of Science of Ahmmadu Bello University and is approved for its contribution to Scientific and literary presentation.

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DEDICATION

This project is dedicated to the memory of my late brother, Dinchang Lohdip, for the love we shared during his short stay on earth.

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ABSTRACT

The kinetics and mechanisms of the oxidation-reduction reactions of diaquotetrakis(2,2'-bipyridine)-μ-oxo-diruthenium-(III) ($RuORu^{4+}$), with BrO_3^-, IO_4^- and SO_3^{2-} have been studied in aqueous perchloric acid ($HClO_4$) solution. At 24.0 ± 1.0°C, I = 1.0M ($NaClO_4$) for BrO_3^- and IO_4^- and I = 2.0M ($NaClO_4$) for SO_3^{2-}, the reaction is first order in both the oxidant and reductant for all the systems with the following empirical rate law;

$$\frac{-d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][XO_m^{n-}]$$

(m = 3, n = 1, 2, X = Br, S.)

(m = 4, n = 1, X = I)

$k_2(BrO_3^-)$ = (8.28 ± 1.56) x $10^{-2}M^{-1}s^{-1}$ at $[H^+]$ = 0.01M

$k_2(IO_4^-)$ = 9.41 ± 1.20$M^{-1}s^{-1}$ at $[H^+]$ = 0.10M

$k_2(SO_3^{2-})$ = (1.34 ± 0.21) x $10^{-3}M^{-1}s^{-1}$ at $[H^+]$ = 0.05M

The rates of the redox reactions strongly depend on acid concentrations and the kinetic data are consistent with the following equation;

$$\frac{-d[RuORu^{4+}]}{dt} = (a + b[H]^{-2})[RuORu^{4+}][XO_m^{n-}]$$

z = 2,1 and -1 for BrO_3^-, IO_4^- and SO_3^{2-} respectively.

The rates of the BrO_3^- and SO_3^{2-} systems are enhanced while the rate of IO_4^- system is inhibited in the presence of CH_3COO^-, $HCOO^-$, NO_3^- and NO_2^- ions. The experimental results obtained for the reactions between $RuORu^{4+}$ and BrO_3^- and IO_4^- are in favour of the outer sphere mechanism and this mechanism has been proposed for each of the two systems.

However, in the $RuORu^{4+}$-SO_3^{2-}system, the experimental evidence suggests the occurence of both inner- and outer-sphere mechanisms. The shift in λmax and the intercept obtained from Michaelis-Menten plot for the SO_3^{2-} system account for the inner sphere path while the outer sphere mechanism is supported by the anion catalysis. Therefore two reaction schemes are proposed to accomodate both mechanisms.

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ABBREVIATIONS

Abbreviation	Name
aq	aqueous
B.D.H	British Drug Houses
bipy, bpy	2,2'-bipyridine
calc.	calculated
E°	redox potential
EDDA	ethylenediaminediacetic acid
EDTA	ethylenediaminetetraacetic acid
en	ethylenediamine
e.s.r	electron spin resonance
G.P.R	General Purpose Reagent
HEDTA	n-(2-hydroxyethyl)ethylenediamine tetraacetic acid
I.S	inner sphere
K	equilibrium constant
k	rate constant
L.R	Laboratory Reagent
n.m.r	nuclear magnetic resonance
obs	observed
O.S	outer sphere
Phen	1,10-phenanthroline
py	pyridine
pyr	pyrazine

Chapter 1

1.0 INTRODUCTION

Oxidation - reduction reactions of metal ions in solution have been extensively studied for the important role they play in chemical, biochemical and technological processes (Iyun, 1982). Detailed knowledge of these electron transfer processes will continue to aid the understanding, development and effective control of a wide area of science and technology. The extensive investigations into the redox systems have been made possible by the use of radio-isotopes and the development of a wide range of techniques for monitoring the rate of electron transfer, as evident from the large number of reviews (Sykes, 1966, 1967; Rosseinskey, 1972; Wilkins, 1974; Burgess, 1978). The range of these techniques now vary from conventional spectrophotometric methods, for slow reactions ($t_{\frac{1}{2}}$ = ca 30 seconds) to continuous and stopped-flow methods for fast reacions ($t_{\frac{1}{2}}$ = milliseconds). These methods have been exhaustively reviewed (Stranks, 1960; Caldin, 1974; Wilkins, 1974), and only a summary is presented below.

1.1 Rate monitoring techniques

1.1.1 Conventional methods

The conventional methods which include photometric, spectrometric, polarometric and radiometric techniques, involve measuring, as a function of time, the concentration of one or

more of the reactants or products or any physical property such as absorbance which is directly related to the concentration [Wilkins, 1974].

1.1.2 Techniques for monitoring the rates of fast reactions

Flow methods

Different flow techniques exist, depending on the treatment given to the reaction after mixing [Caldin, 1964]. In quenched flow method, the reaction solution is quenched after a predetermined time and the quenched solution is analysed by any conventional method, while in the continuous-flow method, the reaction solution is allowed to flow continuously along an observation tube, as the changes in the reaction mixture is monitored at different points along the tube or at a fixed point on the tube.

In the case of stopped-flow, the solutions are forced together through a mixing device and as the mixed solution flows along a tube, it is abruptly stopped so that the solution comes to rest within a few milliseconds. The rate of flow along the observation tube is such that when the solution is stopped, a segment within 1cm of the 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 is relayed to an oscilloscope.

Relaxation methods

These methods are usually applied to reversible reactions with half-lives ($t_{\frac{1}{2}}$) as short as 10^{-9} sec [Eigen and de Maeyer,

1963]. The observed equilibrium is perturbed by rapid variation of a physical parameter such as temperature, pressure or electric field intensity and the time taken to readjust to a new equilibrium position is monitored, which is then related to the rate constants of the forward and backward reactions. The dependence of a particular equilibrium on a chosen external physical parameter largely determines the method of perturbation used for such an equilibrium and hence these methods are referred to as 'temperature-jump', 'pressure-jump' or 'electric-jump' methods (Wilkinson, 1980].

Resonance techniques

In the n.m.r technique, 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 a chemical interaction, results in line broadening. On addition of increasing amount of a reagent, measurement of the corresponding increase in width of the line due to the second reagent can be made. For example, ^{1}H n.m.r line broadening has been used to measure the rate 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 Concept of Electron Transfer (redox) Reactions

1.2.1 Frank-Condon Principle

The actual electron transfer process must satisfy the "Frank-Condon Principle" (restriction), which states that "the

motion of nuclei is so slow (10^{-13} sec.) compared to that of electron (10^{-15}sec.), that an electron transfer occurs without an appreciable movement of the nuclei" [Platzman and Franck, 1954; Sutin, 1966]. This implies that the nuclei are virtually frozen in position or stationary during the time taken for electron transfer.

The operation of the Frank-Condon Principle demands that:
(a) Both the oxidant and reductant must undergo reorganization before electron transfer in such a way that their energies in the transition states become identical, thus minimizing the energy change on electron transfer. The total change in free energy involved in the process can then be represented by equation (1.1) [Marcus, 1956].

$$\Delta\overset{\ddagger}{G} = \Delta\overset{\ddagger}{G}_{\iota} + \Delta\overset{\ddagger}{G}_{i} + \Delta\overset{\ddagger}{G}_{o} \quad \ldots\ldots\ldots\ldots\ldots (1.1)$$

Where $\Delta\overset{\ddagger}{G}_{\iota}$ = Association free energy.

$\Delta\overset{\ddagger}{G}_{i}$ = Inner-sphere reorganization energy.

$\Delta\overset{\ddagger}{G}_{o}$ = Outer-sphere reorganization energy.

(b) No angular momentum 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.

For example, the exchange reaction (1.2)

$$Co(Phen)_3^{2+} + \overset{*}{Co}(Phen)_3^{3+} \longrightarrow Co(Phen)_3^{3+} + \overset{*}{Co}(Phen)_3^{2+} \quad \text{---(1.2)}$$

involves only the transfer of electron from σ_g orbital of one

Cobalt ion to that of the other and has a rate of $1.1M^{-1}s^{-1}$ at 25°C [Baker et al, 1959], whereas the exchange reaction (1.3)

$$Co(NH_3)_6^{2+} + \overset{*}{Co}(NH_3)_6^{3+} \longrightarrow Co(NH_3)_6^{3+} + \overset{*}{Co}(NH_3)_6^{2+} \quad \ldots(1.3)$$

requires simultaneous electron transfer and change in spin multiplicity and thus, it is slow with a rate of $10^{-9}M^{-1}s^{-1}$ at 25°C [Stranks, 1966].

According to the "Frank-Condon Principle", electron migration is viewed as a tunneling process in which the electron passes through the potential energy barrier rather than over it [Basolo and Pearson, 1967]. The result is that the electrons can be transfered at distances much greater than would correspond to actual collision of reactants. Figure (1.1) shows a potential energy diagram illustrating this barrier leakage, where,

U_1 and U_2 = ground states of the electrons in cations 1 and 2 respectively.

d = width of barrier at height of penetration.

w = kinetic energy of the electron

U_o = height of the barrier.

1.3 Types of Electron Transfer Reactions

1.3.1 Homonuclear electron exchange

In homonuclear electron exchange, the transfer of electrons occurs between two identical metal ion centres

existing in different oxidation states. Because the reactant and product concentrations are the same, the only change in free energy is that due to mixing and therefore the overall free energy is approximately zero. Examples of these reactions are given in equations (1.4) and (1.5).

$$\overset{*}{Pt}Cl_6^{2-} + PtCl_4^{2-} \text{ ------> } \overset{*}{Pt}Cl_4^{2-} + PtCl_6^{2-} \quad .....(1.4)$$

$$\overset{*}{Fe}(Phen)_3^{2+} + Fe(Phen)_3^{3+} \text{ ---> } \overset{*}{Fe}(Phen)_3^{3+} + Fe(Phen)_3^{2+} \quad ...(1.5)$$

Isotopic labelling techniques are usually used for monitoring slow exchange reactions of this type and n.m.r spectroscopic methods are employed for fast ones [Wilkin, 1974].

1.3.2 <u>Heteronuclear or Cross reactions</u>

In this type of reactions, the electron transfer is between different metal ion centres and the products are chemically distinct from the reactants. Here, the net change in free energy cannot be zero and in most cases, $\Delta G^\circ < 0$.

Examples are represented in equations (1.6 - 1.9).

$$Co(NH_3)_5X^{2+} + Cr^{2+} + 5H^+ \text{ ----> } CrX^{2+} + Co^{2+} + 5NH_4^+ \quad ....(1.6)$$

$$Co(en)_3^{3+} + Ru(NH_3)_6^{2+} \text{ ----> } Co(en)_3^{2+} + Ru(NH_3)_6^{3+} \quad ....(1.7)$$

$$2Fe^{2+} + Tl^{3+} \text{ ------> } 2Fe^{3+} + Tl^+ \quad .....(1.8)$$

$$2V^{2+} + Br_2 \text{ -------> } 2V^{3+} + 2Br^- \quad .....(1.9)$$

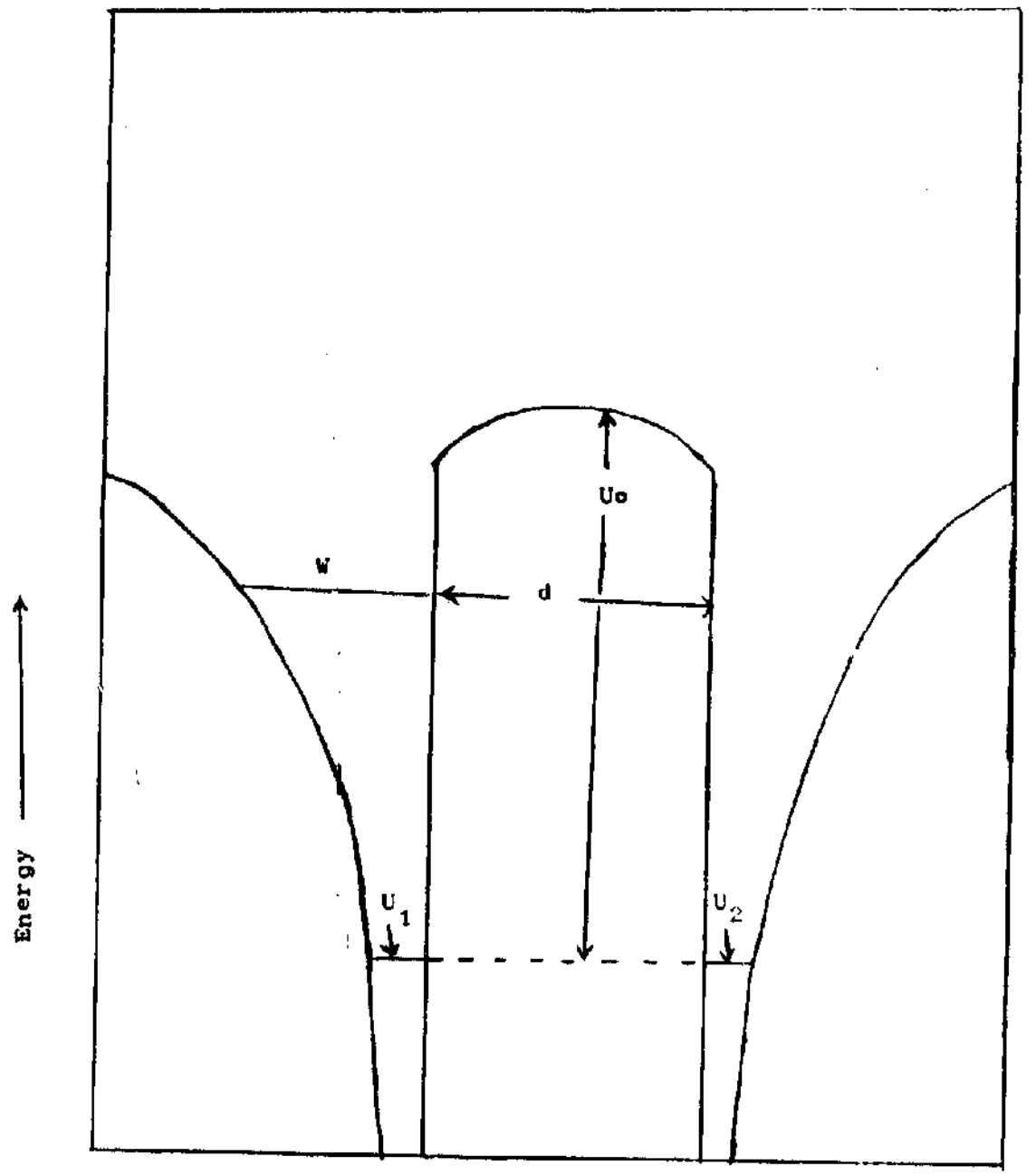


Figure 1.1 Electron Transfer by Penetration of a potential energy barrier.

When the oxidant and reductant undergo equal changes in the oxidation states as in equations (1.6) and (1.7), the reactions are said to be complementary and the stoichiometry is always 1:1. However, when there are unequal changes in oxidation states of the oxidant and the reductant as in equations (1.8) and (1.9), such reactions are termed non-complementary and the stoichiometry is no longer 1:1.

For reactions involving multiple oxidation state changes, the points of mechanistic interst will be;

(i) whether more than one electron are transferred in a single step or in a series of univalent changes and

(ii) whether an intermediate is formed in the process. For example, V(II) has been found to react with Hg(II) to produce V(IV) in a step which involves a direct two-electron transfer, whereas the oxidation reaction involving iodine and triodide occurs in a series of univalent changes with $^{\bullet}I_2^-$ as a transient intermediate [Green and Sykes, 1970]. Direct two-electron paths have also been identified in the Cr(II) reduction of $[Pt(NH_3)_5Cl]^{3+}$ and $Pt(NH_3)_5OH]^{3+}$ [Beattie and Basolo, 1971] and in some binuclear complexes [Isied and Taube, 1973].

1.4 Mechanisms of Redox Reactions

When undertaking the study of the mechanism of electron transfer process, the following questions come to mind:

(i) What is the stoichiometry of the reaction and the composition of the activated complex?

(ii) Is the reaction accompanied by transfer of electrons or atoms and if by atoms, which atoms are transferred?

(iii) Is the rate of electron transfer greater or less than the rate of substitution of the reaction?

(iv) What is the number of electrons that is transferred in a single step for multivalent reactants?

(v) What provides the driving force if the reaction is not thermodynamically feasible?

(vi) Can the products be isolated and identified?

(vii) Is it possible to identify or infer the intermediate formed prior to the act of electron transfer?

(viii) What is the significance of acid-base catalysis (if any) obtained in the rate law; could it be rationalized in terms of the reactants, transition state or products?

Answers to some or all of the above questions lead to one of the distinct mechanisms that have been established for redox reactions: the Inner-sphere and Outer-sphere mechanisms.

1.4.1 Outer sphere Mechanism

The outer sphere mechanism involves electron transfer between two reactants whose coordination spheres remain intact, although not completely undisturbed during the process. An example is given in equation (1.10).

$$\overset{*}{Fe}(Phen)_3^{2+} + Fe(Phen)_3^{3+} \rightarrow \overset{*}{Fe}(Phen)_3^{3+} + Fe(Phen)_3^{2+} \quad \ldots(1.10)$$

In the reaction above, the phenanthroline (Phen) could not become detached from the inert Fe(II) and Fe(III) centres during the course of the rapid redox process, therefore the coordina-

tion shells of the two reactants remain essentially intact before and after the electron transfer [Larsen and Wahl, 1965].

Reactions which follow this pathway are considered to proceed via the following steps:

Step I: Formation of a precursor complex.

$$M^{II}(H_2O)_6^{2+} + M^{III}(NH_3)_5L^{3+} \rightleftharpoons [(H_2O)_6M^{II}..LM^{III}(NH_3)_5]^{4+} \quad (1.11)$$

(Precursor complex)

Step II: Activation of the precursor complex

$$(H_2O)_6M^{II}..LM^{III}(NH_3)_5]^{4+} \rightleftharpoons [(H_2O)_6M^{II}..LM^{III}(NH_3)_5^{4+\ddagger}] \quad (1.12)$$

(activated complex)

Step III: Electron transfer and formation of a successor complex

$$[(H_2O)_6M^{II}..LM^{III}(NH_3)_5^{4+\ddagger}] \longrightarrow (H_2O)_6M^{III}..LM^{II}(NH_3)_5]^{4+} \quad (1.13)$$

(successor complex)

Step IV: Decomposition of successor complex to give the final products.

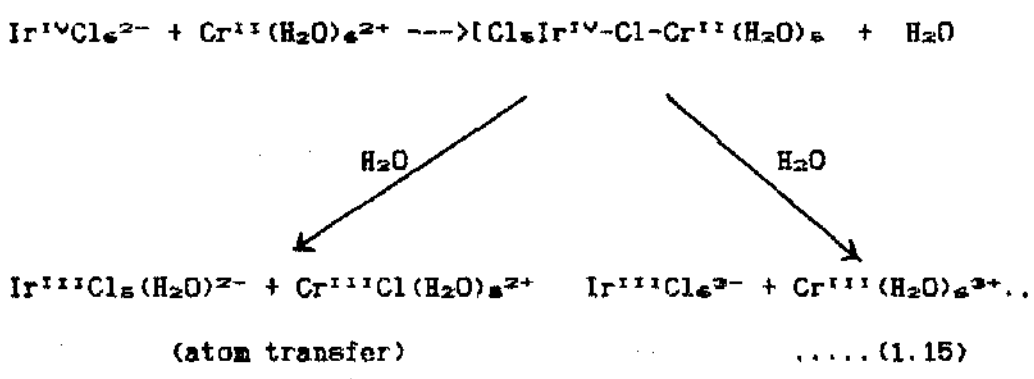
$$[(H_2O)_6M^{III}..LM^{II}(NH_3)_5]^{4+} \longrightarrow M^{III}(H_2O)_6^{3+} + M^{II}(NH_3)_5L^{+} \quad (1.14)$$

Step III is the rate determining step of the reaction.

Most outer sphere oxidants and reductants are relatively inert in the time scale of redox reactions.

1.4.2 Inner sphere Mechanism

The main feature of this mechanism is that substitution occurs at one of the metal centres to give a binuclear ligand-bridged species prior to the transfer of electron. The two reactants are therefore linked by at least one bridging ligand common to their inner coordination shells. Electron transfer then occurs through the bridging ligand which is usually but not always transferred from one metal centre to the other.



The inner sphere mechanism also proceeds through a series of steps given by equations (1.16-1.20).

Step I: Formation of collision complex.

$$L_5M^{III}X^{2+} + M^{II}(H_2O)_6^{2+} \rightleftharpoons [L_5M^{III}X//M^{II}(H_2O)_6]^{4+} \quad \ldots.(1.16)$$

(collision complex)

Step II: Formation of bridged precursor complex.

$$[L_5M^{III}X//M^{II}(H_2O)_6]^{4+} \longrightarrow [L_5M^{III}-X-M^{II}(H_2O)_5]^{4+} + H_2O \ldots(1.17)$$

(precursor complex)

Step III: Activation of the precursor complex, electron transfer and formation of successor complex.

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{4+} \longrightarrow [L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5^{4+\ddagger}] \quad \ldots\ldots (1.18)$$

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5^{4+}]^{*} \longrightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5^{4+\ddagger}] \quad \ldots\ldots (1.19)$$

Step IV: Deactivation of successor complex and formation of products.

$$[L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5^{4+}]^{*} \longrightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{4+}$$

$$\downarrow H_2O$$

$$L_5M^{II}(H_2O)^{2+} + XM^{III}(H_2O)_5^{2+} \quad \ldots\ldots (1.20)$$

The usually encountered rate determining step is step III, which involves the actual transfer of electron(s).

1.5 Diagnosis of the mechanism of redox reactions

One of the primary aims of redox kinetics is to distinquish between the inner sphere and outer sphere mechanisms. Some of the criteria that have been use to achieve this are discussed below:

1.5.1 k redox (k_{redox}) versus k Substitution (k_{sub})

In the inner sphere mechanism, substitution into the coordination shell occurs before electron transfer therefore if

$k_{red} >> k_{sub}$, such a reaction can only occur by the outer-sphere mechanism. An example is the electron exchange reaction between $Fe(Phen)_3^{2+}$ and $\overset{*}{Fe}(Phen)_3^{3+}$, [Larsen and Wahl, 1965].

$$Fe(Phen)_3^{2+} + \overset{*}{Fe}(Phen)_3^{3+} \dashrightarrow Fe(Phen)_3^{3+} + \overset{*}{Fe}(Phen)_3^{2+} \quad ...(1.21)$$

The rate constants for the substitution of phen. are $7.5 \times 10^{-8} s^{-1}$ for $\overset{*}{Fe}(Phen)_3^{2+}$ and $5.01 \times 10^{-8} s^{-1}$ for $Fe(Phen)_3^{3+}$, while K exchange is $10^{8} M^{-1} s^{-1}$. In this example, the outer sphere mechanism is operative because $k_{red} >> k_{sub}$. For a reaction in which $k_{sub} >> k_{red}$, and in the presence of a suitable bridging ligand, the inner sphere mechanism may operate.

1.5.2 Product identification

One of the most important features of the inner sphere mechanism is that electron transfer takes place through a bridging ligand. When the bridging ligand is transferred from one metal centre to another after the act of electron transfer, it provides an evidence in support of the inner sphere mechanism. In the study of the reaction between Cr^{2+} and Co^{3+}, Taube and co-workers (1953) were able to associate the product $CrCl^{2+}$ with a binuclear intermediate of the form $[(NH_3)_5Co\text{-}Cl\text{-}Cr^{4+}]$ and appropriately proposed the inner sphere mechanism.

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \longrightarrow [(NH_3)_5Co\text{-}Cl\text{-}Cr]^{4+}$$

$$\downarrow H^+$$

$$CrCl^{2+} + Co^{2+} + 5NH_4^+ \quad .....(1.22)$$

This criterion must be applied with caution because;

(i) Atom transfer does not occur in all reactions that proceed via an inner sphere mechanism.

(ii) The products of the reactions of some reductants like Fe^{2+}, V^{2+} and Eu^{2+}, hydrolyse rapidly, making the detection difficult, except in few cases, for example $Co(NH_3)_5SCN^{2+}/V^{2+}$ system, where the stopped-flow technique has been used [Davies and Espenson, 1969; Sykes and Green, 1970; Green et al, 1971].

1.5.3 Identification of binuclear intermediate

The inner sphere mechanism presupposes that a binuclear intermediate is formed between two reactants prior to electron transfer [Basolo and Pearson, 1967; Al-Jallal and Sulfab, 1983]. Depending on the life time of the intermediate, its detection can be accomplished by the use of ordinary spectrophotometry or by stopped-flow techniques. If the identification of the intermediate is possible then it serves as a criterion for assigning the inner sphere mechanism. Although the identification of a binuclear intermediate is necessary, it is not a sufficient condition for the diagnosis of an inner sphere mechanism, because the mere presence of an intermediate does not automatically mean that this species plays a direct role in the

redox process.

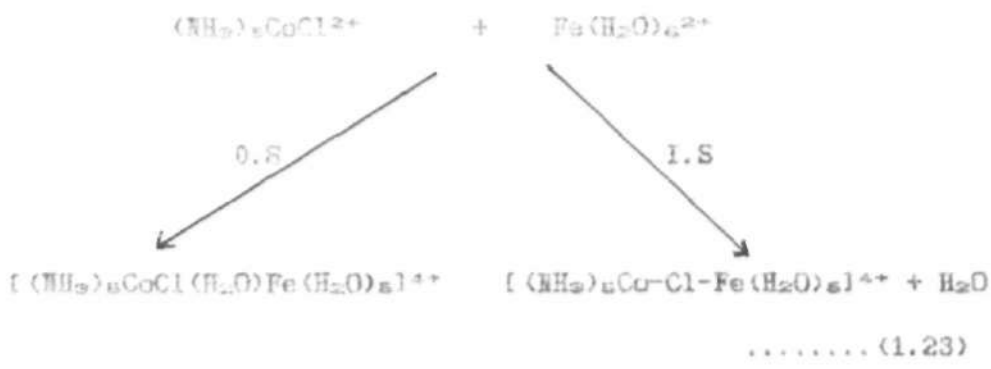
1.5.4 Reactivity Pattern

If a wide variety of complexes of the general type $Co(NH_3)_5X^{2+}$ ($X = Cl^-$, F^-, Br^-, NO_3^-), is reacted with another metal ion, the rates of reactions for inner sphere mechanism would be expected to be sensitive to the nature of X (since it is the bridging ligand), while in the case of outer sphere mechanism, the rates would be similar irrespective of the identity of X [Sykes, 1967; Shea and Haim, 1973]. Therefore when the reactions of such a series of complexes are found to be independent of the nature of X, then the outer sphere mechanism can be said to operate.

The effects of added anions also gives a clue to the type of mechanism involved in a reaction [Adegite et al, 1977; Przystas and Sutin, 1973; Pennington and Haim, 1967]. For example, if a reaction is catalysed by the presence of added anions, it suggests an outer sphere pathway.

1.5.5 Activation Parameters:

Although there seems to be no direct relationship between the activation parameters such as $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$, etc, and the type of mechanism, their signs and magnitudes can be used in support of or against a particular mechanism. For example, negative value of $\Delta H^{\neq}$ indicates the formation of a precursor complex as in inner sphere mechanism [Wilkins, 1974]. The volume of activation, $\Delta V^{\neq}$, can also be used as a support for the inner sphere pathway.



.....(1.23)

The volume of activation is expected to increase in the case of inner sphere mechanism because the effective volume of free water molecules is more than that of coordinated water molecules.

1.5.6 Marcus Theory

In the outer sphere mechanism, the weak interaction between the reactants has permitted its theoretical treatments and correlation between kinetic and thermodynamic parameters [Sutin, 1966; Diebler and Sutin, 1968]. The most widely used of these treatments is the Marcus Theory [Marcus, 1956]. When work terms are small, the theory predicts that for the reaction (1.24),

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2 \quad .....(1.24)$$

and related isotopic exchange reactions (1.25) and (1.26)

$$\overset{*}{Ox}_1 + Red_1 \rightleftharpoons \overset{*}{Red}_1 + Ox_1 \quad .....(1.25)$$

$$Ox_2 + Red_2 \rightleftharpoons Red_2 + Ox_2 \quad \ldots\ldots\ldots (1.26)$$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \quad \ldots\ldots\ldots (1.27)$$

$$\text{where } \log f = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)}$$

k_{12} and K_{12} are the rate and equilibrium constants respectively for the cross reaction, k_{11}, k_{22} are appropriate rate constants for isotopic exchange, and Z is the collision frequency ($10^{11}M^{-1}s^{-1}$ for homogeneous reactions).

Thus, from Marcus equation, the theoretical rate constant can be calculated from equation (1.28)

$$k = Ze^{-\Delta G^{\ddagger}/RT} \quad \ldots\ldots\ldots (1.28)$$

$\Delta G^{\ddagger}$ = Gibbs free energy for the cross reaction.

A reasonable agreement between $k_{calc.}$ and $k_{obs.}$ is usually taken as evidence in support of the outer sphere mechanism but an absence of the correlation does not give absolute evidence for inner sphere mechanism. For f = 1 and for small values of k_{12},

$$\Delta G^{\ddagger}_{12} = 0.50\Delta G^{\ddagger}_{11} + 0.50\Delta G^{\ddagger}_{22} + 0.5\Delta G^{0}_{12} \quad \ldots\ldots\ldots (1.29)$$

So that for a series of reactions, a plot of $\Delta G^{\ddagger}_{12}$ versus ΔG^{o}_{12} gives a slope of 0.50 if the reaction is of the outer sphere type.

1.6 Objectives of the Project

Ruthenium complexes occupy an important position in chemistry, biochemistry and chemical technology from their wide range of applications. For example, they have been reported to effect a variety of organic oxidations even under mild conditions [Thompson and Meyer, 1982]. These complexes, particularly the oxo-bridged type, have large extinction coefficients in the visible region and are relatively stable towards photo-dissociation. Their relatively high energy transfer ability has also provided a basis for the design of artificial systems used in the splitting of water with solar energy (Bolletta et al, 1980].

Haim and co-workers have recently undertaken the kinetic studies of some ligand-bridged complexes of Ru(III) [Akhtar and Haim and references therein 1988], but there has been no published kinetic results on the oxo-bridged Ru(III) dimers. So far, only the synthesis and characterization of a series of oxo-bridged Ru(III) complexes have been accomplished [Weaver et al, 1975]. These dimers, which are of the form $[(LL)_2 X RuORu X (LL)_2]^{n+}$ (LL = bipy or phen, X = Cl^-, NO_2^- or H_2O), have been identified as good redox agents in chemical synthesis and in biological systems [Meyer et al, 1981; Weaver et al, 1975].

There is therefore the need to establish the factors that govern the nature of the reactivity of these systems. And so in

this project, the redox reactions of $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ and some oxy-anions are being investigated as part of an effort to collect data which would give an insight into the kinetics and mechanisms of the reactions of the complex with the oxy-anions of interest. The information that would be obtained can then be compared to those of its monomeric analogues and related systems that have been reported. It is also hoped that the knowledge so gained can be utilized in the development of redox catalysis and the design of artificial systems for solar energy generation.

Chapter 2

2.0 LITERATURE REVIEW

2.1 Ligand-bridged complexes of Ruthenium

A series of mixed-valence complexes of Ru(III) has been prepared [Krentzien and Taube, 1976; Tom and Taube, 1975], and their properties compared to simple monomeric analogues. In the study of these ligand-bridged complexes, emphasis has been placed on the nature and the extent of metal-metal interactions across the bridging ligands and the consequences of such interactions on the physical and chemical properties of such systems [Miller and Meyer, 1971; Weaver et al, 1975]. For example, the extent of delocalization between the ruthenium sites in the ligand-bridged systems depends on the oxidation state of the metal site and on the effects of the bridging and non-bridging ligands [Tom and Taube, 1975].

Recently, a programme to study the reactivity of mixed-valence binuclear complexes was started by Haim and co-workers, (1988). The report on pyrazine-bridged ruthenium dimers indicates that the metal-metal overlap occurs by the metal-ligand mixing due to the large Ru-Ru distance (6.9A°). However, the study of ruthenium bridged by some heterocyclic ligands indicates no metal-metal interactions across these heterocycles [Sullivian and Meyer, 1979]. An example is one involving $[(Ru(bipy)_2Cl)_2Ph_2PCH_2Ph_2]^{3+}$ in which the transition is due to

metal-metal charge transfer.

Since this work is concerned with the reactions of the oxo-bridged ruthenium systems, it is pertinent to consider the nature of these complexes in more details.

2.2 Oxo-bridged complexes of Ruthenium(III)

Oxo-complexes of transition metals are strongly oxidizing and often used in synthetic organic chemistry [Meyer et al, 1981]. Because of their role as redox agents in chemical and biological systems, there is a need to establish the factors that govern the nature of their reactivities which will help in the development of redox catalysis. High valent oxo-complexes of ruthenium, for example, those containing polypyridyl ligands have been used as oxidative catalysts [Chi-Ming et al, 1986] and those derived from trans - $[Ru(bipy)_2(H_2O)_2]^{2+}$ have been shown to play an important role in the photolytic splitting of water [Taqui et al, 1986].

The properties of ligand bridged transition metal complexes can differ significantly depending on the nature and/or extent of metal-metal interaction [Weaver et al, 1975].

There are cases in which;

(i) There is a strong, direct metal-metal bonding,

(ii) Strong metal-metal interactions exist, but through a bridging ligand,

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

(iv) There is no evidence for metal electronic interaction.

Complexes of the first transition metals have been shown to

exhibit weak metal-metal interactions and the interactions seem to be stronger for second and third row metals [Weaver et al, 1975].

As stated in chapter one, a series of oxo-bridged complexes $[(LL)_2XRuORuX(LL)_2]^{n+}$ (LL = bipy or phen, X = Cl^-, NO_2^- or H_2O), which fall into Robin and Day Class III, (Robin and Day, 1967), have some unusual physicochemical properties when compared to their monomeric analogues [Weavers et al, 1975]. These properties have been suggested to arise from chemically significant interactions between the two Ru(III) ions across the oxide bridge. Because of the strong Ru-O-Ru interactions, the identity of the separate Ru(III) ions is lost in determining the physical and chemical properties of such systems. It is therefore necessary to treat them as molecular Ru-O-Ru systems with distinct chemical and physical properties of their own. The electron spectral data of some of these complexes are represented in Table (2.1).

One of the conclusions from a series of studies on the oxo-bridged Ru(III) dimers is that the oxo-group can support strong electron interaction between the metal sites, which can in turn lead to an extensive reversible redox chemistry [Baumann and Meyer, 1980]. 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 systems.

The spectral and chemical properties of Ru-O-Ru have been found to be similar to those of Os-O-Os but different from those of Fe(III) systems. For example, Ru-O-Ru and Os-O-Os have

Table 2.1

*Electron spectral data of $[(LL)_2XRuORuX(LL)_2]^{n+}$ (LL = bipy or Phen, X = Cl^-, NO_2^-, H_2O) in acetonitrile

Compound	λmax(nm)	ε	μ
$[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$	672	17900	1.87
	298	39000	
	244	65900	
$[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$	660	25000	
	410	2900	
	284	53000	
$[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$	632	25700	1.80
	284	4890	
	244	38400	
$[(Phen)_2(H_2O)RuORu(H_2O)(Phen)_2]^{4+}$	660	17600	1.70
	264	87000	
$[(Phen)_2(NO_2)RuORu(NO_2)(Phen)_2]^{2+}$	640	25300	1.80
	264	88000	

*Weaver et al, 1975.

ε = molar extinction coefficient

μ = magnetic moment

strong metal-metal interaction, while the metal-metal interaction in Fe(III) ions is insignificant to effect similar changes in electronic and chemical properties [Khedekar et al, 1967; Lewis et al, 1968; Schugar et al, 1972]. This is probably due to the lesser d-orbital extension of Fe(III) when compared to Ru(III) and Os(III).

Most of the reported kinetic studies on ruthenium are those involving the ammine complexes (Adegite et al, 1979; Lee and Early, 1981; Chalipoyil et al, 1977), and recently, the pyrazine bridged mixed ruthenium dimers have also been studied (Akhtar and Hain and references therein, 1988). However, the oxo-dimers of Ru(III) are now receiving some attention [Iyun and Adegite, 1988]. For example, the anion assisted dissociation of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ has been investigated [Iyun, 1988]. A great deal of kinetic work still needs to be done on the oxo-bridged Ru(III) complexes to be able to classify them into mechanistic pathways. (Most of the earlier research interest has been on characterization; i.e crystallographic, bonding and electrochemical properties of these dimers [Early and Fealey, 1971; Weaver et al, 1975].)

Since this project is aimed at studying the redox reactions of $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ and some oxy-anions, a review of the reactions of the anions is considered below:

2.3 Reactions of Oxy-anions

There has been a number of kinetic investigations into the mechanisms and activity patterns of redox reactions involving complex ions and oxy-anions [Shakhashili and Gordon, 1969], and

the rates of oxygen exchange and redox reactions were found to depend strongly on acid concentration [Birk and Kozub, 1973]. For a number of oxy-anions SO_3^{2-}, SO_4^{2-} [Hoering and Kennedy, 1957], ClO_3^- [Hoering et al, 1958], ClO_4^-, BrO_3^-, IO_4^-, IO_3^- [Birk and Kozub, 1973], NO_3^- and NO_2^- [Anbar and Guttman, 1961; Anbar and Taube, 1954], the rates of oxygen exchange and reduction by a species R, generally have rate terms of the forms $k[XO_m^{n-}][H^+]$ and $k[XO_m^{n-}][R][H^+]$ respectively (X = Cl, Br, I, S, N....; m = 2,3, or 4, n = 1 or 2). One way of looking at the $[H^+]$ dependence is that the protons enhance the cleavage of the bond between the oxide ions from the central atoms [Edwards, 1964].

For oxy-anions that are derived from small and or highly charged central atoms, the predominant rate law term for exchange is $k[XO_m^{n-}][H^+]^2$ and this has been observed for NO_3^-, NO_2^-, ClO_4^-, and BrO_3^- [Edwards, 1954]. For example, chloride ion has been shown to catalyse the oxygen exchange between water and NO_3^- and BrO_3^- with the following rate law.

$$\text{Rate} = k[XO_3^-][Cl^-][H^+]^2 \quad \ldots\ldots\ldots \quad (2.1)$$

But when the central atom is large and or less highly charged, the rate law shows first order dependence of $[H^+]$ [Baloga and Harley, 1963]. An example is the reaction of IO_4^- with the following rate law;

$$\text{Rate} = k[IO_4^-][H^+] \quad \ldots\ldots\ldots \quad (2.2)$$

Although IO_4^- is thermodynamically a poorer oxidant than BrO_3^-, it is much more reactive, presummably because of the lability of its oxygens due to the larger size of iodine [Olsen et al, 1973].

The mechanisms for the reactions of these oxy-anions with a variety of metal ion complexes have been a subject of discussion in recent years [Gordon and Buchacek, 1972; Huchital and Rodges, 1973; Birk, 1973; Birk and Kozub, 1973, 1978; Sulfab, 1976; Sulfab and Abu-Shady, 1977; Ige and Amire, 1985]. Depending on the nature of the metal ion complex and the oxy-anion, both inner and outer-sphere mechanisms have been proposed.

The oxy-anions of interest in this work are BrO_3^-, IO_4^- and SO_3^{2-} and therefore require more detailed treatment here.

2.3.1 Oxidation Reactions of Bromate (BrO_3^-) ion.

Bromate ion redox reactions with a variety of metal ions have been studied [Thompson and references therein, 1971]. For example, its reactions with $Fe(CN)_6^{4-}$, $[Fe(bipy)(CN)_4]^{2-}$, $[Fe(bipy)_2(CN)_2]$, Hg^0 and $Ru(CN)_6^{4-}$ have been shown to have both a direct path and an autocatalytic path caused by the $Br-BrO_2$ reaction [Birk, 1978] and the rate can be accomodated by the general equation (2.3).

$$\frac{-d[BrO_3^-]}{dt} = (k + k_H[H^+]^2)[BrO_3^-][M^{n+}] \quad \ldots\ldots\ldots \quad (2.3)$$

Values of k and k_H for these and other metal ions at 25°C are given in table (2.2).

The results obtained from the BrO_3^-/Fe(II) reactions, in conjunction with Marcus correlation, suggested that both terms in the rate law are probably due to outer sphere mechanism [Birk and Kozub, 1978]. But earlier investigation has also shown evidence for the occurence of an inner sphere pathway, possibly involving substitution of Fe^{2+} rather than on the BrO_3^- [Birk and Kozub, 1973].

Of all the reactions of BrO_3^- with metal ion complexes that have been studied, Fe(II) systems have received more attention. An example is $Fe(CN)_6^{4-}/BrO_3^-$ system [Birk, 1973, Birk and Kozub, 1973]. In the presence of excess BrO_3^-, the overall stoichiometry is given in equation (2.4)

$$BrO_3^- + 5Fe(CN)_6^{4-} + 6H^+ \longrightarrow 5Fe(CN)_6^{3-} + 3H_2O + \tfrac{1}{2}Br_2 \quad \ldots(2.4)$$

The following sequence of reactions is said to operate with equation (2.8) as the rate determining step.

$$Fe(II) + BrO_3^- \xrightarrow[2H^+]{k_1} Fe(III) + BrO_2 + H_2O \quad \ldots\ldots(2.5)$$

$$4Fe(II) + BrO_2 + 4H^+ \xrightarrow{\text{fast}} 4Fe(III) + \tfrac{1}{2}Br_2 + 2H_2O \quad \ldots(2.6)$$

$$Fe(II) + \tfrac{1}{2}Br_2 \xrightarrow[\text{fast}]{k_2} Fe(III) + Br^- \quad \ldots\ldots(2.7)$$

$$Br^- + BrO_3^- + 2H^+ \xrightarrow[4H^+,\ 4Br^-]{k_3} 3Br_2 + 3H_2O \quad \ldots\ldots(2.8)$$

Table 2.2

Values of k and k_H at 25°C for the reduction of BrO_3^- by some metal ions.

Metal ion	k, $M^{-1}s^{-1}$	k_H, $M^{-1}s^{-1}$	Ionic strength
$Fe(CN)_6^{4-}$	0.00125	0.193	0.5M
$Fe(bipy)(CN)_4^{2-}$	0.0062	0.227	0.5M
$Fe(bipy)_2(CN)_2$	0.029	0.755	0.5M
$Fe(bipy)_3^{2+}$	<0.0042	< 0.15	0.5M
Fe^{2+}	0.372	-	0.5M
VO^{2+}	4.93	-	2.0M
U^{4+}	12.5	3.2	2.0M
Hg°	3.7	2.0	1.0M
$IrCl_6^{3-}$	-	10.2	0.5M

Table 2.3

Values of a and b for the Reduction of BrO_3^- by metal ions at 25°C

Complex	E°, Oxidation	10^3a, $M^{-1}s^{-1}$	$b, M^{-2}s^{-1}$	I, M	Ref.
$Fe(bpy)(CN)_4^{2-}$	-0.65	6.2	0.227	0.5	f
$Fe(bpy)_2(CN)_2$	-0.79	29.5	0.755	0.5	f
$Fe(bpy)_3^{2+}$	-1.07	4.2[c]	0.15[c]	0.5	f
$Co^{III}V$	-1.00	0.26[d]	0.000045[d]	2.0	g
$RuORu^{4+}$		55.3[e]	5.09[e]	1.0	This work

[c]Estimated value, the reaction follows a different rate law.

[d]Value at 24.5°C, [e]Value at 24.0 ± 1.0°C

[f]Birk and Korub, 1978, [g]Ayoko et al, 1989.

However, when Fe(II) is in excess the stoichiometry becomes 6:1 during most of the reaction and will only change to 5.1 when bromine starts to accumulate. When these conditions are made, the rate equation reduces to equation (2.9).

$$\frac{-d[Fe(II)]}{dt} = 6k_1[Fe(II)][BrO_3^-] + 6k_2[Br^-][BrO_3^-][H^+]^2 \quad ...2.9$$

$k_1 = 1.25 \times 10^{-2} + 0.193[H^+]^2 M^{-1}s^{-1}$

$k_2 = 2.8 M^{-3}s^{-1}$, T = 25°C, I = 0.5M

The second order dependence on $[H^+]$ in this reaction can be explained in term of displacement of H_2O from $H_2BrO_3^+$ either prior to or in the rate determining step [Birk and Kozub, 1978].

$$BrO_3^- + 2H^+ \longrightarrow H_2BrO_3^+ \text{ (or } BrO_2^+ + H_2O) \quad .....(2.10)$$

$$Fe(II) + H_2BrO_3^+ \longrightarrow Fe(III) + BrO_2 + H_2O \quad ....(2.11)$$

This displacement then results into a binuclear species containing the reducing agent and BrO_3^- ion [Birk, 1973].

Although, BrO_3^- is known to undergo a 2-equiv-change as in the oxidation of Hg_2^{2+} dimer, 1-equiv-changes have also been observed in other systems [Sykes et al, 1976]. For example, the rate law for direct reduction of BrO_3^- by Fe(II) is consistent with the first electron transfer being rate determining.

The reduction of BrO_3^- by $Fe(Phen)_3^{2+}$ in H_2SO_4 has also been

investigated and the rate found to be dependent on the concentration ratio of the reactants [Koros et al, 1975]. For example, at $[Fe(Phen)_3^{2+}] = [BrO_3^-]$, the rate law is given by equation (2.12).

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}] \quad \ldots\ldots\ldots (2.12)$$

$$k = (7.54 \pm 0.42) \times 10^{-5} s^{-1}$$

while at $[Fe(phen)_3^{2+}] < [BrO_3^-]$, the reaction is autocatalytic and the rate law is described by equation (2.13).

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][BrO_3^-]^{2/3}[H_2SO_4]^{3/5} \quad \ldots\ldots\ldots (2.13)$$

$$k = (1.74 \pm 0.28) \times 10^{3} M^{-3} s^{-1}$$

2.3.2 Oxidation Reactions of Periodate (IO_4^-) ion

Periodate ion oxidation of metal ion complexes has been intensively studied [Sulfab, 1976; El-Eziri and Sulfab, 1977, Kassim and Sulfab, 1977; Sulfab and Abu-Shady, 1977], and in most cases it seems to prefer the inner sphere mechanism [Sulfab and Kassim, 1981; Sulfab and Abdel-Khalek, 1983]. This mechanism has been supported by the spectrophotometric identification of Co(III) intermediate products in the oxidation of Co(II) complexes of EDTA, HEDTA and EDDA [Sulfab and Kassim, 1977].

Symons (1955) has investigated and reported the oxidation of Fe(II) by IO_4^- to proceed via one-electron transfer steps. The polymerization of added acrylonitrile confirmed the formation of free radicals (I(VI)) resulting from one-electron transfer. But since IO_4^- is a two-electron oxidant (I(VII) - I(V)), a concurrent two electron transfer cannot be ruled out [El-Eziri and Sulfab, 1977] and therefore it is possible for the two electrons to be abstracted from one Fe(II) with the formation of unstable Fe(IV) as with some two-equivalent oxidants or from two Fe(II) [Sutin et al, 1965]. One of such systems [Sulfab, 1976] is characterized by the following stoichiometry;

$$2Fe(CN)_6^{4-} + IO_4^- + 2H_2O \longrightarrow 2Fe(CN)_6^{3-} + IO_3^- + 2OH^- + H_2O \quad \ldots\ldots(2.14)$$

At constant acid (pH 7.72) the rate law obeys equation (2.15)

$$-\frac{d[IO_4^-]}{dt} = k_2[Fe(CN)_6^{4-}][IO_4^-] \quad \ldots\ldots\ldots(1.15)$$

Like with other oxy-anions, the rate of oxygen exchange and redox reactions of IO_4^- also depend strongly on acid concentration [Birk and Kozub, 1973]. Therefore, the dependence of k_2 (equation 2.15) on $[H^+]$ is given by equation (2.16) and the final rate represented by equation (2.17).

$$k_2 = k_2' + k_3[H^+] \quad \ldots\ldots\ldots(2.16)$$

$$\frac{-d[IO_4^-]}{dt} = (k_2' + k_3[H^+])[Fe(CN)_6^{4-}][IO_4^-] \quad .....(2.17)$$

Different species of periodate ion exist in aqueous solution [Benson, 1968]. These species include H_6IO_6, $H_4IO_6^-$, $H_3IO_6^{2-}$ and IO_4^- are involved in the following equilibria (2.18 - 2.21).

$$H_4IO_6^- + H^+ \overset{k_1}{\rightleftharpoons} H_5IO_6, \quad k_1 = 1.98 \times 10^3\ M^{-1} \quad .... (2.18)$$

$$IO_4^- + 2H_2O \overset{k_H}{\rightleftharpoons} H_4IO_6^-, \quad k_H = 0.025 \quad .....(2.19)$$

$$H_3IO_6^{2-} + H^+ \overset{k_2}{\rightleftharpoons} H_4IO_6^-, \quad k_2 = 5.0 \times 10^9 M^{-1} \quad .....(2.20)$$

$$IO_4^- + H^+ \overset{k_3}{\rightleftharpoons} HIO_4, \quad k_3 = 150 \pm 10 M^{-1} \quad .....(2.21)$$

k_1, k_H and k_2 are values at I = 0, T = 25°C while k_3 is at I = 1.0M, T = 25°C.

At pH 4.2 and I = 0.1M, 99.8% of periodate in aqueous solution is present in the form of $H_4IO_6^-$ and IO_4^- [Kustin and Lieberman, 1964]. It would then be expected that the reactive species be IO_4^- and $H_4IO_6^-$, but rate laws of some systems include the other species [Sulfab and Howlett, 1976] as in the rate law below (2.22).

Rate = $(k_a[IO_4^-] + k_b[H_4IO_6^-] + k_c[H_3IO_6^{2-}])[Fe(CN)_6^{4-}]$...(2.22)

However, in most of the cases, IO_4^- and $H_4IO_6^-$ are the reactive species, especially with a series of Co(II) complexes [Wilkin

and Yelin, 1970; Al-Jallal and Sulfab and references therein, 1983].

IO_4^- has also been used in the oxidation of organic compounds, particularly in the oxidation of phenols [Radhaknishnamnt et al, 1976] and glycols [Sulfab and references therein, 1976]. For example, the oxidation of 1,2-diols by IO_4^- proceeds by way of a covalent link involving a cyclic intermediate [Sulfab, 1974] which corresponds to an inner sphere mechanism.

However, the electron transfer in $Fe(Phen)_3^{2+}/IO_4^-$ system has been reported to occur simultaneously via both inner - and outer - sphere pathways [Ige and Amire, 1985]. The inner sphere path which is the predominant pathway at low acid (0.02 - 0.15M), occurs by a single step two-electron transfer, while the outer sphere electron transfer process occurs at high acid (< 0.20M). Therefore the possibility of the occurence of the outer sphere mechanism can not be ruled out for the reaction of IO_4^- ion.

2.3.3 Reduction Reactions of Sulphite (SO_3^{2-}) ion

The sulphite ion has received a lot of attention as a powerful reductant in the past few decades [Benson, 1968]. The ion has been known to reduce metal ions and other oxidants by a variety of mechanisms and with varying stoichiometry [Russel and Yost, 1944]. The stoichiometry and products of the reaction allow a distinction to be made between one-equivalent and two-equivalent oxidizing agents examplified by equations (2.23) and (2.24), the products being dithionate ($S_2O_6^{2-}$) and sulphate

(SO_4^{2-}) ions respectively [Higginson and Marshall, 1957; Davies et al, 1969].

$$SO_3^{2-} \xrightarrow{-e^-} SO_3^{-} \longrightarrow \tfrac{1}{2}S_2O_6^{2-} \quad \ldots\ldots (2.23)$$

$$SO_3^{2-} \xrightarrow{-2e^-} SO_3 \ (i.e\ SO_4^{2-}) \quad \ldots\ldots\ldots\ldots (2.24)$$

The stoichiometry of the redox reaction depends largely on the lability of the metal ion complexes involved [Veprek-Siska et al, 1966]. For example, substitution inert complexes which behave as 1-equivalent oxidants, give SO_4^{2-} as product but substitution labile ones react with a lower non-integral stoichiometry, giving $S_2O_6^{2-}$ as an additional product.

$$SO_3^{2-} + 2M(n) \longrightarrow SO_4^{2-} + 2M(n-1) \quad \ldots\ldots (2.25)$$

$$SO_3^{2-} + (1-x)M(n) \longrightarrow xSO_4^{2-} + \tfrac{1}{2}(1-x)S_2O_6^{2-} + (1-x)M(n-1) \quad \ldots\ldots (2.26)$$

where x lies between zero and unity.

A group of researchers have earlier reported that free SO_3^{2-} ions are always oxidized to SO_4^{2-} without $S_2O_6^{2-}$ [Higginson and Marshall, 1957] or with very negligble amount of $S_2O_6^{2-}$ [Veprek-Siska et al, 1966]. But more recently, the formation of $S_2O_6^{2-}$ in addition to SO_4^{2-} as oxidation products of SO_3^{2-} has been established [Dennis et al, 1983], confirming earlier reports [Haight et al, 1965, Lister and Rosenblum, 1963].

The most intensively studied oxidation reaction of SO_3^{2-} is that involving Fe(III) complexes e.g $Fe(CN)_6^{3-}$ [Murray, 1968; Lancaster and Murray, 1971]. This reaction was believed to involve the intermediate $[Fe(CN)_5SO_3]^{4-}$, with the subsequent formation of SO_4^{2-} [Veprek-Siska and Wagnereva, 1965; Veprek-Siska et al, 1966], but this claim was later disproved by Swinehart (1967). When the species $[Fe(CN)_5SO_3]^{4-}$ was prepared and analysed, its reactivity was found to be different from that predicted by Veprek-Siska and so the outer sphere formation of SO_3^- radical ions is favoured.

Two reaction schemes have been proposed for the reduction of $Fe(CN)_6^{3-}$ by SO_3^{2-} in aqueous solution.

Scheme I

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \underset{\text{slow}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5(CN.SO_3]^{5-} \quad \ldots\ldots\ldots (2.27)$$

$$(Fe(CN)_6]^{3-} + [Fe(CN)_5(CN.SO_3)]^{5-} \xrightarrow[\text{fast}]{k_2} [Fe(CN)_6]^{4-} + [Fe(CN)_5(CN.SO_3)]^{4-} \quad \text{--------} (2.28)$$

$$(Fe(CN)_5(CN.SO_3)]^{4-} + H_2O \xrightarrow[\text{slow}]{k_3} [Fe(CN)_6]^{4-} + SO_4^{2-} + 2H^+ \quad \ldots\ldots (2.29)$$

Scheme II

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \underset{}{\overset{k_4}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + SO_3^- \quad \ldots\ldots (2.30)$$

$$[Fe(CN)_6]^{3-} + SO_3^- \xrightarrow[\text{fast}]{K_5} [Fe(CN)_5(CN.SO_3]^{4-} \quad \ldots\ldots (2.31)$$

$$Fe(CN)_5(CN.SO_3)^{4-} + H_2O \xrightarrow[\text{slow}]{k_c} [Fe(CN)_6]^{4-} + SO_4^{2-} + 2H^+ \quad \ldots\ldots(2.32)$$

The later scheme has been substantiated and found to be similar to the mechanism proposed earlier for the reaction between $Fe(CN)_6^{3-}$ and NO_2^- [Davies and Stedman, 1968].

In an effort to give more insight into the mechanism of the reaction of SO_3^{2-}, Dennis and co-workers (1983) have investigated $Mo(CN)_8^{3-}$-SO_3^{2-} and $V(CN)_6^{3-}$-SO_3^{2-} systems and established the occurence of the outer sphere mechanism in both cases with the following stoichiometry.

$$2M(CN)_6^{3-} + SO_3^{2-} \longrightarrow 2M(CN)_6^{4-} + SO_4^{2-} \quad \ldots\ldots(2.33)$$

M = Mo(V), V(V)

A similar mechanism has also been proposed to operate in the reaction between SO_3^{2-} and $IrCl_6^{2-}$ [Stapp and Carlyle, 1974]. The net reactions can be described by equations (2.34) and (2.35) and the rate law by (2.36).

$$2IrCl_6^{2-} + HSO_3^- + H_2O \longrightarrow 2IrCl_6^{3-} + SO_4^{2-} + 3H^+ \quad \ldots\ldots(2.34)$$

$$2IrCl_6^{2-} + 2HSO_3^- \longrightarrow 2IrCl_6^{3-} + S_2O_6^{2-} + 2H^+ \quad \ldots\ldots(2.35)$$

$$\frac{-d[IrCl_6^{2-}]}{dt} = \frac{k[HSO_3^-]}{[H^+]} \quad \ldots\ldots(2.36)$$

The rate law does not however suggest the product of the rate determining step; the products could be $IrCl_6^{3-}$ and SO_3^- or IrS^{VIII} complex as indicated in equations (2.37) and (2.38).

$$IrCl_6^{4-} + SO_3^{2-} \text{ -------> } IrCl_6^{3-} + SO_3^- \quad \text{.....(2.37)}$$

$$IrCl_6^{4-} + SO_3^{2-} \text{ -------> } IrS^{VIII} \quad \text{.....(2.38)}$$

Based on evidence from the rate law, stoichiometry and the inertness of $IrCl_6^{2-}$, the outer sphere mechanism was proposed for this system. (Consistent with earlier report [Brown and Higginson, 1972].)

Chapter 3

3.0 EXPERIMENTAL

3.1 Materials and Reagents

All reagents and solvents were used without further purification.

3.1.1 Diaquotetrakis (2,2'-bipyridine)-μ-oxo-diruthenium(III) perchlorate, $[(bipy)_2H_2ORuORuH_2O(bipy)_2](ClO_4)_4$

The oxo-bridged complex, $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$, ($RuORu^{4+}$), was prepared, purified and characterized according to the method outlined by Meyer and Coworkers [Weaver et al, 1975; Meyer and Godwin, 1971] as follows: Cis-Dichlorobis (2,2'-bipyridine) ruthenium(II), (2.00g, 4.13mmole) was suspended in distilled water (80cm^3) containing silver nitrate (1.76g, 10.36mmole, 2.51 equiv). The mixture was refluxed for 8 hours, cooled to room temperature and centrifuged. The supernatant liquid was filtered by suction into a fine frit to remove chloride and silver metal.. The filtrate was heated on a steam bath and treated with a saturated solution of sodium perchlorate ($NaClO_4$) until precipitation began to occur. Slow cooling to 0°C produced the desired material, which was collected by suction filtration, washed with a small portion of cold water and air dried. The salt was recrystallized from hot water containing small amount of $NaClO_4$. (The dark microcrystallined

solid gave a deep green solution in water and acetonitrile.) The yield was 1.45g or 54% of theoretical (theoretical yield = 2.69g). The electronic spectral properties of the prepared complex were consistent with the literature values [Weaver et al, 1975].

3.1.2 Preparation of Standard Sodium bromate ($NaBrO_3$) Solution

About 15g $NaBrO_3$ (B.D.H, Analar) were dried at 120°C for 2 hours and allowed to cool in a dessicator, from which a 1.0M solution was prepared in 100cm³ distilled water [Vogel, 1978]. A portion of the solution was treated with excess potassium iodine (KI) in acid medium and the liberated iodine was titrated against $Na_2S_2O_3$ solution previously standardized against KIO_3 [Birk and Kozub, 1973].

3.1.3 Preparation of standard sodium periodate ($NaIO_4$) solution

The solution was obtained by dissolving an accurate weight of $NaIO_4$ (B.D.H, Analar) in flasks wrapped with aluminium foil to avoid photochemical decomposition [Symons, 1955; Vivekanandam and Ramachandran, 1983). The $NaIO_4$ solution was standardized as follows: A 100cm³ portion of the solution (containing about 0.2g) was acidified with concentrated H_2SO_4. SO_2 was then passed into the solution until a colourless solution was obtained and the excess SO_2 boiled off. Ammoniacal solution of the mixture was precipitated with $AgNO_3$ solution. The precipitate was collected, washed with 1% HNO_3 and finally with little water. It was dried in the oven at 105-110°C until a constant weight was obtained. The concentration of the stock

solution was calculated based on the following equation:

$$Ag^{+} + 4SO_3^{2-} + IO_4^{-} \longrightarrow 4SO_4^{2-} + AgI \quad \ldots\ldots(3.1)$$

3.1.4 Preparation of Standard Sodium Sulphite (Na_2SO_3) Solution

The sulphite solution was prepared by dissolving an appropriate amount of Na_2SO_3 (B.D.H, L.R) in distilled water and standardized by iodometric method [Vogel, 1978]. 25cm³ of standard 0.1M iodine solution was pipetted into a 350cm³ conical flask, then 5cm³ of 2.0MHCl and 150cm³ distilled water were added. 20cm³ of 0.1M Na_2SO_3 solution was added slowly into the mixture with constant stirring. The excess iodine was titrated with standard (0.1M) $Na_2S_2O_3$ solution using starch indicator. The iodometric method of determination is based on the following equations:

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2H^{+} + 2I^{-} \quad \ldots\ldots(3.2)$$

$$HSO_3^{-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 3H^{+} + 2I^{-} \quad \ldots\ldots(3.3)$$

3.1.5 Preparation of 0.1M $Na_2B_4O_7.10H_2O$ solution

3.746g of $Na_2B_4O_7.10H_2O$ (B.D.H. Analar) were accurately weighed, dissolved in 100cm³ volumetric flask and made up of the mark with distilled water to give a 0.1M solution. (This solution was used as a primary standard for $HClO_4$).

3.1.6 Preparation of standard perchloric Acid ($HClO_4$) Solution

A stock solution (5.0M) of perchloric acid was obtained

by dilution from concentrated $HClO_4$ (B.D.H, Analar). About 0.1M solution was prepared from the stock and titrated against standard 0.1M $Na_2B_4O_7.10H_2O$ solution, using methyl orange indicator. The concentration of the $HClO_4$ was calculated from the following equation:

$$B_4O_7^{2-} + 2H^+ + 5H_2O \rightleftharpoons 4H_3BO_4 \quad \ldots\ldots\ldots \quad (3.4)$$

3.1.7 Preparation of Standard Sodium perchlorate ($NaClO_4$) Solution

A known weight of $NaClO_4$ (B.D.H, G.P.R) was dissolved in distilled water and standardized by gravimetric method as follows: $2cm^3$ portions of $NaClO_4$ stock solution were taken in preweighed bottles, dried at 105-110°C and cooled in a dessicator until constant weights were obtained. The weights obtained after drying $2cm^3$ portions were used to calculate the actual concentration of the solution.

3.1.8 Preparation of 0.1M KIO_3 solution (Primary Standard)

5.35g of KIO_3 (B.D.H, Analar), previously dried at 105-110°C and cooled in a dessicator, was accurately weighed and dissolved in $250cm^3$ of distilled water to give a 0.1M solution.

3.1.9 Preparation of standard 0.1M sodium thiosulphate ($Na_2S_2O_3$) Solution

About 26g of $Na_2S_2O_3.5H_2O$ (B.D.H, Analar) were weighed and dissolved in $1dm^3$ distilled water. The solution was standardized against 0.1M KIO_3 as follows: $20cm^3$ of 0.1M KIO_3

and 5cm³ of M-H_2SO_4 were taken in a conical flask and a saturated solution of KI was added to the mixture. The liberated I_2 was titrated against a portion of the $Na_2S_2O_3$ solution using starch solution as indicator.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad \ldots\ldots\ldots (3.5)$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \ldots\ldots\ldots (3.6)$$

3.1.10 Preparation of 0.1M Iodine (I_2) Solution

About 20g of iodate free KI (B.D.H, Analar) were dissolved in 30-40cm³ of distilled water in a glass stopped 1dm³ graduated flask and 12.7g of iodine (B.D.H, Analar) was transferred into the concentrated KI solution. The glass stopper was inserted into the flask and shaken in the cold until all the iodine dissolved. The solution was then allowed to acquire room temperature and made up to the mark with distilled water. It was standardized against $Na_2S_2O_3$ solution and kept in a cool dark place.

3.1.11 Nitron Reagent ($C_{20}H_{16}N_4$)

The reagent was prepared by dissolving 5g of nitron (B.D.H, G.P.P) in 500cm³ of 5% acetic acid and stored in a dark bottle. (The mono-acid base nitron, $C_{20}H_{16}N_4$, forms a fairly insoluble crystalline nitrate, $C_{20}H_{16}N_4.HNO_3$, which was used for the quantitative determination of nitrates.)

3.1.12 CH_3COONa, HCOONa, $NaNO_3$, $NaNO_2$ and Na_2SO_4 Solutions

The solutions of CH_3COONa, HCOONa, $NaNO_3$, $NaNO_2$ and Na_2SO_4 were prepared by dissolving known weights of the respective salts in known volumes of distilled water. (The salts were B.D.H, L.R. except Na_2SO_4 which was B.D.H, Analar.)

3.2 Stoichiometric studies

The stoichiometries of the reactions were determined by spectrophotometric titration. Reaction mixtures containing various concentrations of $RuORu^{4+}$ (0.25-12.5 x 10^{-6}M) and constant concentration of each oxyanion (1.0 x 10^{-5}M), $[H^+]$ = 0.05M, I = 1.0M (BrO_3^-, IO_4^-), I = 2.0M (SO_3^{2-}), were allowed to stand until the reactions had gone to completion. The absorbances of the solutions were then measured at 650nm.

3.3 Kinetic Measurements

The rate of reaction of $RuORu^{4+}$ with each of the oxyanions (BrO_3^-, IO_4^- and SO_3^{2-}) was studied by monitoring the decrease in the absorbance of the dimer ($RuORu^{4+}$) at 650nm. All kinetic measurements were made under pseudo-first-order conditions, with the respective oxyanions in more than 100 fold excess over $[RuORu^{4+}]$ at 24.0 ± 1.0°C and I = 1.0M ($NaClO_4$) for BrO_3^- and IO_4^- and I = 2.0M ($NaClO_4$) for SO_3^{2-}, unless otherwise indicated.

Chapter 4

4.0 RESULTS

4.1 Stoichiometry

The spectrophotometric determination of the stoichiometries of the three systems did not yield any results. All the reaction mixtures gave almost the same absorbances from the measurements taken after every 24 hours for a period of 3 months. The difficulty encountered in this respect may be attributed to the very high extinction coefficient of the oxo-complex (25,000$M^{-1}cm^{-1}$ at 660nm). Because of the intense green colour of $RuORu^{4+}$ solutions, there was no significant change in absorbance in the presence of the low concentrations of the oxyanions and so the determination of the stoichiometries was unsuccessful.

4.2 Determination of order with respect to $[RuORu^{4+}]$ and $[XO_m^{n-}]$

The rates of the reactions were measured under conditions in which (XO_m^{n-}) was at least 100 fold excess over $[RuORu^{4+}]$. Pseudo-first-order plots of $\log(A_t - A_\infty)$ versus time were linear to between 50 and 80% completion of reaction. (A_t and A_∞ are the absorbances of the complex at time t and the end of the reaction respectively.) Typical plots of these systems are shown in Figures (4.1 - 4.3). The linearity of each of these plots shows that the reactions are first order in $[RuORu^{4+}]$.

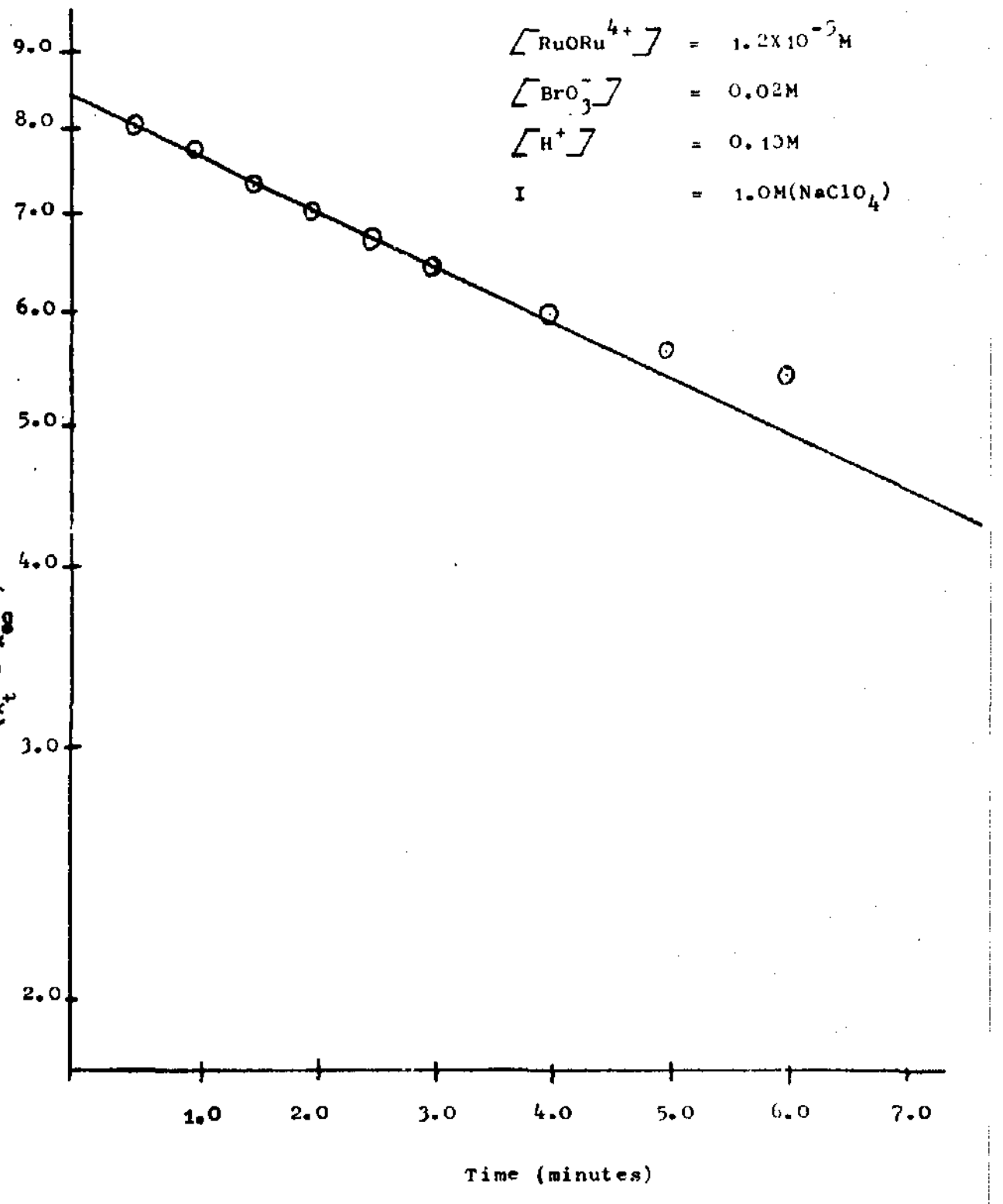


Figure 4.1 Pseudo-first-order plot for the redox reaction between $RuORu^{4+}$ and BrO_3^-

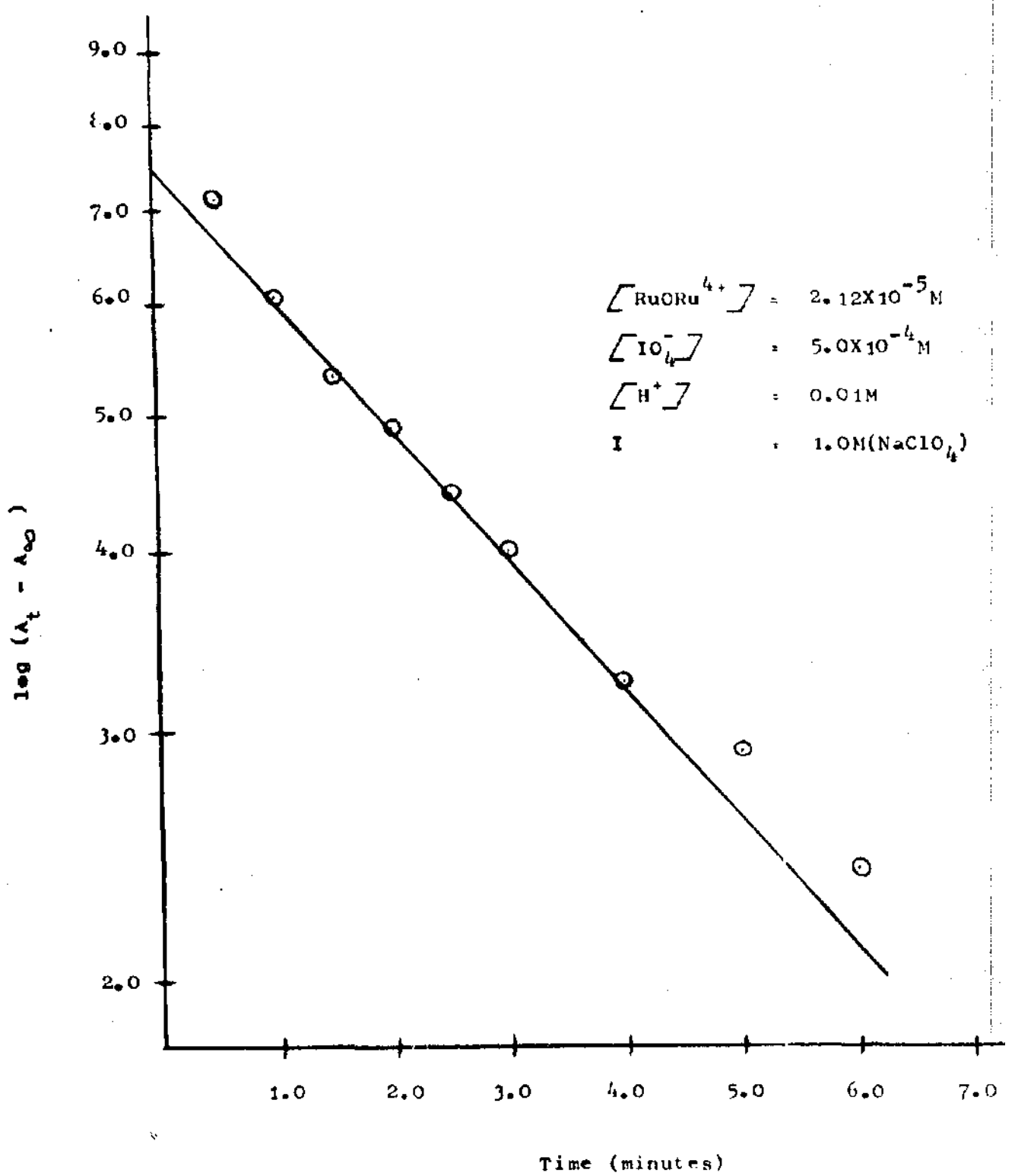


Figure 4.2 Pseudo-first-order plot for the redox reaction between $RuORu^{4+}$ and IO_4^-.

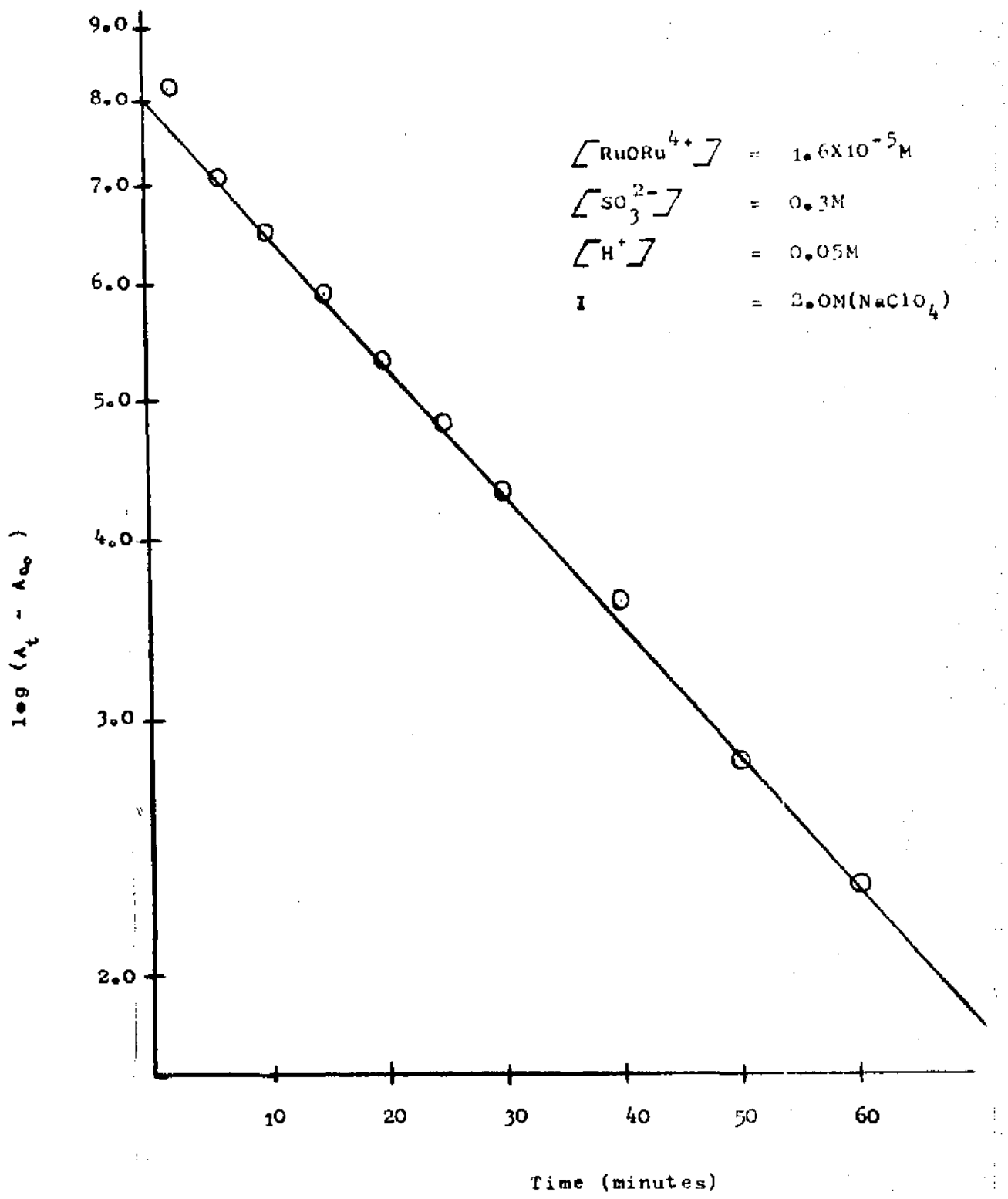


Figure 4.3: Pseudo-first-order plot for the redox reaction between $RuORu^{4+}$ and SO_3^{2-}

Plots of $\log K_{obs}$ versus $\log[XO_m^{n-}]$ were also linear with slopes of 1.03 (BrO_3^-), 0.77 (IO_4^-) and 1.08 (SO_3^{2-}) confirming that the reactions were also first order in $[XO_m^{n-}]$. Therefore, the rate equation for each of the reactions is represented by equation (4.1)

$$\frac{-d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][XO_m^{n-}] \quad \ldots\ldots\ldots\ldots \quad (4.1)$$

where $k_2 = k_{obs}/[XO_m^{n-}]$

k_{obs} = Pseudo-first-order rate constant

k_2 = Second-order rate constant

The second-order rate constants, calculated from $k_2 = k_{obs}/[XO_m^{n-}]$, were fairly constant, supporting first order dependence on $[XO_m^{n-}]$. Typical plots of $\log k_{obs}$ versus $\log[XO_m^{n-}]$ and the second-order rate constants determined from these plots are given in Figures (4.4 - 4.6) and Tables (4.1 - 4.3) respectively.

For $RuORu^{4+}$ - BrO_3^- system,

$k_2 = (8.28 \pm 1.56) \times 10^{-2} M^{-1}s^{-1}$ at $[H^+] = 0.01M$,

$I = 1.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0°C$.

For $RuORu^{4+}$ - IO_4^- system

$k_2 = 9.41 \pm 1.20 M^{-1}s^{-1}$ at $[H^+] = 0.10M$, $I = 1.0M$ ($NaClO_4$)

$T = 24.0 \pm 1.0°C$

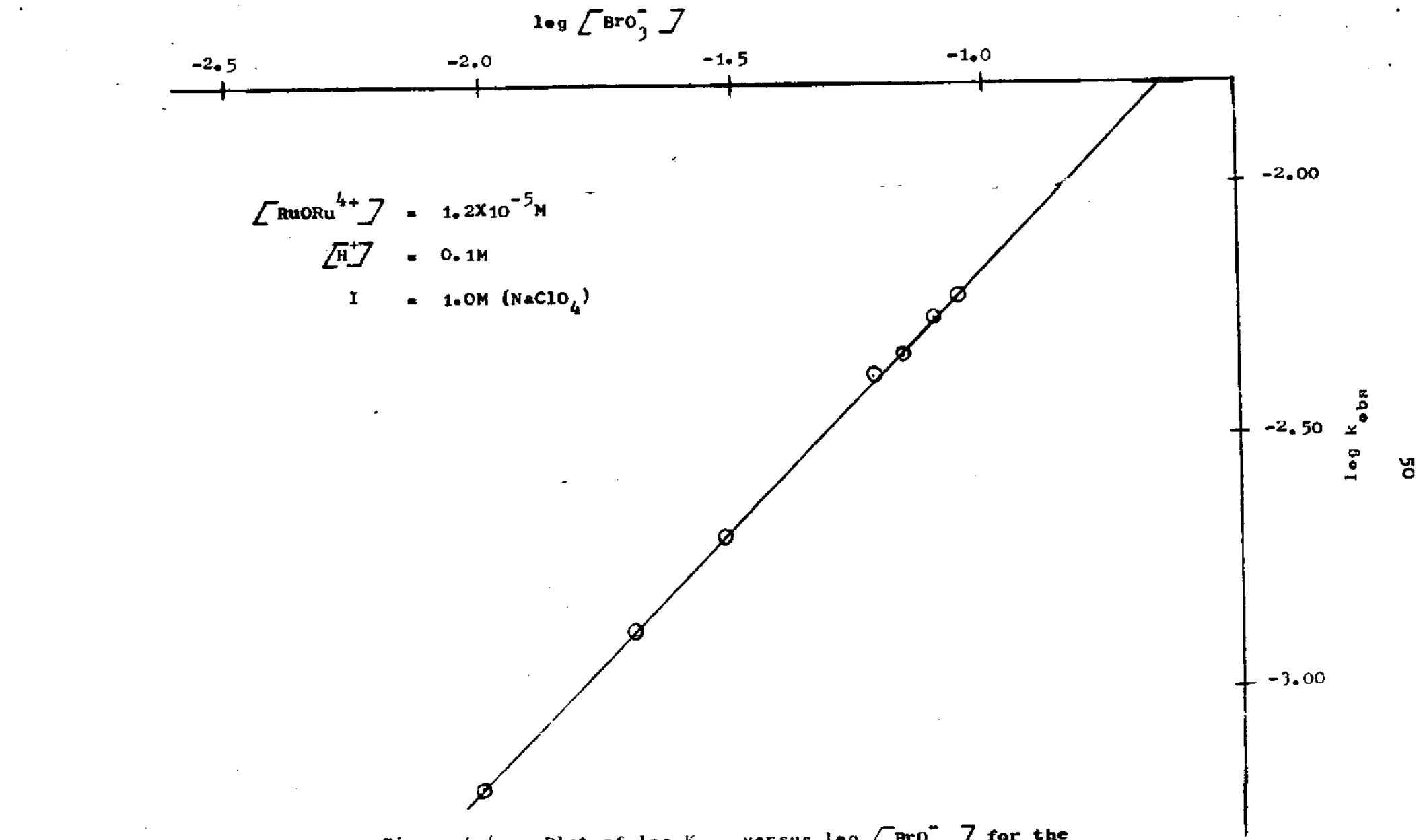


Figure 4.4 Plot of log K_{obs} versus log $[BrO_3^-]$ for the reaction of $RuORu^{4+}$ and BrO_3^-

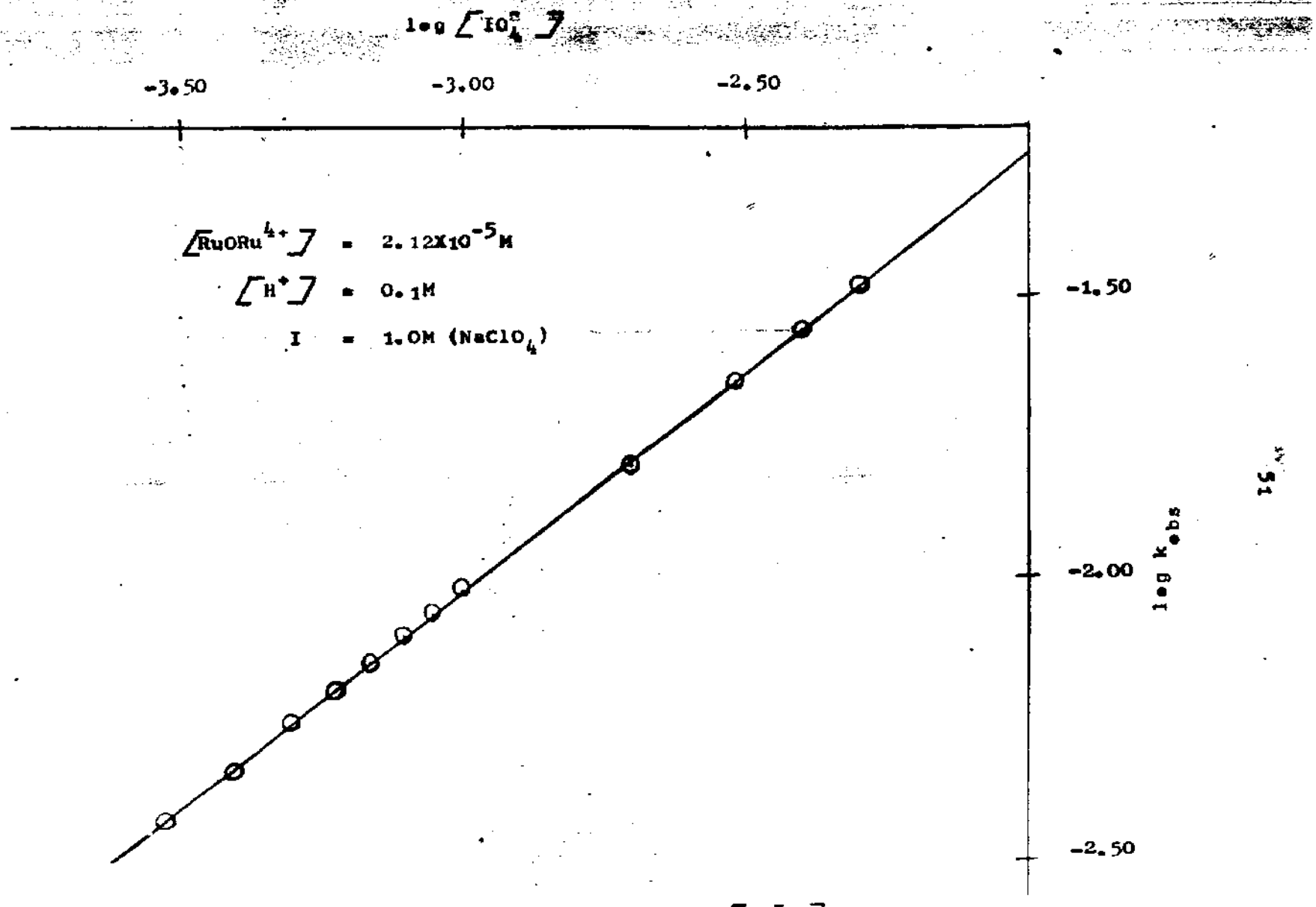


Figure 4.5: Plot of log k_{obs} versus log $[IO_4^-]$ for the reaction of $RuORu^{4+}$ and IO_4^-

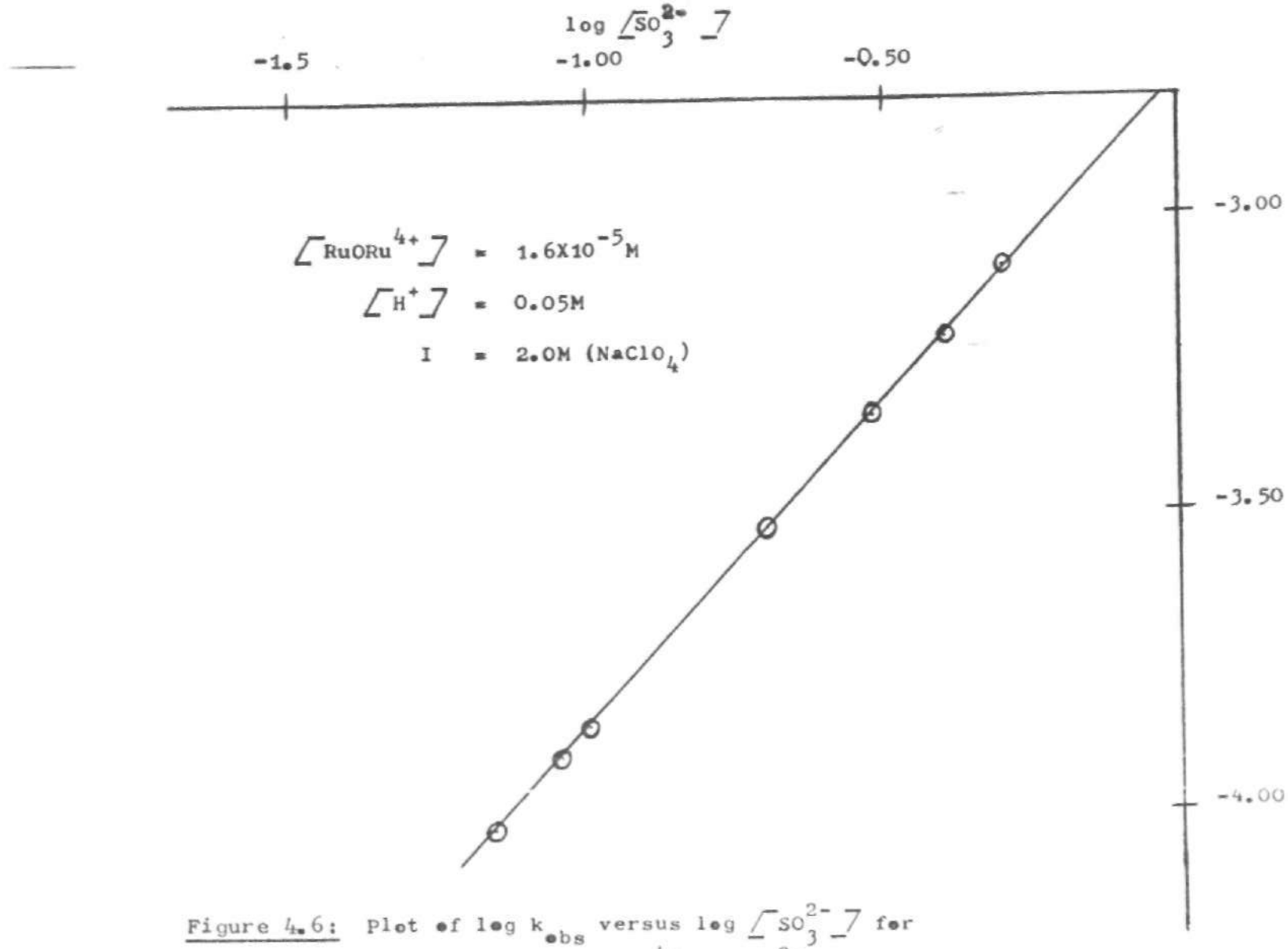


Figure 4.6: Plot of log k_{obs} versus log $[SO_3^{2-}]$ for the reaction of $RuORu^{4+}$ and SO_3^{2-}

Table 4.1

Pseudo-first-order and Second-order rate constants for the reaction of $RuORu^{4+}$ and BrO_4^-

$[RuORu^{4+}] = 1.2 \times 10^{-5}M$, $I = 1.0M$ ($NaClO_4$)

$T = 24.0 \pm 1.0^{o}C$ $\lambda max = 650nm$

$10^{2}[BrO_4^-]$, M	$[H^+]$, M	$10^{3}k_{obs}$, s^{-1}	$10^{2}k_2$, $M^{-1}s^{-1}$
2.0	0.01	1.34	6.70
5.0	0.01	5.43	10.86
6.0	0.01	5.39	8.98
7.0	0.01	5.34	7.63
8.0	0.01	6.43	8.04
9.0	0.01	5.78	6.42
1.0	0.10	0.65	6.51
2.0	0.10	1.34	6.50
3.0	0.10	1.90	6.33
6.0	0.10	5.66	9.43
7.0	0.10	4.26	6.08
8.0	0.10	6.68	8.38
9.0	0.10	4.67	5.19

Table 4.2

Pseudo-first-order and second-order rate constants for the reaction of $RuORu^{4+}$ and IO_4^-

$[RuORu^{4+}] = 2.12 \times 10^{-5}M$, $I = 1.0M$ ($NaClO_4$),

$T = 24.0 \pm 1.0^{\circ}C$, $\lambda max = 650nm$

$10^4[IO_4^-]$, M	$[H^+]$, M	$10^3 k_{obs}$, s^{-1}	k_2, $M^{-1}s^{-1}$
3.0	0.1	2.48	8.26
4.0	0.1	3.93	9.93
5.0	0.1	5.28	10.56
6.0	0.1	5.34	8.89
7.0	0.1	8.17	11.68
8.0	0.1	7.94	9.92
9.0	0.1	7.22	8.03
10.0	0.1	9.69	9.69
20.0	0.1	16.20	8.12
30.0	0.1	30.90	10.30
40.0	0.1	31.21	7.30
50.0	0.1	48.50	9.69

Table 4.3

Pseudo-first-order and second order rate constants for the reaction of $RuORu^{4+}$ and SO_3^{2-}

$[RuORu^{4+}] = 1.6 \times 10^{-4}$M, $I = 2.0$M($NaClO_4$),

$T = 24.0 \pm 1.0$°C, $\lambda_{max} = 650$nm

$[SO_3^{2-}]$, M	$[H^+]$, M	$10^4 k_{obs}$, s^{-1}	$10^3 k_2$, $M^{-1}s^{-1}$
0.05	0.05	0.61	1.23
0.07	0.05	0.93	1.33
0.09	0.05	1.46	1.62
0.10	0.05	1.72	1.72
0.20	0.05	2.72	1.36
0.30	0.05	3.53	1.18
0.40	0.05	6.20	1.55

and for $RuORu^{4+}$ - SO_3^{2-} system,

k_2 = (1.43 ± 0.21) x $10^{-3}M^{-1}s^{-1}$ at $[H^+]$ = 0.05M

I = 2.0M ($NaClO_4$), T = 24.0 ± 1.0°C.

4.3 Effect of hydrogen ion on the rates of the reactions of $RuORu^{4+}$ and XO_m^{n-}.

The influence of $[H^+]$ on the rates of the reactions between each of the oxy-anions and $RuORu^{4+}$ was investigated by determining the rate constants in the acid range 0.01 - 0.50M. (Both $[RuORu^{4+}]$ and $[XO_m^{n-}]$ were kept constant at 24.0 ± 1.0°C and I = 1.0M ($NaClO_4$) for BrO_3^- and IO_4^- systems) and I = 2.0M ($NaClO_4$) for the SO_3^{2-} system.) The rate constants were found to be dependent on the hydrogen ion concentration in each case. Values of the acid dependent rate constants (k_H) are given in Tables (4.4 - 4.6).

Least squares analyses of plots of k_H versus $[H^+]^z$ (z = 2,1 and -1 for BrO_3^-, IO_4^- and SO_3^{2-} respectively) were linear with an intercept in each case. (Figures 4.7 - 4.9). The rate constants can thus be represented by equation (4.2)

$$k_H = a + b[H^+]^z \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

and the overall rate equation can be written as;

$$\frac{-d[RuORu^{4+}]}{dt} = (a + b[H^+]^z)[RuORu^{4+}][XO_m^{n-}] \quad \ldots\ldots\ldots (4.3)$$

Table 4.4

Acid dependent rate constants for the reaction of $RuORu^{4+}$ and BrO_3^-

$[RuORu^{4+}] = 1.2 \times 10^{-5}M$, $[BrO_3^-] = 0.08M$

$I = 1.0M(NaClO_4)$, $T = 24.0 \pm 1.0^{o}C$, $\lambda max = 650nm$

$[H^+]$, M	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, $M^{-1}s^{-1}$
0.01	4.34	5.43
0.03	4.65	5.81
0.04	5.36	6.70
0.05	5.30	6.63
0.06	6.12	7.65
0.07	6.30	7.88
0.09	7.64	9.55

Table 4.5

Acid dependant rate constants for the oxidation of $RuORu^{4+}$ by IO_4^- ion

$[RuORu^{4+}] = (2.12 \times 10^{-5}M$, $[IO_4^-] = 5.0 \times 10^{-4}M$,

$I = 1.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0°C$, $\lambda max = 650nm$.

$[H^+]$, M	$10^3 k_{obs}$, s^{-1}	k_2, $M^{-1}s^{-1}$
0.01	3.88	7.76
0.02	4.77	9.54
0.03	4.23	11.40
0.04	6.08	12.16
0.06	7.27	14.54
0.07	7.73	15.46
0.08	7.78	15.56
0.09	8.89	17.78

Table 4.6

Acid dependent rate constants for the reaction of $RuORu^{4+}$ and SO_3^{2-}

$[RuORu^{4+}] = 1.6 \times 10^{-5}M$, $[SO_3^{2-}] = 0.10M$,

$I = 2.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0^{o}C$, $\lambda max = 650nm$

$[H^+]$, M	$10^4 k_{obs}$, s^{-1}	$10^3 k_2$, $M^{-1}s^{-1}$
0.03	1.46	1.46
0.05	1.25	1.25
0.07	1.13	1.13
0.09	0.80	0.80
0.10	0.37	0.37
0.20	0.51	0.51
0.30	0.31	0.31
0.40	0.45	0.45
0.50	0.44	0.44

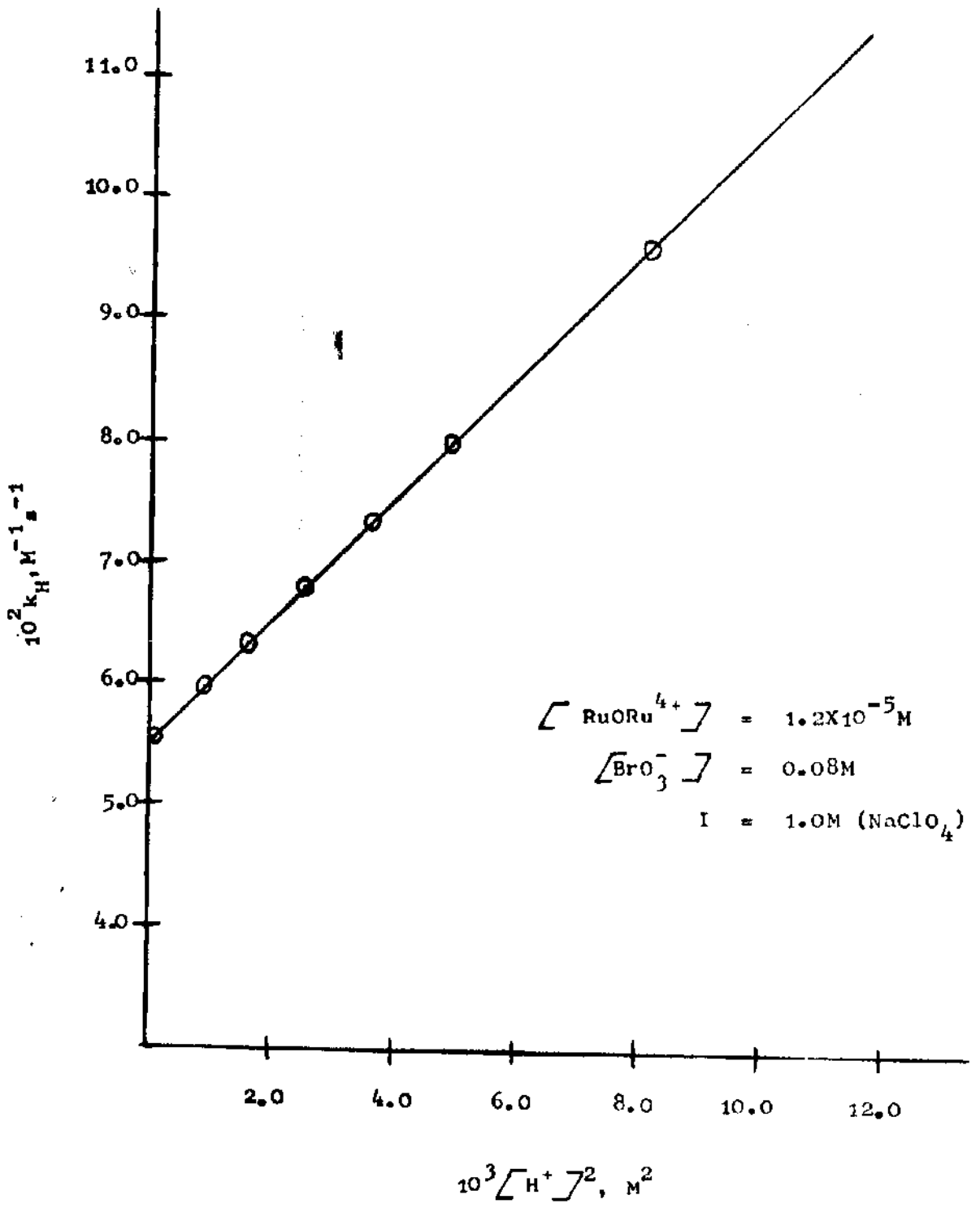


Figure 4.7: Plot of k_H versus $[H^+]^2$ for the redox reaction between $RuORu^{4+}$ and BrO_3^-

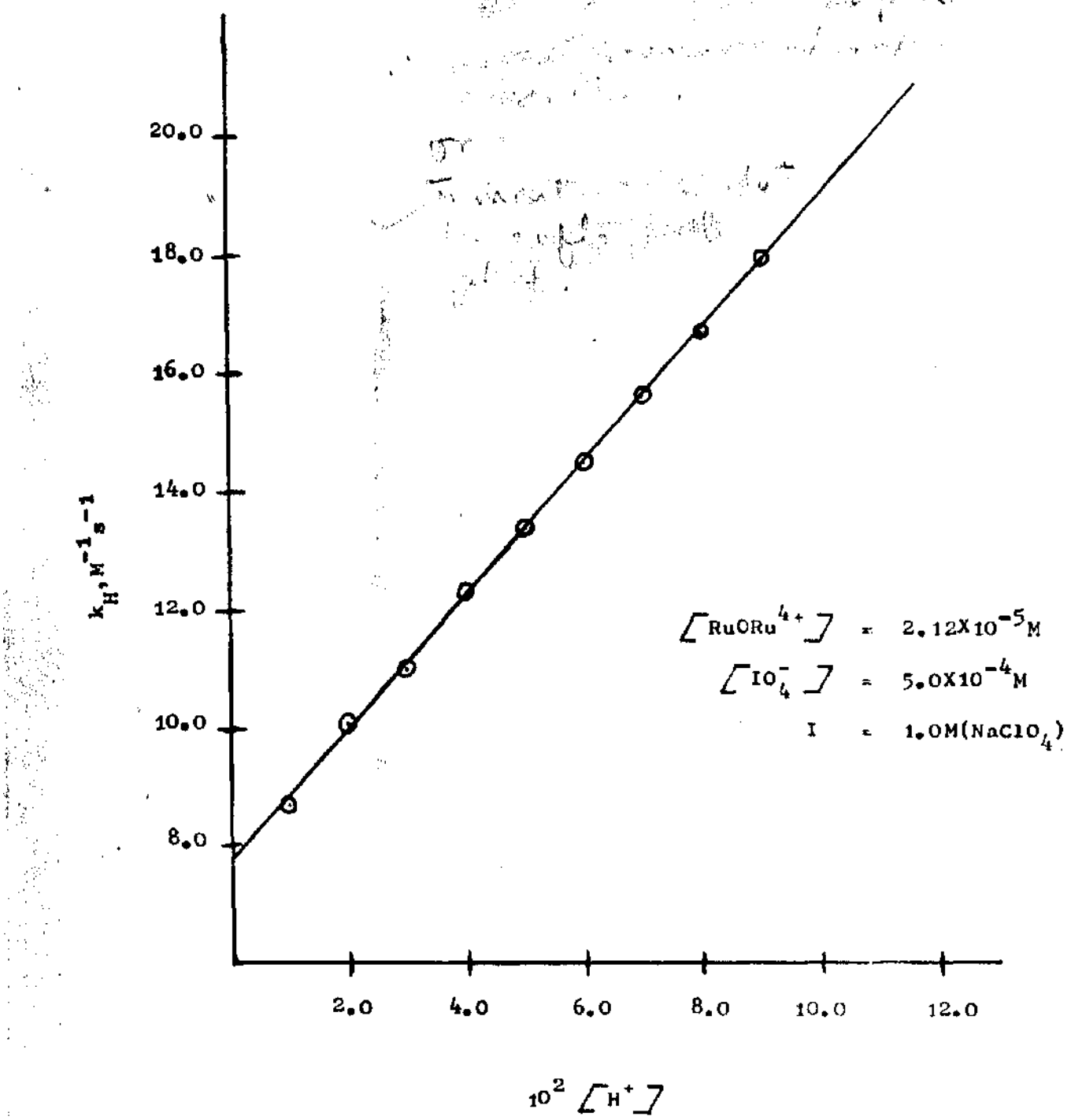


Figure 4.8: Plot of k_H versus $[H^+]$ for the redox reaction between $RuORu^{4+}$ and IO_4^-.

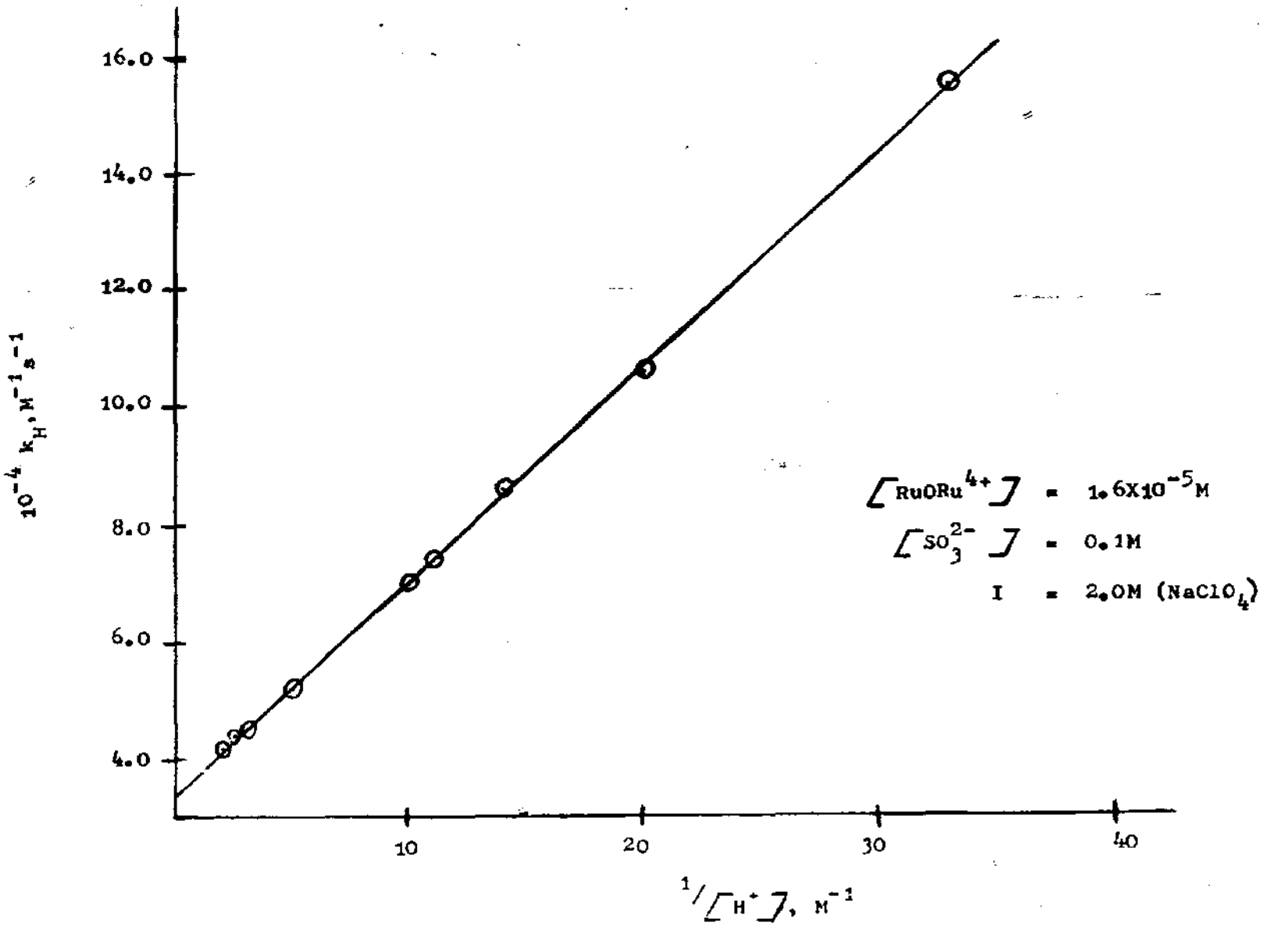


Figure 4.9: Plot of k_H versus $[H^+]^{-1}$ for the redox reaction between $RuORu^{4+}$ and SO_3^{2-}

a and b are intercept and slope respectively, whose values are given below for each of the systems at 24.0 ± 1.0°C.

RuORu^{4+} - BrO_3^- system

a = 5.53 x $10^{-2}M^{-1}s^{-1}$, b = $5.09M^{-2}s^{-1}$

at I = 1.0M ($NaClO_4$), $[H^+]$ = 0.01 - 0.09M.

RuORu^{4+} - IO_4^- system

a = $7.75M^{-1}s^{-1}$, b = 1.13 x $10^{2}M^{-2}s^{-1}$

at I = 1.0M ($NaClO_4$), $[H^+]$ = 0.1 - 0.5M

RuORu^{4+} - SO_3^{2-} system

a = 3.4 x $10^{-4}M^{-1}s^{-1}$, b = 6.37 x $10^{-6}s^{-1}$

at I = 2.0M ($NaClO_4$), $[H^+]$ = 0.03 - 0.50M.

4.4 Effect of added anions on the rates of the reactions of RuORu^{4+} and IO_4^-

Keeping the concentrations of all other reactants constant, (I = 1.0M for BrO_3^- and IO_4^-, and I = 2.0M for SO_3^{2-}), the effect of added anions on the rates of the reactions was investigated for $[X^-]$ = 0.008 - 0.05M (X = $HCOO^-$, CH_3COO^-, NO_3^- and NO_2^-). (From preliminary investigations, the added anions have been shown not to react with either the complex or oxyanions.) The anion dependent rate constants ($^nk_2$) are given in Tables (4.7 - 4.9).

The rate constants for RuORu^{4+} - BrO_3^- and RuORu^{4+} - SO_3^{2-} reactions were found to increase while those of RuORu^{4+} - IO_4^- decreased with increase in the concentrations of the appropriate

Table 4.7

Anion-dependent rate constants (^{x}k) for the reaction of $RuORu^{4+}$ and BrO_3^-

$[RuORu^{4+}] = 1.2 \times 10^{-5}M$, $[BrO_3^-] = 0.02M$

$I = 1.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0^{o}C$, $\lambda max = 650nm$

$[H^+]$, M	$10^2[X^-]$, M	$10^3 \times k_{obs}$, s^{-1}	$10^{2x} \times k_2$, $M^{-1}s^{-1}$
	$X = HCOO^-$		
0.05	0.8	1.55	7.75
0.05	1.0	1.78	8.9
0.05	2.0	1.44	7.20
0.05	3.0	1.63	8.15
	$X^- = NO_3^-$		
0.05	1.0	1.93	9.65
0.05	2.0	2.18	10.90
0.05	3.0	2.30	11.50
0.05	5.0	2.25	11.25
	$X^- = CH_3COO^-$		
0.05	0.8	3.14	15.70
0.05	2.0	3.39	16.95
0.05	4.0	4.09	20.45

Table 4.8

Anion-dependent rate constants (^{x}k) for the reaction of $RuORu^{4+}$ and IO_4^-

$[RuOTu^{4+}] = 2.12 \times 10^{-5}M$, $[IO_4^-] = 5 \times 10^{-4}M$, I = 1.0M ($NaClO_4$), T = 24.0 ± 1.0°C λmax = 650nm

$[H^+]$, M	$[X^-]$, M	$10^3 \times k_{obs}$, s^{-1}	$^{x}k_2$, $M^{-1}s^{-1}$
		$X^- = 10^2[HCOO^-]$	
0.05	0.7	3.21	6.42
0.05	0.9	3.28	6.56
0.05	1.0	3.05	6.10
0.05	3.0	2.06	4.12
0.05	4.0	2.01	4.02
0.05	5.0	1.43	2.86
		$X^- = 10^2[CH_3COO^-]$	
0.05	2.0	3.11	6.22
0.05	3.0	3.04	6.08
0.05	6.0	1.75	3.50
0.05	8.0	1.56	3.12
0.05	10.0	1.17	2.34
		$X^- = 10^2[NO_3^-]$	
0.05	0.3	3.63	7.26
0.05	0.5	3.57	7.13
0.05	0.9	3.47	6.93
0.05	2.0	3.29	6.58
0.05	6.0	2.91	5.83
0.05	8.0	3.00	6.00
0.05	20.0	2.06	4.12

Table 4.9

Anion-dependent rate constants (^{x}k) for the reaction of $RuORu^{4+}$ and SO_3^{2-}

$[RuORu^{4+}] = 1.6 \times 10^{-5}M$, $[SO_3^{2-}] = 0.1M$, $I = 2.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0°C$, $\lambda max = 650nm$

$[H^+]$, M	$[X^-]$, M	$10^4 \times k_{obs}$, s^{-1}	$10^3 \times k_2$, $M^{-1}s^{-1}$
		$X^- = NO_2^-$	
0.05	0.01	0.07	0.07
0.05	0.05	0.84	0.84
0.05	0.09	1.10	1.10
0.05	0.10	1.25	1.25
0.05	0.20	1.75	1.75
0.05	0.30	2.30	2.30
0.05	0.40	2.69	2.69
		$X^- = HCOO^-$	
0.05	0.10	1.55	1.55
0.05	0.20	1.54	1.54
0.05	0.30	1.94	1.94
0.05	0.40	2.16	2.16
0.05	0.50	2.54	2.54

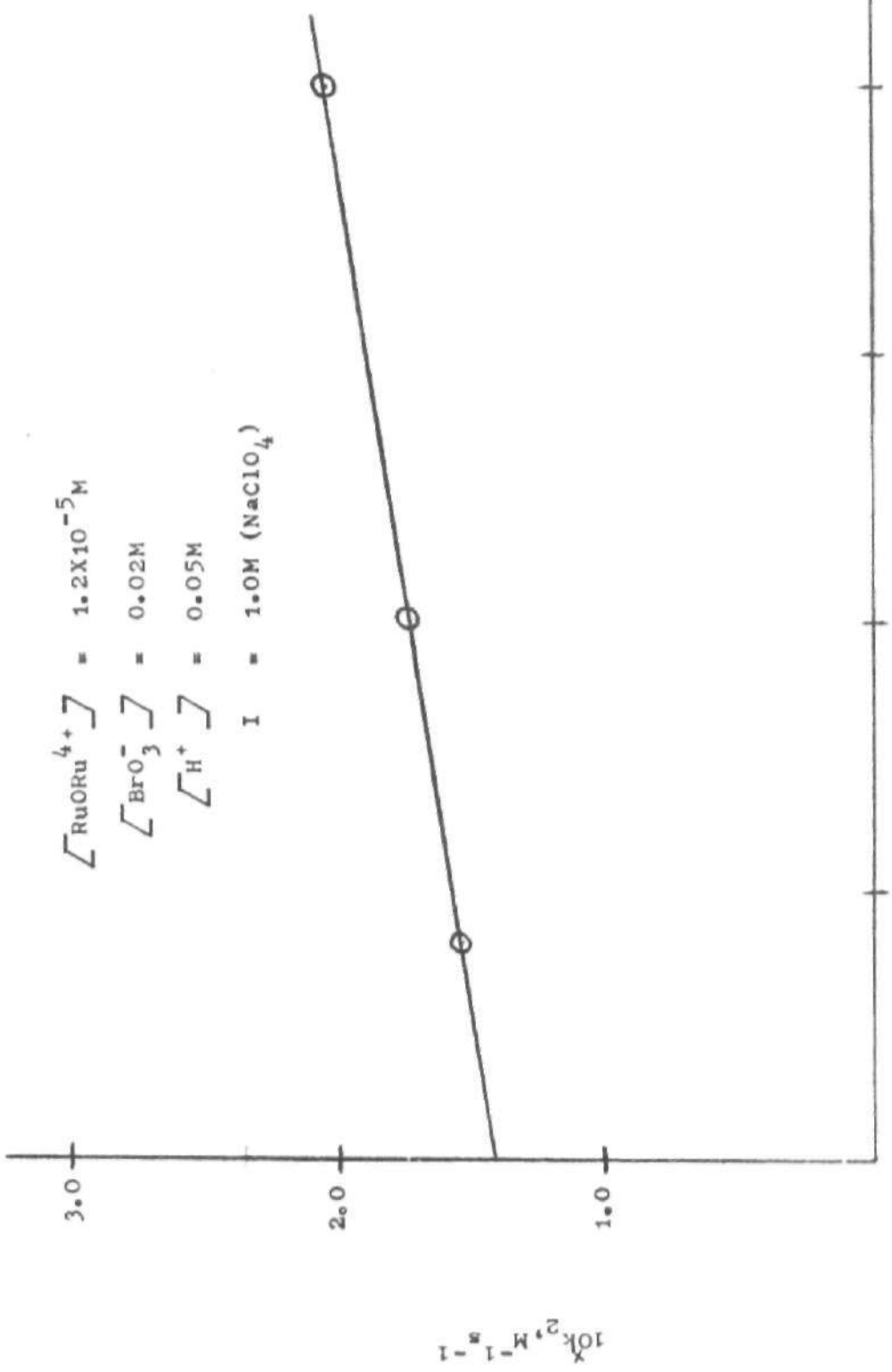


Figure 4.10: Plot of $^{X}k_2$ versus $[CH_3COO^-]$ for the redox reaction between $RuORu^{4+}$ and BrO_3^-

$[RuORu^{4+}]$ = 1.2×10^{-5} M

$[BrO_3^-]$ = 0.02M

$[H^+]$ = 0.05M

I = 1.0M ($NaClO_4$)

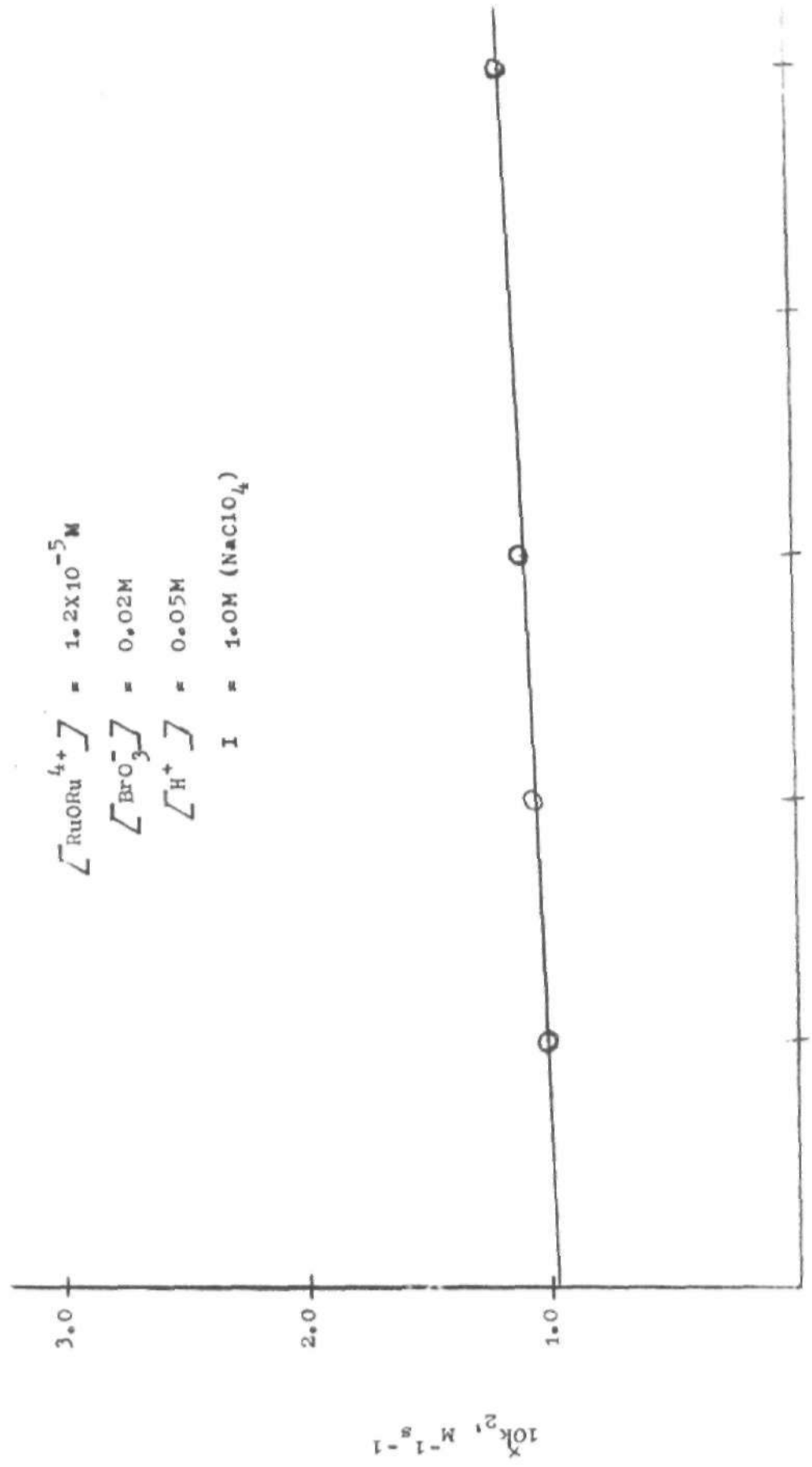


Figure 4.11: Plot of $^{\chi}k_2$ versus $[NO_3^-]$ for the redox reaction between $RuORu^{4+}$ and BrO_3^-

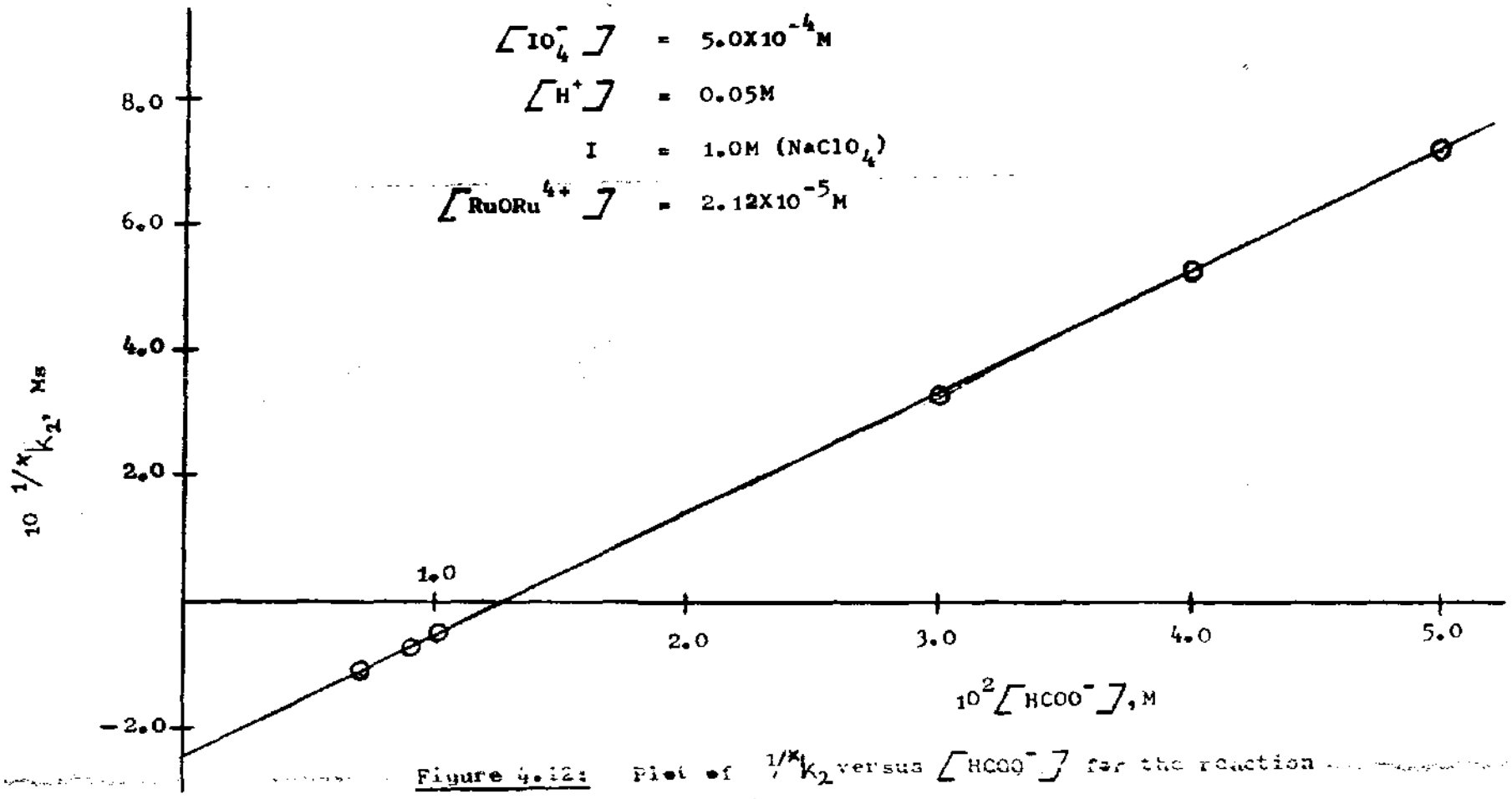


Figure 4.12: Plot of $^{1}/_{k_2}$ versus $[HCOO^-]$ for the reaction of $RuORu^{4+}$ and IO_4^-.

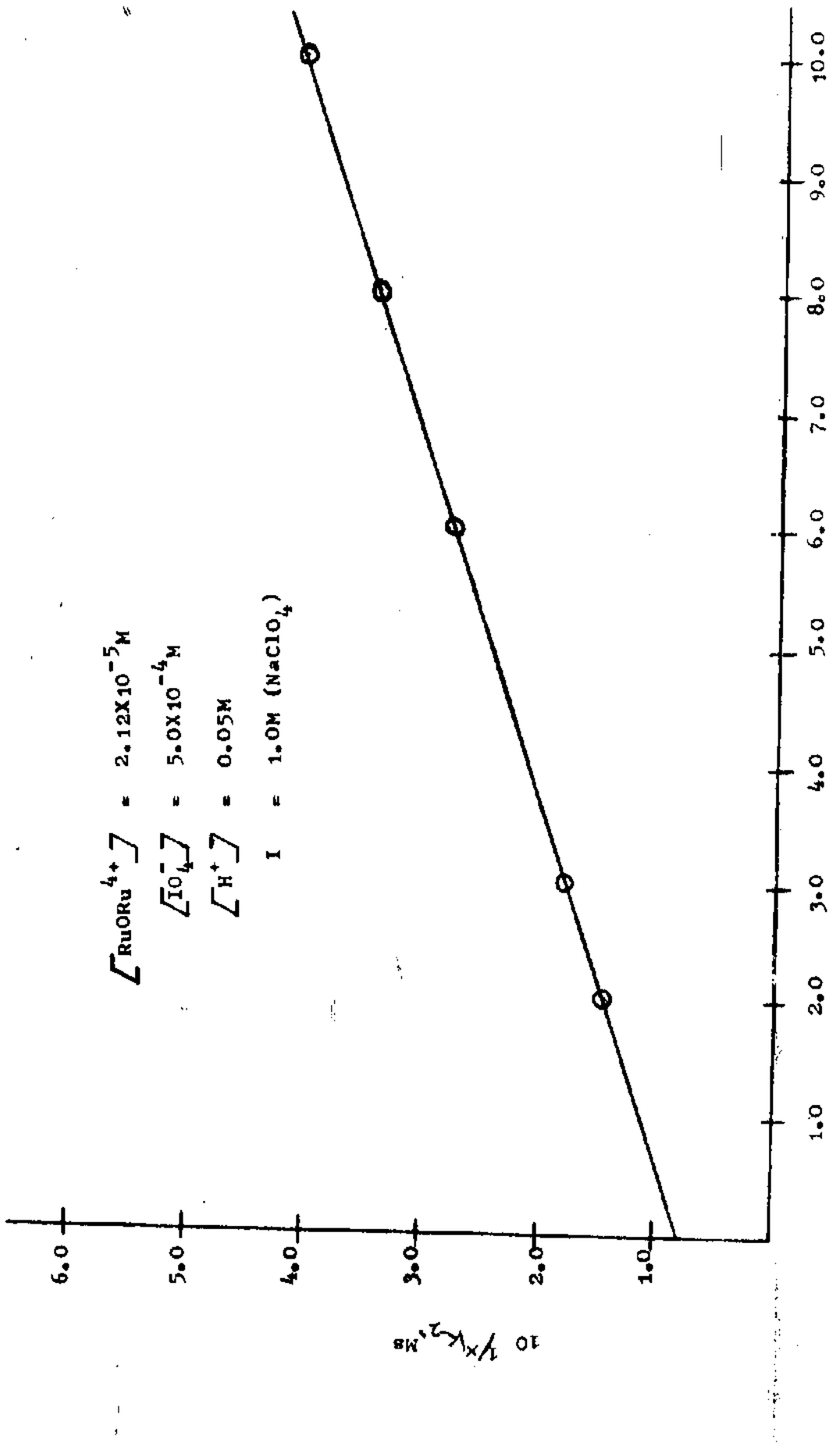


Figure 4.13: Plot of $1/k_{2,ms}$ versus $[CH_3COO^-]$ for the reaction of $RuORu^{4+}$ and IO_4^-.

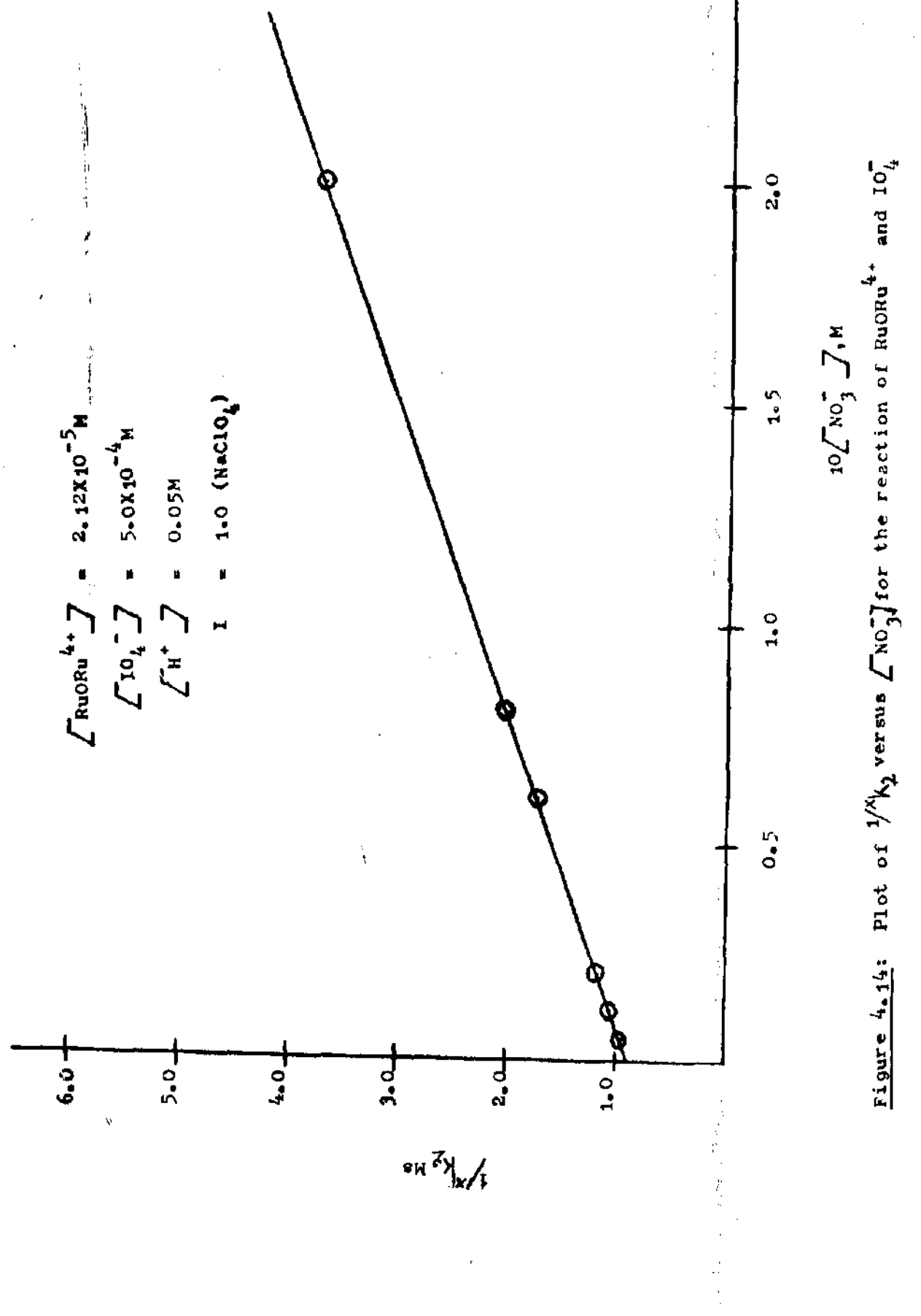


Figure 4.14: Plot of $1/\chi_{K_2}$ versus $[NO_3^-]$ for the reaction of $RuORu^{4+}$ and IO_4^-

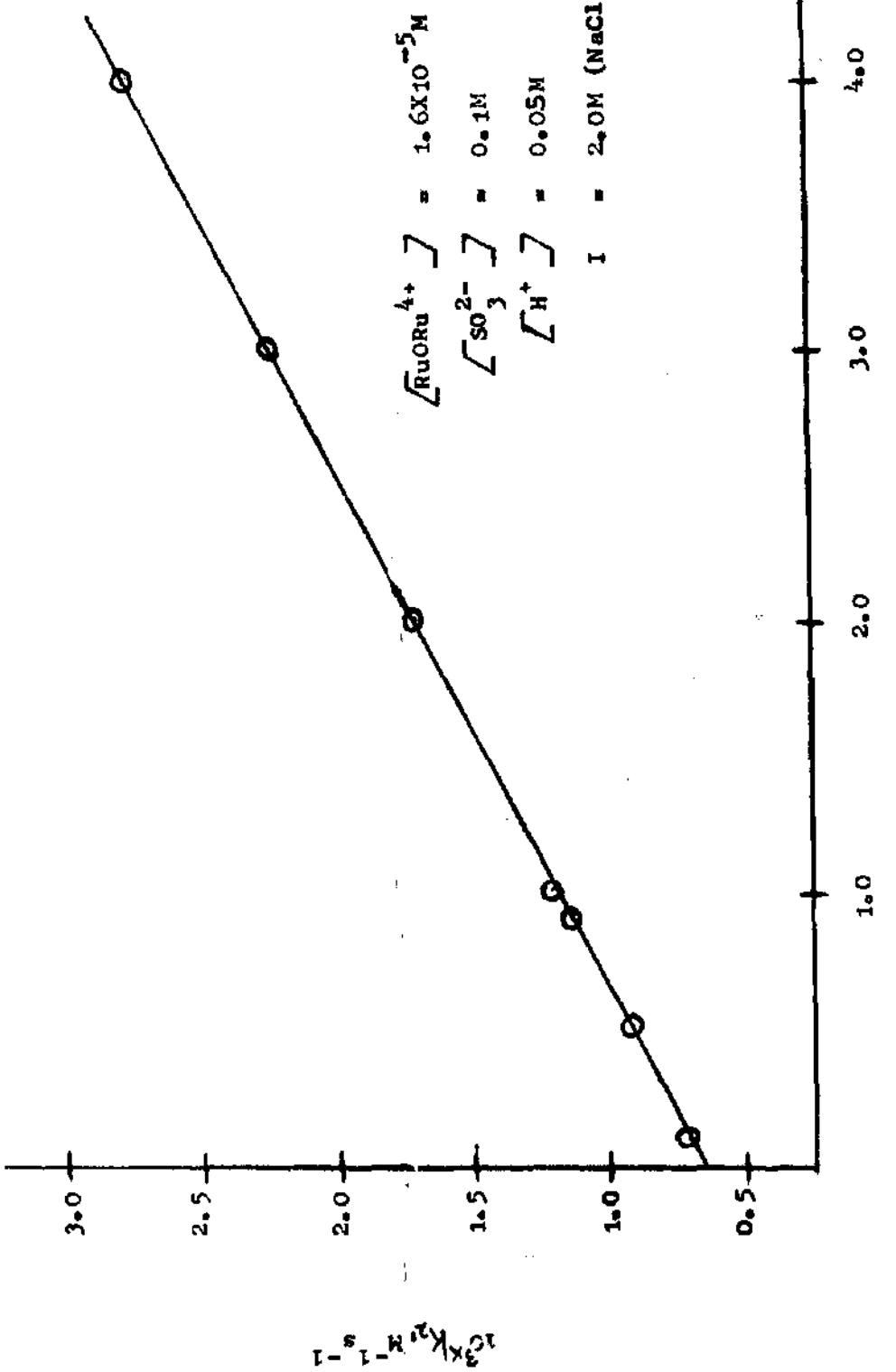


Figure 4.15: Plot of k_2 versus $[NO_2^-]$ for the redox reaction between $RuORu^{4+}$ and SO_3^{2-}

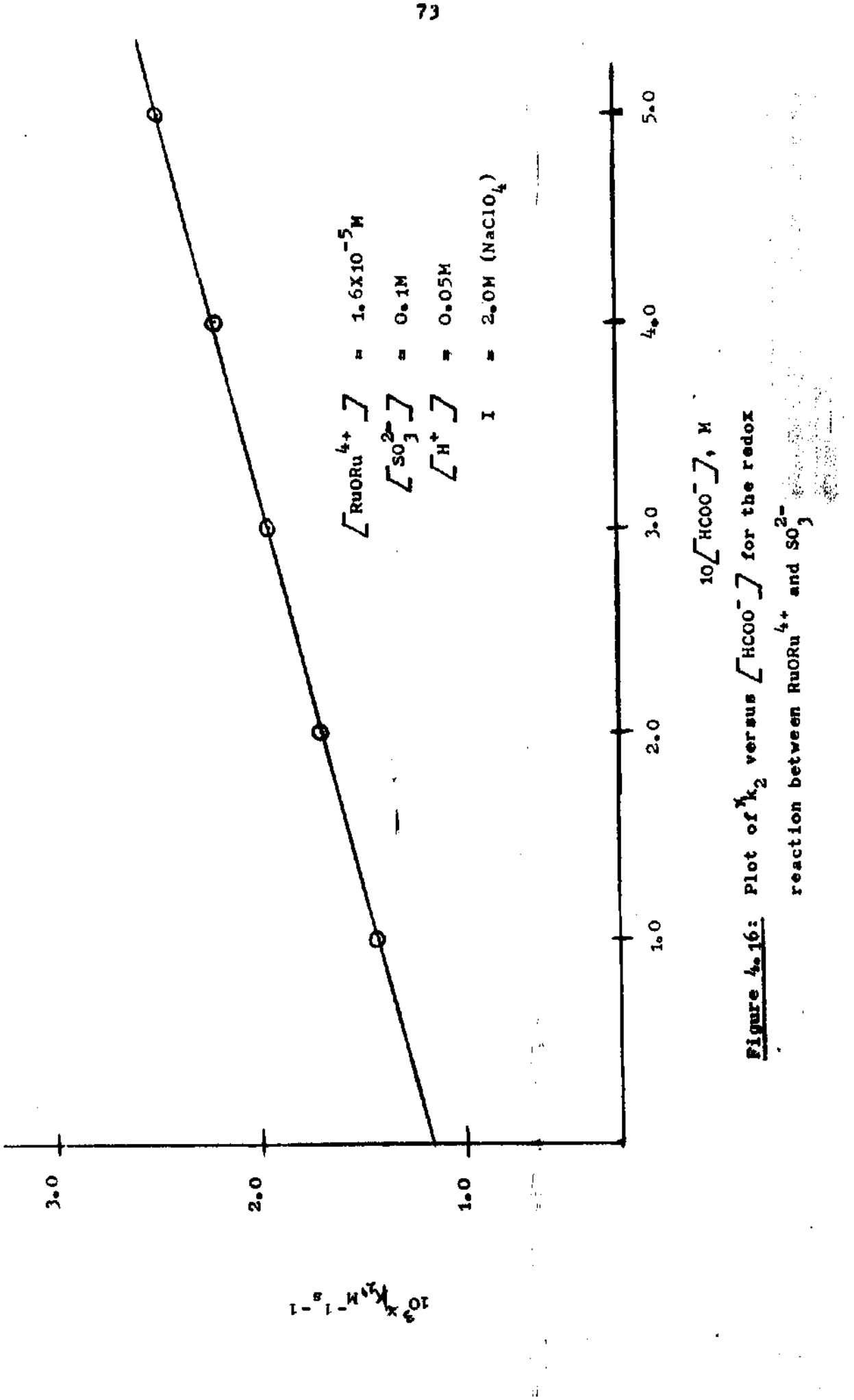


Figure 4.16: Plot of k_2 versus $\lceil HCOO^- \rceil$ for the redox reaction between $RuORu^{4+}$ and SO_3^{2-}

added anions. Plots of $^{x}k_2$ versus [X^-] for BrO_3^- and SO_3^{2-} and $1/^{x}k_2$, versus [X^-] for IO_4^- reactions were linear (figures 4.10 - 4.16) and fitted equations (4.4) and (4.5). ($^{x}k_2$ = anion-dependent second-order rate constants.)

$$^{x}k_2 = p + q[X^-], \ (BrO_3^-, SO_3^{2-}) \quad \ldots\ldots\ldots (4.4)$$

$$1/^{x}k_2 = p + q[X^-], \ (IO_4^-) \quad \ldots\ldots\ldots\ldots\ldots (4.5)$$

Where for $RuORu^{4+}$ - BrO_3^-

$p(CH_3COO^-) = 0.14M^{-1}s^{-1}$, $q(CH_3COO^{-1}) = 1.58M^{-1}s^{-1}$

$p(NO_3^-) = 9.80 \times 10^{-2}M^{-1}s^{-1}$, $q(NO_3^-) = 0.37M^{-2}s^{-1}$

$[RuORu^{4+}] = 1.2 \times 10^{-5}M$, $[BrO_3^-] = 0.02M$, $[H^+] = 0.05M$

$I = 1.0M$ ($NaClO_4$) and $T = 24.0 \pm 1.0^{o}C$.

For $RuORu^{4+}$ - IO_4^-,

$p(HCOO^-) = -0.25Ms$, $q(HCOO^-) = 19.27s$

$p(CH_3COO^-) = 7.80 \times 10^{-2}Ms$, $q(CH_3COO^-) = 2.23s$

$p(NO_3^-) = 8.90 \times 10^{-2}Ms$, $q(NO_3^-) = 1.42s$

$[RuORu^{4+}] = 2.12 \times 10^{-5}M$, $[IO_4^-] = 5.0 \times 10^{-4}M$, $[H^+] = 0.05M$,

$I = 1.0M$ ($NaClO_4$) and $T = 24.0 \pm 1.0^{o}C$.

and for $RuORu^{4+}$ - SO_3^{2-}

$p(NO_3^-) = 6.60 \times 10^{-4}M^{-1}s^{-1}$, $q(NO_3^-) = 5.24 \times 10^{-3}M^{-2}s^{-1}$

$p(NO_2^-) = 1.16 \times 10^{-3}M^{-1}s^{-1}$, $q(NO_2^-) = 2.59 \times 10^{-3}M^{-2}s^{-1}$

$(RuORu^{4+}] = 1.6 \times 10^{-5}M$, $[SO_3^{2-}] = 0.1M$, $[H^+] = 0.05M$

$I = 2.0M$ ($NaClO_4$) and $T = 24.0 \pm 1.0^{o}C$.

4.5 Activation parameters for $RuORu^{4+}$ - BrO_3^- system

The rate of the reaction between $RuORu^{4+}$ and BrO_3^- was measured at various temperatures and the plot of $\log(k_2/T)$ versus 1/T was obtained (figure 4.17), from which the activation parametres were calculated. The values of the rate constants at different temperatures and the activation parameters are given in Table (4.10). (Acivation parameter studies could not be carried out for other systems due to the break down of the thermostat attached to the spectrophotometer.)

4.6 Tests for intermediate complex

4.6.1 Spectrophotometric test

These measurements were undertaken to find out whether a spectroscopically determinable intermediate complex was formed between the $RUORu^{4+}$ and each of the oxyanions during the reactions. Solutions of the reactants were mixed and their spectra recorded after one minute in each case, over a range of wavelengths (600 - 700nm). A similar run was made for the complex alone. From the spectra (Figure 4.18), there is no appreciable shift in wavelength from 650nm for the BrO_3^- and IO_4^- systems but there is a 10nm shift in the case of the SO_3^{2-} system. This suggests that an intermediate complex is formed in the reaction between $RuORu^{4+}$ and SO_3^{2-}, although, the possibility for the formation of such cannot be ruled out in the other cases.

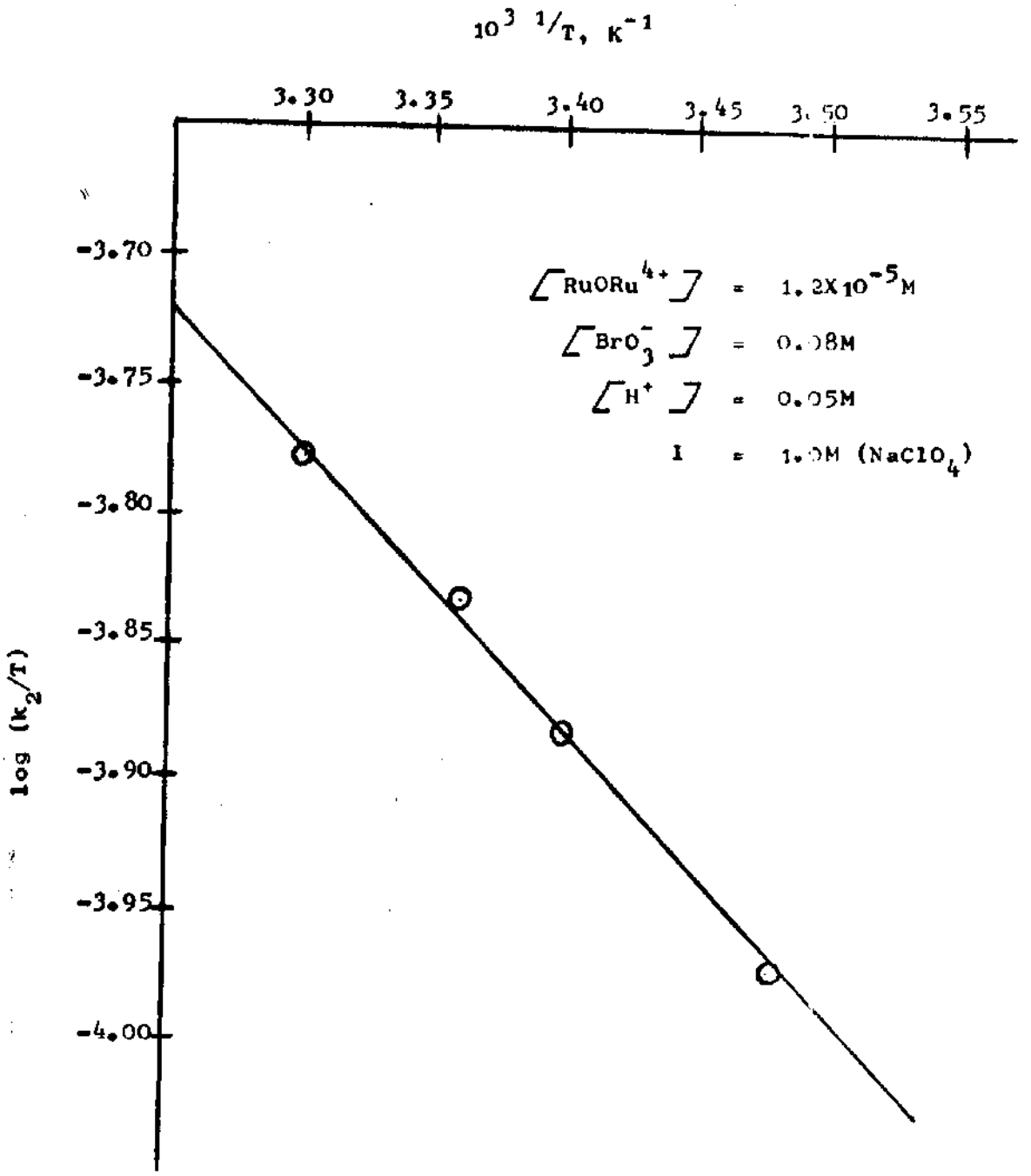


Figure 4.17: Plot of log (k_2/T) versus ^{1}/T for the reaction of $RuORu^{4+}$ and BrO_3^- ions

Table 4.10

Temperature-dependent rate constants and the corresponding *constant parameters for the reaction of $RuORu^{4+}$ and BrO_3^-

$[RuORu^{4+}] = (1.2 \pm 0.1) \times 10^{-5}M$, $[H^+] = 0.05M$,

$I = 1.0M$ ($NaClO_4$), $\lambda max = 650nm$

$[BrO_3^-]$	T°C	$10^2 k_{obs}, s^{-1}$	$10^2 k_2, M^{-1}s^{-1}$
0.05	14.6	1.76	3.52
0.05	20.4	1.81	3.64
0.05	24.8	2.32	4.64
0.05	29.8	2.70	5.40
0.08	14.6	2.25	2.81
0.08	20.4	2.59	3.24
0.08	24.8	4.41	5.51
0.08	29.8	4.47	5.86

$\Delta H^{\neq} = 21.06 KJmol^{-1}$

$\Delta S^{\neq} = -198.27 Jmol^{-1}K^{-1}$

*Values obtained at 24.8°C, $[BrO_3^-] = 0.08M$

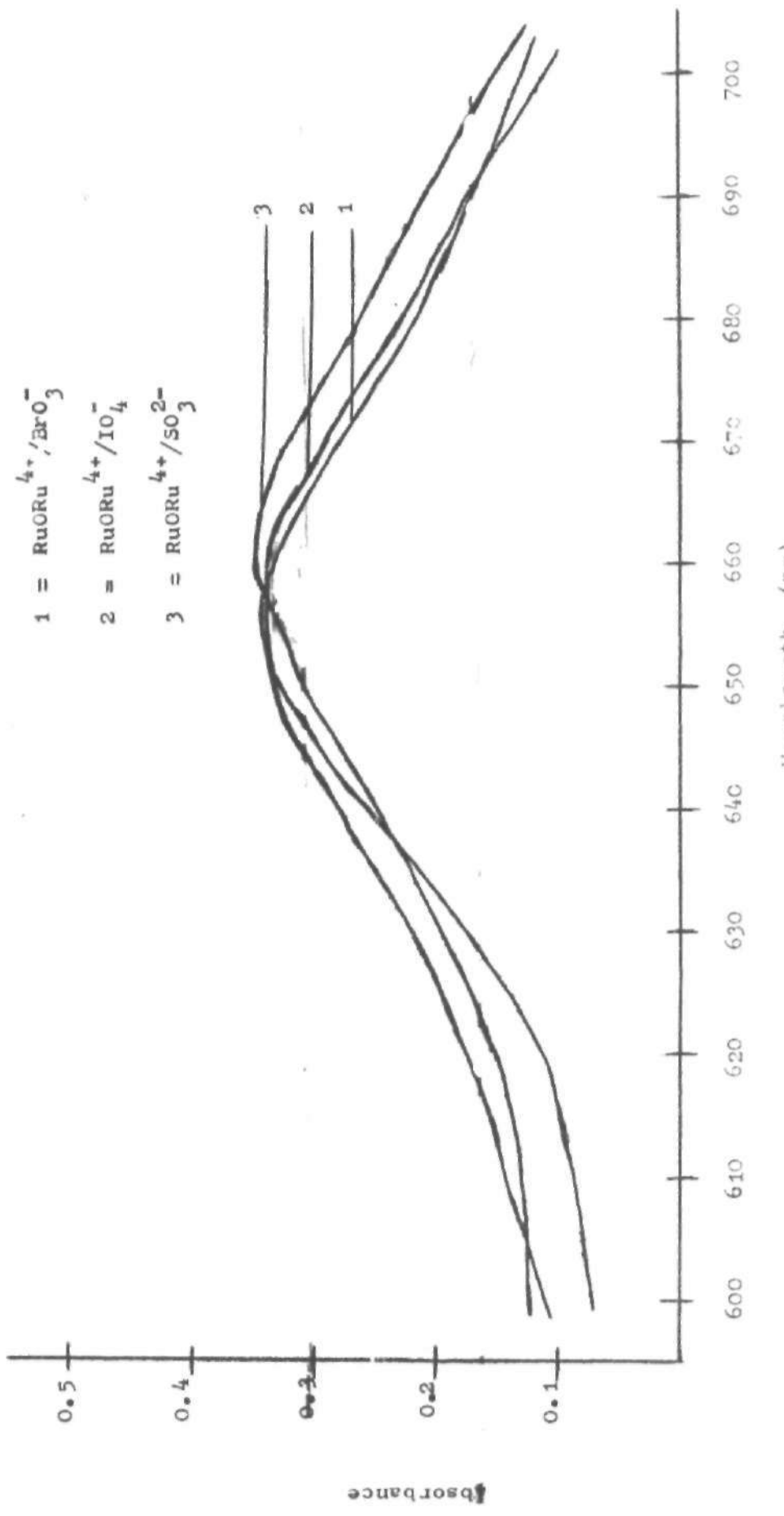


Figure 4.18: Spectra of $RuORu^{4+}/XO_m^{n-}$ mixtures recorded at 1 minute from the time of initiation of the reactions.

4.6.2 Michaelis-Menten Plot

Least squares analyses of the plots of $1/k_{obs}$ versus $1/[XO_m^{n-}]$ gave straight lines and are represented in Figures (4.19 - 4.21). For the BrO_3^- system, the line passes through the origin while the IO_4^- and SO_3^{2-} systems have insignificant intercepts, which suggest the possibility for the formation of an intermediate in the reactions involving IO_4^- and SO_3^{2-} ions.

4.7 Product Analysis

Hints about the possible pathway for the redox reactions of $RuORu^{4+}$ could be obtained from the isolation and characterization of the products, but in this work, only spectra of the reaction products were obtained and these are presented in Figure (4.22). Because of the absence of available data on the possible products, it was not possible to identify the individual products in these reactions.

4.8 Stability of $RuORu^{4+}$

The absorbance of the solution of $RuORu^{4+}$ was monitored over a period of more than 3 months and no significant change in absorbance was observed. Similar process was carried out for the $RuORu^{4+}$ in acid (0.01 - 0.1M), in the presence of both acid and some anions and similar results were obtained. This shows the stability of the complex in water, acid and in the presence of both acid and anions.

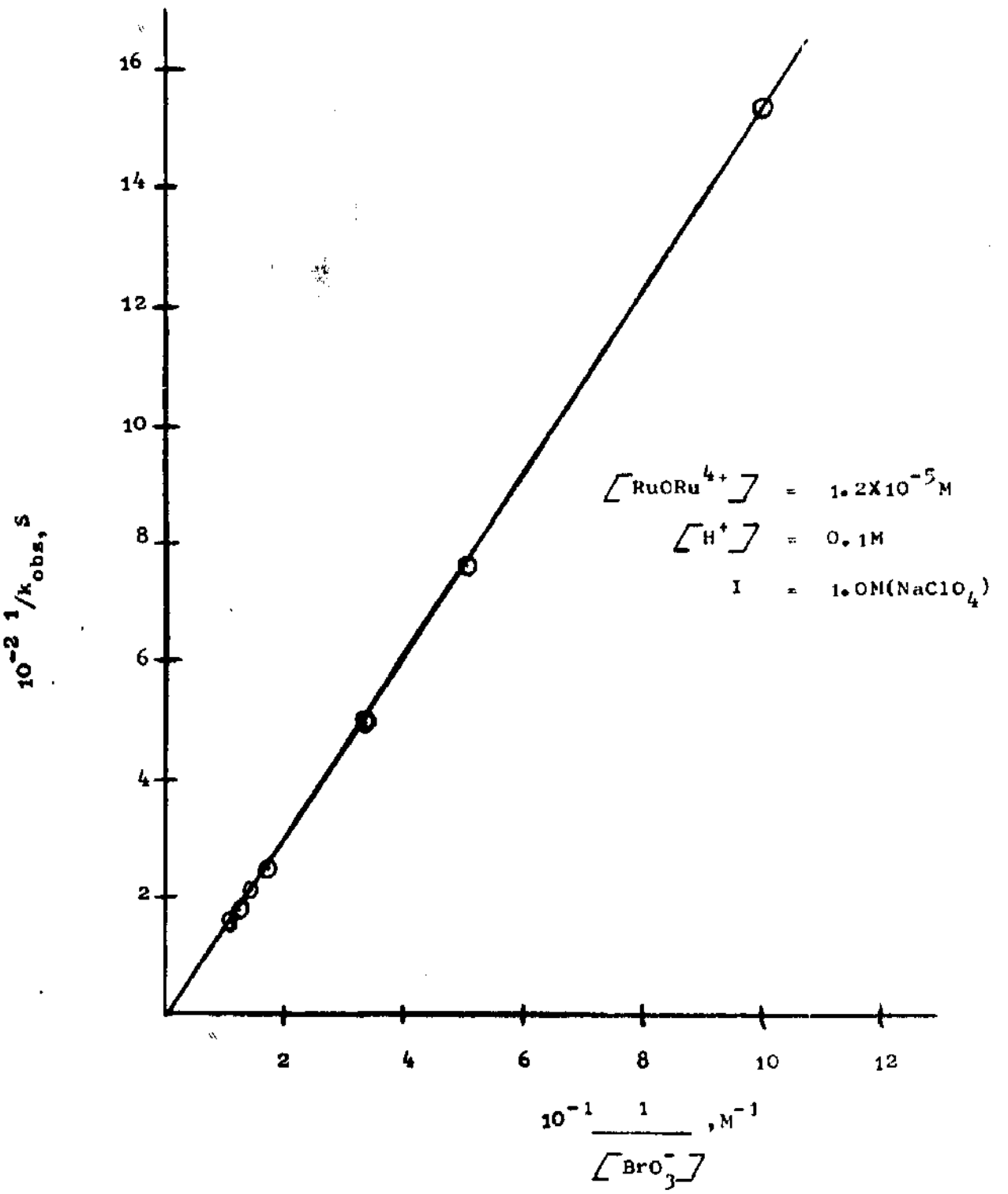


Figure 4.19: Michaelis-Menten Plot ($^1/k_{obs.}$ Vs $^1/[BrO_3^-]$) for the reaction of $RuORu^{4+}$ and BrO_3^-.

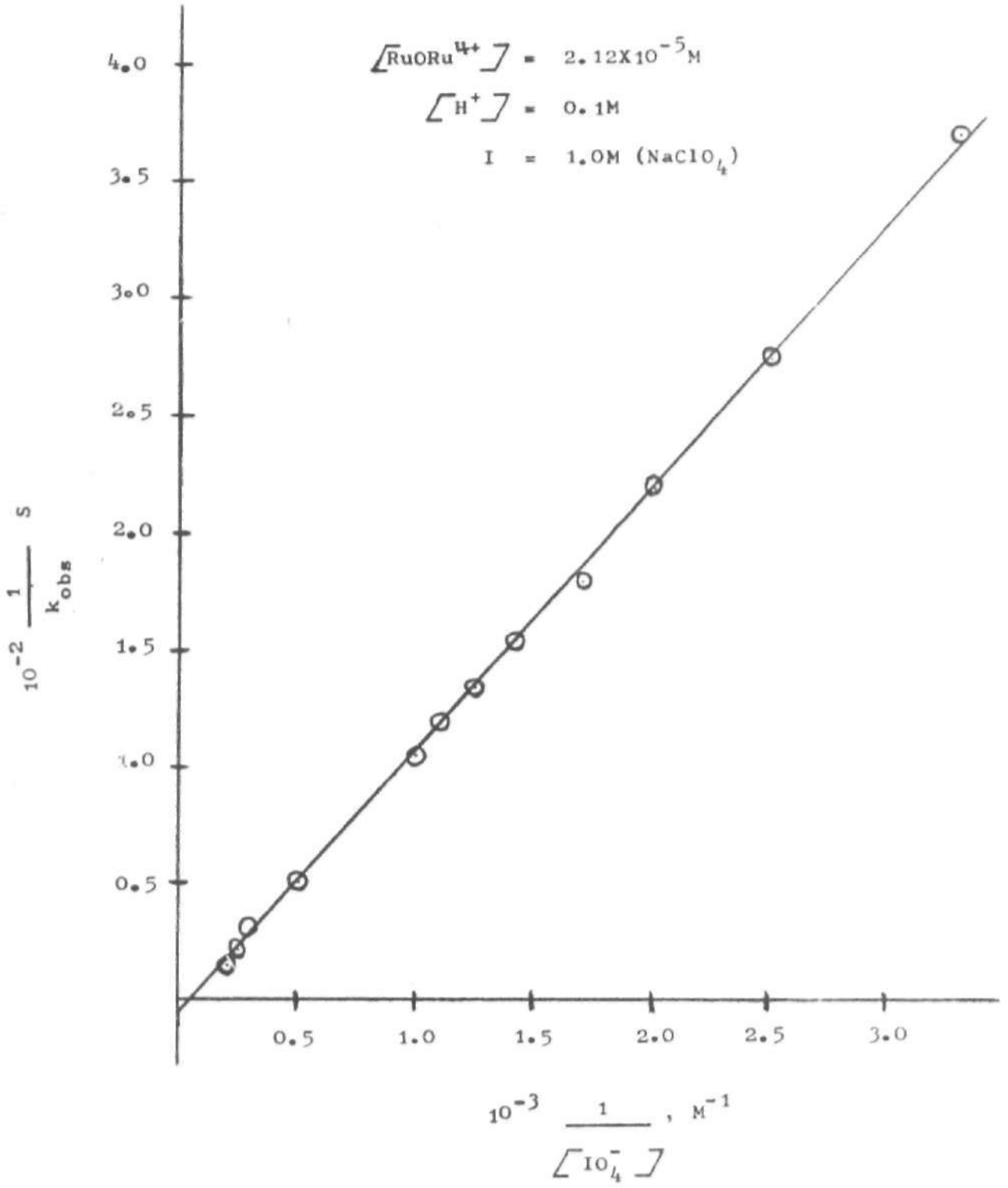


Figure 4.20: Michaelis-Menten Plot ($^1/k_{obs}$ Vs $^1/\lceil IO_4^- \rceil$) for the reaction of $RuORu^{4+}$ and IO_4^-.

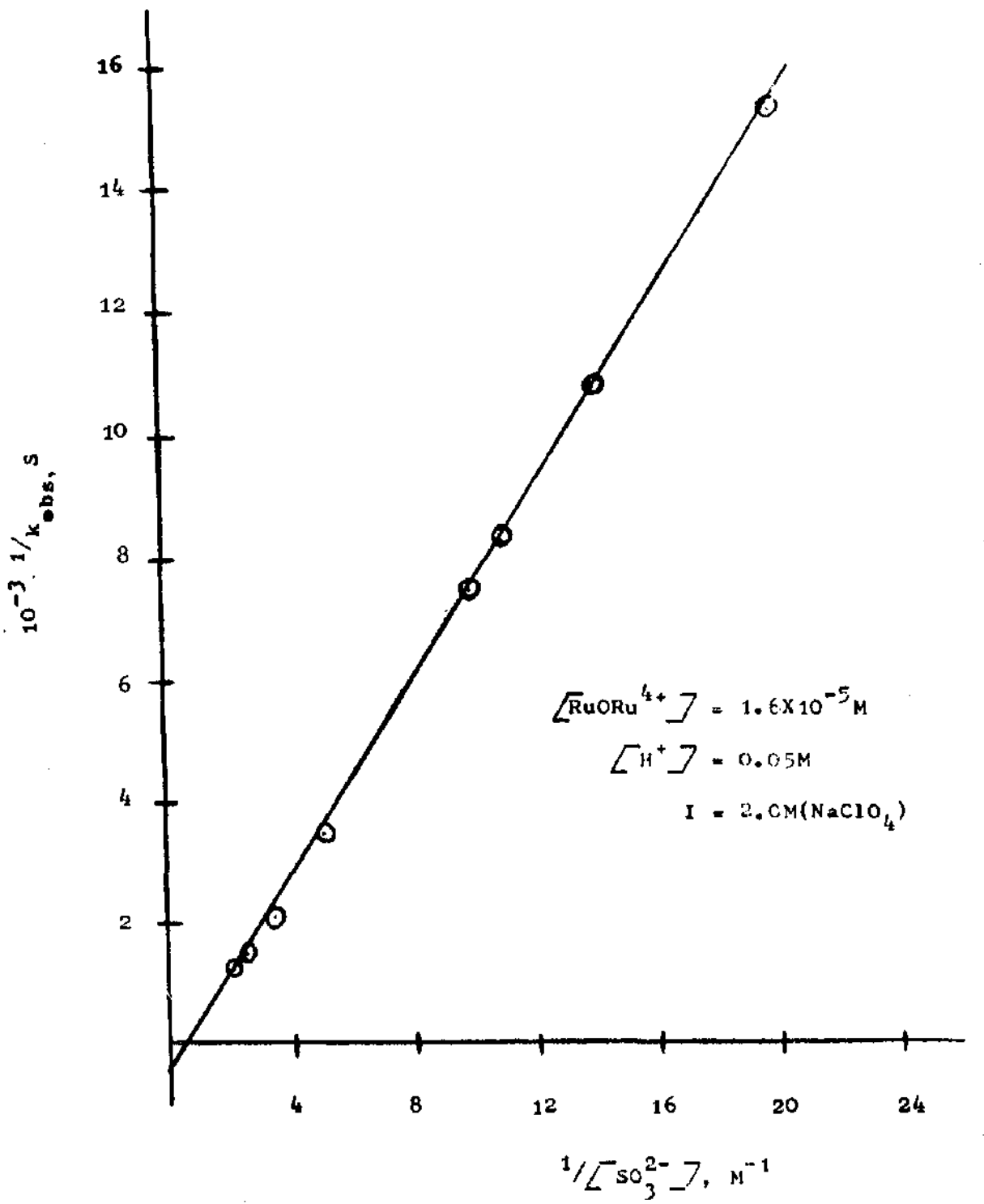


Figure 4.21: Michaelis-Menten Plot ($1/k_{obs}$ Vs $1/[SO_3^{2-}]$ for the reaction of $RuORu^{4+}$ and SO_3^{2-}

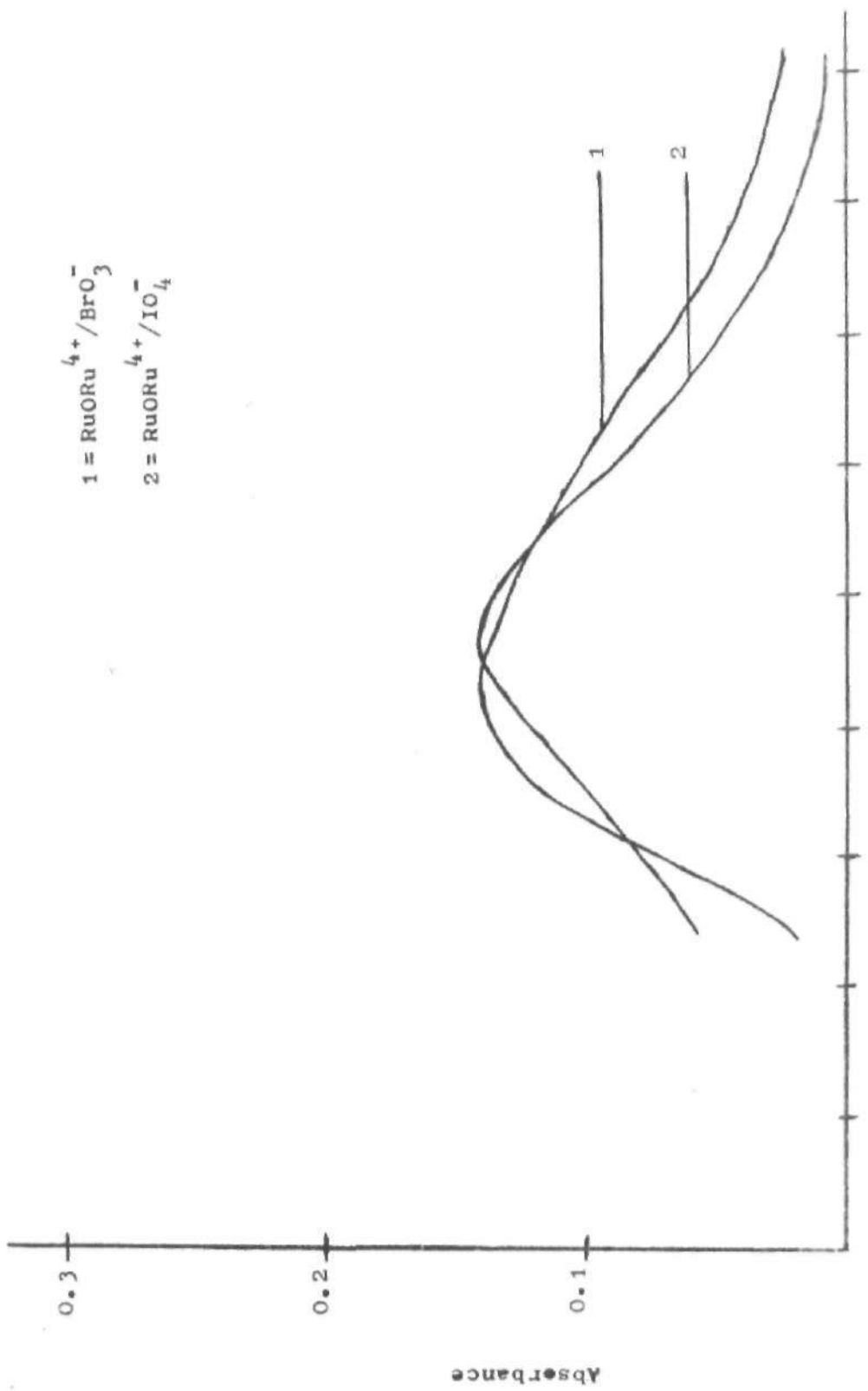


Figure 4.22 Spectra of the final products of the redox reactions between $RuORu^{4+}$ and BrO_3^- and IO_4^-

Chapter 5

5.0 DISCUSSION

5.1 $RuORu^{4+}$ - BrO_3^- System

From kinetic studies, the reaction between $RuORu^{4+}$ and BrO_3^- has been shown to have first order dependence on each of the reactant concentrations as illustrated by equation (5.1).

$$\frac{-d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][BrO_3^-] \quad \ldots\ldots\ldots (5.1)$$

Under the experimental conditions employed in this study, k_2 was evaluated to be $(8.28 \pm 1.56) \times 10^{-2} M^{-1}s^{-1}$ at $24.0 \pm 1.0^{o}C$.

The rate of oxygen exchange and redox reactions of many oxyanions have been reported to depend strongly on acid concentration [Birk and Korub, 1973, 1978; Basolo and Pearson, 1968]. In this study, the rate of reaction exhibits a second order dependence on $[H^+]$.

$$\frac{-d[RuORu^{4+}]}{dt} = (a + b[H^+]^2)[RuORu^{4+}][BrO_3^-] \quad \ldots\ldots\ldots (5.2)$$

The stability of the oxo-complex in both aqueous and acid media indicates that the dimer cannot be protonated and the $[H^+]$ dependence is attributed to the protonation of BrO_3^- ion [Melvin

and Gordon, 1973]. This is in keeping with the fact that the $[H^+]^2$ term commonly encountered in reactions of BrO_3^- has been attributed to the formation of $H_2BrO_3^+$, which reacts with the reductant in the rate determining step or dissociates to H_2O and BrO_2^+, prior to the rate determining step [Birk, 1973, 1978; Birk and Kozub, 1973, 1978; Thompson, 1971; Thompson and Knight, 1973].

The reaction scheme proposed below reasonably accounts for experimental results.

$$BrO_3^- + 2H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2BrO_3^+ \text{ (or } BrO_2^+ + H_2O) \quad \ldots\ldots \quad (5.3)$$

$$H_2BrO_3^+ + RuORu^{4+} \xrightarrow{k_2} \text{Products} \quad \ldots\ldots\ldots\ldots\ldots (5.4)$$

$$BrO_3^- + RuORu^{4+} \xrightarrow{k_3} \text{Products} \quad \ldots\ldots\ldots\ldots\ldots (5.5)$$

(The identity of the products in equations (5.4) and (5.5) are not specified because the products of the redox reactions have not yet been identified).

If the steady state approximation is applied to reactions (5.3 - 5.5), the rate of disappearance of $RuORu^{4+}$ may be expressed by equation (5.6).

$$\frac{-d[RuORu^{4+}]}{dt} = \frac{k_1 k_2 [H^+]^2 [RuORu^{4+}][BrO_3^-]}{k_{-1} + k_2[RuORu^{4+}]} + k_3[RuORu^{4+}][BrO_3^-] \quad \ldots\ldots\ldots\ldots (5.6)$$

If $k_{-1} >> k_2[RuORu^{4+}]$ then,

$$\frac{-d[RuORu^{4+}]}{dt} = \{k_a + Kk_2[H^+]^2\}[RuORu^{4+}][BrO_3^-] \quad \ldots\ldots\ldots \quad (5.7)$$

$K = k_1/k_{-1}$ is ca. $10^{-11}M^{-1}$ [Birk, 1978]

Equation (5.7) is analogous to equation (5.2) consistent with plot of k_{obs} versus $[H^+]$ (figure 4.7), with $k_a = a$ and $Kk_2 = b$; a and b are calculated to be $5.53 \times 10^{-2}M^{-1}s^{-1}$ and $5.09M^{-3}s^{-1}$ respectively at 24.0 ± 1.0°C.

One of the most important questions in BrO_3^- reactions is whether the acid dependent and independent paths occur by the inner- or outer-sphere mechanism. In some cases, the reaction has been interpreted in terms of parallel outer- and inner-sphere pathways, with the acid independent path occuring via the outer sphere mechanism. The occurence of the inner sphere path in such reactions may be attributed to the displacement of water molecule from $H_2BrO_3^+$, which leads to the formation of a binuclear species containing the reductant and BrO_2^+ [Birk, 1973]. In other cases, two parallel outer sphere paths have been proposed, as in the reduction of BrO_3^- by some Fe(II) and Ce(IV) complexes [Birk and Kozub, 1978].

In this present study, the experimental results are more in support of the outer sphere mechanism. For example, the electronic spectra of the solutions containing mixtures of $RuORu^{4+}$ and BrO_3^- did not show a clear shift in the λmax of $RuORu^{4+}$ (Figure 4.16). Michaelis-Menten plot (Figure 4.19) was

also linear without an intercept. These observations support the absence of spectrophotometric and kinetic evidence for intermediate complex formation during the reaction, suggesting that the reaction occured by the outer sphere mechanism [Prakask et al, 1979; Ayoko, 1989].

Further support for the outer sphere mechanism is evident from the catalysis of the rate by acetate and nitrate ions (Table 4.7), since anion catalysed reactions are thought to be a characteristic of outer sphere reactions [Adegite et al, 1977; Przystas and Sutin, 1973; Penning and Haim, 1967].

Although, there seems to be no direct relationship between activation parameters such as $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$, etc, and the type of mechanism, they can throw some light in support of or against a particular mechanism. For example, negative value of $\Delta H^{\neq}$ ($\Delta H^{\neq} < 0$) shows the presence of a precursor characteristic to the inner sphere mechanism [Wilkins, 1974]. Therefore the positive value of $\Delta H^{\neq}$ (21.06 $KJmol^{-1}$) for this reaction is thought to be an additional evidence in support of the outer sphere mechanism.

It appears that the absence of spectrophotometric and kinetic evidence for intermediate complex and anion catalysis of the rate, favour the outer sphere mechanism for both pathways in the reaction. In this respect, the reaction is similar to those of BrO_3^- with some Fe(II) complexes, $IrCl_6^{2-}$ and $Co^{II}W$ [Birk, 1978; Birk and Kozub, 1978; Ayoko et al, 1989]. The rate constants obtained at 25°C for those reactions as well as the redox potentials of the reductants were compared with corresponding values of the present system (Table 2.3). Unfort-

unately, the absence of a definite redox potential for the $[Ru^{III}ORu^{III}]^{4+}$ -----> $[Ru^{IV}ORu^{IV}]^{6+}$ couple prevents the application of Marcus type of correlation to this reaction.

5.2 $RuORu^{4+}$ - IO_4^- system

The first-order dependence on each of the reactant (concentrations) is common in the reactions of IO_4^- ion [El-Eziri and Sulfab, 1977; Kassim and Sulfab, 1977], and has been observed in this present system.

$$\frac{-d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][IO_4^-] \quad \ldots\ldots\ldots\ldots (5.8)$$

First order dependence on $[H^+]$ has also featured prominantly in IO_4^- redox reactions with some metal ion complexes [Ige and Amire and references therein, 1985; El-Eziri and Sulfab, 1977; Kassim and Sulfab, 1977]. This type of $[H^+]$ dependence was observed in this present study and related to k_2 as follows:

$$k_2 = a + b[H^+] \quad \ldots\ldots\ldots\ldots\ldots\ldots (5.9)$$

$k_2 = 9.41 \pm 1.2 M^{-1}s^{-1}$, $[H^+] = 0.10 - 0.50M$

$I = 1.0M$ ($NaClO_4$), $T = 24.0 \pm 1.0°C$

This suggests the existence of two parallel pathways for the reaction, involving a protonated and an unprotonated species, both reacting to form products. However, the protonated path has been shown to predominate [Melvin and Gordon, 1973; Birk and Kozub, 1978].

In aqueous solutions, periodate exists as H_5IO_6, $H_4IO_6^-$, $H_3IO_6^{2-}$ and IO_4^- [Benson, 1968] and forms a set of equilibria illustrated by equations (2.20 - 2.23) in chapter two. However, $H_4IO_6^-$ and IO_4^- are the dominant and reactive species in acid (pH 4.2), I = 0.1M [Kustin and Lieberman, 1964]. Kassim and Sulfab (1977) have earlier attributed the first order dependence on $[H^+]$ to the equilibrium below.

$$IO_4^- + H^+ \rightleftharpoons HIO_4$$

Taking into consideration the rapid equilibrium below

$$[H^+] + L^- \rightleftharpoons HL$$

where L^- stands for total periodate ($H_4IO_6^-$ and IO_4^-), and the results of this investigation, the following reaction scheme is proposed for the $RuORu^{4+}$ - IO_4^- system.

$$H^+ + L^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HL \quad \text{.....(5.10)}$$

$$RuORu^{4+} + HL \xrightarrow{k_2} \text{Products} \quad \text{.....(5.11)}$$

$$RuORu^{4+} + L^- \xrightarrow{k_3} \text{Products} \quad \text{.....(5.12)}$$

The application of the steady state approximation to equations (5.10 - 5.12) leads to equation (5.13).

$$\frac{-d[RuORu^{4+}]}{dt} = \frac{k_1 k_2 [H^+][RuORu^{4+}][L^-]}{k_{-1} + k_2[RuORu^{4+}]} + k_3[RuORu^{4+}][L^-] \quad \ldots (5.13)$$

Provided $k_{-1} >> k_2[RuORu^{4+}]$, equation (5.13) reduces to equation (5.14)

$$\frac{-d[RuORu^{4+}]}{dt} = (k_3 + Kk_2[H^+])[RuORu^{4+}][L^-] \quad \ldots\ldots\ldots (5.14)$$

$$K = k_1/k_{-1}$$

Equation (5.14) is analogous to equation (4.3) which is consistent with the plot of k_{obs} versus $[H^+]$ (Figure 5.8), where $a = k_3$ and $b = Kk_2$. Under the experimental conditions employed in this investigation, a and b are computed to be $7.75 M^{-1}s^{-1}$ and $1.13 \times 10^{-2} M^{-1}s^{-1}$ respectively at $24.0 \pm 1.0^{o}C$.

Most of the IO_4^- oxidation reactions so far studied seem to prefer the inner sphere mechanism (Sulfab, 1976; El-Eziri and Sulfab, 1977; Kassim and Sulfab, 1977; Sulfab and Abu-shady, 1977; Al-Jallal and Sulfab, 1983). This mechanism has been confirmed by the identification of Co^{III} intermediate products in the reactions of Co^{II}complexes of EDTA, HEDTA and EDDA (Sulfab and Kassim, 1977, 1981). More recently, Ige and Amire (1985) have reported the oxidation of $Fe(Phen)_3^{2+}$ to occur simultaneously via both inner- and outer-sphere pathways: the

former occuring by a single-step two-electron transfer at low acid (0.02 - 0.15M) and the later via two single-electron transfer at high acid (0.2M). The preference of the inner sphere path by most Fe(II) complexes towards IO_4^- can be attributed to the very labile nature of Fe(II) where substitution into its inner coordination shell is very likely, with the IO_4^- oxygen(s) acting as bridging atom(s) [El-Eziri and Sulfab, 1977].

In this study, the Michaelis-Menten plot (Figure 4.20) has an insignificant intercept suggesting the possibility of the formation of an intermediate as in the inner sphere mechanism. In an effort to confirm the presence of an intermediate in this reaction, the electronic spectra of solutions containing mixtures of $RuORu^{4+}$ and IO_4^- were run. There was no clear shift in λmax of $RuORu^{4+}$ (Figure 4.18), which suggests the absence of an intermediate and therefore the reaction is most likely to occur by the outer sphere mechanism. Although this evidence does not completely rule out the possibility of the formation of an intermediate, the inner sphere pathway is not a major route for the reaction.

The occurence of the outer sphere pathway is supported by the inhibitive effects of formate, acetate and nitrate ions (Table 4.8) on the rate constants of the reaction [Pennington and Haim, 1967; Przystas and Sutin, 1973; Adegite et al, 1977]. In keeping with the experimental results, the outer sphere mechanism is hereby proposed for the reaction of $RuORu^{4+}$ and IO_4^-.

5.3 $RuORu^{4+}$ - SO_3^{2-} system

Like with other systems considered in this work, the $RuORu^{4+}$ - SO_3^{2-} reaction exhibits first-order dependence on each of the reactant concentrations.

$$\frac{-d[RuORu^{4+}]}{dt} = k_2[RuORu^{4+}][SO_3^{2-}] \quad \ldots\ldots\ldots\ldots \quad (5.15)$$

Inverse acid pathways have featured prominantly in most kinetic studies of ascorbic acid with some metal complexes [Pelizzetti et al. 1976, 1978; Adjad et al. 1977]. Similar dependence has also been observed for $PtCl_6^{2-}$ - SO_3^{2-} system [Sen Gupta, 1987] and in this present system. Thus,

$$\frac{-d[RuORu^{4+}]}{dt} = (a + b[H^+]^{-1})[RuORu^{4+}][SO_3^{2-}] \quad \ldots (5.16)$$

Under the experimental conditions, k_2, a and b have been calculated to be $(1.43 \pm 0.21) \times 10^{-3} M^{-1}s^{-1}$, $3.40 \times 10^{-4} M^{-1}s^{-1}$ and $6.37 \times 10^{-5} s^{-1}$ respectively.

The inverse $[H^+]$ dependence has been attributed to the equilibrium system illustrated by equation (5.17), which is said to exist in aqueous solution of SO_3^{2-} ions [Stapp and Carlyle, 1974; Dennis et al. 1983; Sen Gupta, 1987]. (The major species in aqueous solution being HSO_3^-.)

$$SO_3^{2-} + H^+ \underset{}{\overset{k}{\rightleftharpoons}} H{:}SO_3^- \rightleftharpoons HOSO_2^- \quad \ldots\ldots\ldots (5.17)$$

I II

$k = 1.0 \times 10^{7}$.

The decrease in rate constants with increase in $[H^+]$ shows that the SO_3^{2-} ion is much more reactive than HSO_3^- ion. The lower reactivity of HSO_3^- ions has been attributed to the fact that in I, the lone pair of electrons is held up by the H^+, while in II, the electron density will be withdrawn from the sulphur atom by the H^+ ion [Connick et al, 1982]. Equation (5.16) also reveals two parallel pathways for this reaction involving HSO_3^- and SO_3^{2-} species. Both pathways can occur by by inner sphere or the outer sphere or simultaneously via both inner sphere and outer sphere mechanisms [Ige and Amire, 1985].

Most oxidation reactions of SO_3^{2-} are believed to proceed by the inner sphere mechanism. For example, the reaction between SO_3^{2-} and $Fe(CN)_6^{3-}$ involves the intermediate $[Fe(CN)_5\text{-}SO_3]^{4-}$, with the subsequent formation of SO_4^{2-} [Veprek-Siska and Wagnerova, 1965; Veprek-Siska et al, 1966]. In this present system, spectrophotometric measurements (figure 1.18) suggest the presence of an intermediate which is confirmed by the intercept obtained on the Michaeclis-Menten plot (figure 4.21). Based on this evidence, a reaction scheme consistent with the inner sphere mechanism is proposed below.

$$HSO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + SO_3^{2-} \quad \text{.....(5.18)}$$

$$SO_3^{2-} + RuORu^{4+} \xrightarrow{k_2} RuORu.SO_3^{2+} \quad \text{.....(5.19)}$$

$$RuORu.SO_3^{2+} + SO_3^{2-} \xrightarrow{k_3} \text{Products} \quad \ldots\ldots(5.20)$$

$$RuORu^{4+} + HSO_3^- \xrightarrow{k_4} \text{Products} \quad \ldots\ldots(5.21)$$

Applying the steady state approximation to the above scheme, equation (5.22) is obtained.

$$\frac{-d[RuORu^{4+}]}{dt} = \frac{k_1 k_2 [RuORu^{4+}][HSO_3^-]}{k_{-1}[H^+] + 2k_2[RuORu^{4+}]} + k_4[RuORu^{4+}][HSO_3^-] \quad \ldots\ldots(5.22)$$

If $k_{-1}[H^+] >> 2k_2[RuORu^{4+}]$,

$$\frac{-d[RuORu^{4+}]}{dt} = (k_4 + Kk_2[H^+]^{-1})[RuORu^{4+}][HSO_3^-] \quad \ldots\ldots(5.23)$$

$K = k_1/k_{-1}$

Equations (5.16) and (5.23) are similar with $k_4 = a$, $Kk_2 = b$.

However, the outer sphere paths have also featured in the reactions of SO_3^{2-} with $Mo(CN)_6^{3-}$ and $W(CN)_6^{3-}$ [Dennis et al, 1983] and $IrCl_6^{2-}$ [Stapp and Carlyle, 1974]. The evidence for the occurence of the outer sphere mechanism in the present system is obtained from the anion catalysis of the reaction. Therefore an alternative reaction scheme is also proposed to accomodate the outer sphere path as follows;

$$HSO_3^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H^+ + SO_3^{2-} \quad \ldots\ldots(5.18)$$

$$SO_3^{2-} + RuORu^{4+} \xrightarrow{k_6} \text{Products} \quad \ldots\ldots (5.24)$$

$$HSO_3^{-} + RuORu^{4+} \xrightarrow{k_7} \text{Products} \quad \ldots\ldots (5.25)$$

Applying steady state approximation to equations (5.18), (5.24) and (5.25), will lead to equation (5.26)

$$\frac{-d[RuORu^{4+}]}{dt} = \frac{k_5K_6[HSO_3^-][RuORu^{4+}]}{k_{-5}[H^+] + k_6[RuORu^{4+}]} + k_7[HSO_3^-][RuORu^{4+}] \quad \ldots (5.26)$$

Provided that $k_{-5}[H^+] \gg k_6[RuORu^{4+}]$,

$$\frac{-d[RuORu^{4+}]}{dt} = (k_7 + Kk_6[H^+]^{-1})[HSO_3^-][RuORu^{4+}] \quad \ldots\ldots (5.27)$$

$K = k_5/k_{-5}$

Equation (5.27) is also similar to equations (5.16), (k_7 = a, Kk_6 = b) and (5.23)

The two reaction schemes proposed are consistent with the experimental results and therefore the reaction between $RuORu^{4+}$ and SO_3^{2-} can be said to proceed by both inner and outer sphere mechanisms similar to that between $Fe(Phen)_3^{2+}$ and IO_4^- [Ige and Amire, 1985]. An unequivocal statement on which of the two mechanisms predominates will await further work on the oxo-complex.

5.4 Summary and Conclusion

The redox reactions of the synthesized oxo-bridged complex ($RuORu^{4+}$) were studied with BrO_3^-, IO_4^- and SO_3^{2-} ions in aqueous perchloric acid. The rates of these reactions showed various forms of hydrogen ion dependences, characteristic of most oxyanion reactions [Birk and Kozub, 1973]. For example, BrO_3^- ion showed second order, IO_4^- had first order and SO_3^{2-} exhibited inverse first order dependences on $[H^+]$. The rates were also influenced by the presence of some added anions. For example, in the BrO_3^- and SO_3^{2-} systems, the added anions had catalytic effects on the rates while an inhibitive effect was observed for the IO_4^- reaction.

The experimental results obtained for the reactions of $RuORu^{4+}$ with BrO_3^- and IO_4^- were in favour of the outer sphere mechanism and therefore the mechanism was proposed for each of the two systems. However, in the $RuORu^{4+}$-SO_3^{2-} system, the experimental data provided evidence for the occurence of both inner and outer sphere mechanisms and therefore two reaction schemes were proposed accordingly.

Although these reactions show some similarities, the nature of a particular oxyanion gives its reactions some characteristic properties. For example, SO_3^{2-} ion has been shown to exhibit a weak intermediate complex formation [Veprek-Siska et al, 1966] and in this present system, the presence of an intermediate was confirmed. In another example, the rates of reactions of oxyanions derived from large and or less highly charged central

atoms are faster than those from small and or highly charged atoms [Edwards, 1954; Baloga and Earley, 1963]. This trend was observed in the titled reactions in this work as follows; $k_2(IO_4^-)$ =9.41$M^{-1}s^{-1}$ > $k_2(BrO_3^-)$ = 8.28 x $10^{-2}M^{-1}s^{-1}$ > $k_2(SO_3^{2-})$ = 1.43 x $10^{-3}M^{-1}s^{-1}$.

For the BrO_3^- system, the activation parameters were determined and the values are as follows; $\Delta H^{\neq}$ = 21.06KJmol^{-1} and $\Delta S^{\neq}$ = -198.27J$K^{-1}mol^{-1}$. (This determination was not carried out for the other systems due to breakdown of the equipment.) The determination of the stoichiometries of the reactions did not yield any results because of the very high extinction coefficient of $RuORu^{4+}$. Similarly, the isolation and identification of the redox products have not been possible.

5.5 Suggestions for further work

For better understanding of the redox reactions of this complex, more work should be carried out in the following areas;

(i) Isolation and identification of the products of the reactions.

(ii) Stoichiometry and kinetic stability of the complex.

(iii) Determination of the redox potentials of the oxo-bridged complex i.e for $[Ru^{III}ORu^{III}]^{4+}$ ----> $[Ru^{IV}ORu^{IV}]^{6+}$ and $[Ru^{III}ORu^{III}]^{4+}$ -----> $[Ru^{II}ORu^{II}]^{2-}$ couples.

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