KINETICS AND MECHANISMS OF THE ELECTRON TRANSFER REACTIONS OF THE μ-OXO- BRIDGED IRON(III) COMPLEX, $Na_4[(FeEDTA)_2O].12H_2O$ WITH SOME THIOLS

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A RESEARCH PROJECT SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN INORGANIC CHEMISTRY

BY

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PG/M.Sc/07/42713

SUPERVISOR: PROFESSOR P.O. UKOHA

FEBRUARY, 2013

DEDICATION

·To Almighty God and his Son Jesus Christ

·To my twins ï Chibuike and Chisom Ibeh

CERTIFICATION

This is to certify that Ezennodebe, Grace a postgraduate student in the Department of Pure and Industrial Chemistry with Registration Number PG/MSc/07/42713, has satisfactorily completed the requirements for the course and research project for the degree of Master of Science in Inorganic Chemistry in the University of Nigeria, Nsukka. The work embodied in this project report is original and has not been submitted in part or in full to any other programme in this or any other university.

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Industrial Chemistry)

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ABBREVIATION

ACGIH	American Conference of Government Industrial Hygienists
BDH	British Drug House
bipy	2,2ȏbipyridine
DMF	Dimethylformadide
E^o	Redox Potential
EDTA	Ethylenediamine tetraacetic acid
en	ethylenediamine
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
ET	Electron Transfer
HAT	Hydrogen Atom Transfer
IS	Inner-sphere
IR	Infra red
k	Rate constant
K	equilibrium
Log	logarithm
NMR or nmr	Nuclear Magnetic Resonance
obs	observed
OS	Outer-sphere
PCET	Proton-Coupled Electron Transfer
PT	Proton Transfer
tga	Thioglycolic acid
UV/VIS	Ultraviolet/ Visible
Ð	Infinity

ABSTRACT

The kinetics and mechanisms of the redox reactions of μ-oxo-bridged iron(III) complex ion $Na_4[(FeEDTA)_2\ O].12H_2O$ denoted as $Fe_2\ O^{4+}$, with the thiols-2-mercaptobenzothiazole(MBSH), 2-mercaptophenol(PhSH), 2-mercaptoacetic acid (MSH), and l-cysteine (RSH) have been investigated in aqueous perchloric acid medium at $[H^+]=1\times10^{-4}$ mol dm^{-3},I=0.05mol dm^{-3}($NaClO_4$) and at T =27.0±0.1^oC. The reactions were monitored under pseudo-first order condition .The rate of reaction was first-order in reductant and oxidant for all the systems giving overall second ï order reactions. The inorganic and organic products of the reaction between Fe_2O^{4+} -MBSH, PhSH, MSH and RSH and oxidants were found to be Fe(II) ions and disulphides respectively. The stoichiometries of Fe_2O^{4+} -MBSH, PhSH, MSH, and RSH was determined by mole ratio method and was found to be 1:2 for all the systems. The reactions of the thiols (MBSH.PhSH,MSH and RSH) had an inverse dependence on hydrogen ion concentration ,and so the general rate law can be given as follows

$$\frac{d[Fe_2O^{4+}]}{dt} = (a + b)\,[H^+]^{-1})\,[Fe_2O^{4+}]\,[\text{reductant}]$$

Changes in ionic strength of the reaction medium had a negative effect on the rate of reaction of Fe_2O^{4+} - MBSH and RSH and positive effect in the reaction of Fe_2O^{4+} - PhSH and MSH. Reduction of Fe_2O^{4+} by MBSH, PhSH, MSh and RSH showed no dependence on dielectric constant because decrease of dielectric constant did not change $k_{obs.}$ CH_3COO^-,/NO_3^-/Cl^-/SO_4^{2-}/K^+ and Mg^{2+},were used to determine the effect of catalysis on Fe_2O^{4+}-MBSH,PhSH,MSH and RSH reactions and there was decrease in catalysis. The effect of temperature on the rate of reduction of Fe_2O^{4+} with reductants was studied and was found to have negative entropy which confirmed the formation of binuclear complexes at the activated complex. The results of the study indicate that the reactions of Fe_2O^{4+} and thiols probably occur by the outer-sphere mechanism.

CHAPTER ONE

1.0 Introduction

There has been a great deal of interest in the chemistry of oxo-bridged complexes of Fe^{3+} [1,2,3,4,5,6,7,8]. This most probably stems from the fact that structures of these complexes are closely related to biological systems such as the protein hemerythrin and ferriporphyrin[6]. It is well known that on account of the presence of sulfyhdryl groups in thiols, they possess marked reducing properties and are readily oxidized to disulphide[7]. Sulfydydryl compounds have also been utilized in identifying low molecular weight cellular metabolites which could serve as detoxifying agents against metal poisoning[5]. Many metal complexes of thiols had been synthesized and found promising in metal chelation therapy. Also reports abound regarding the role played by RSH/RSSR couples in mediating redox potentials at biological sites[3].

Kinetic data has been published on the oxidation of ß-mercaptoacetic acid by $enH_2[(FeHEDTA)_20].6H_20$[3], oxidation of ß-mercaptoacetic acid by trioxoiodate(v)[11], reduction of iron(III) complex,$enH_2[(FeHEDTA)_2O].6H_2O$ by thiosulphate ions in acid medium[12]. These reactions produced no detectable stable intermediates and were rationalized on the basis of outer-sphere electron transfer mechanism. In the reaction of tetraoxoiodate (VII) and L-cysteine, the reaction was shown to have direct acid dependence and negative Bronsted-Debye salt effect[11].

Bioinorganic processes have exposed the inorganic reaction mechanists to the outer fringes of catalysis, to the fact that the main criterion for most catalytic action is a site which has similar electronic characteristics to those of the active site of the catalyst for the reaction under consideration. Consequent on this, prerequisites establishing the structure of the reactant and the product(s); the coordination sphere of the complex being robust and making sure that the only reactive site is the one pertinent to the elementary reaction under investigation should be

pursued[6]. Also the reaction being studied must be stoichiometric and as simple as possible, in order that the maximum mechanistic information can be obtained from it.

The role played by ligands in electron transfer reactions cannot be overlooked since ligand substitution as well as electron transfer attend most redox reactions. This phenomenon influences the reactivity of a particular metal as well as its stability in any oxidation state. These are factors that are dependent on the free energy change for such intramolecular electron transfer process[13-16].

Favourable change in free energy and activation energy in a redox process lead to a spontaneous reaction and results in change in oxidation state of at least two of the reactants. Mechanistically, these reactions follow one of the pathways, inner-or outer-sphere, although some other complex reactions operate by simultaneous inner-and outer-sphere mechanisms.[17, 18] These facts make it imperative that the inorganic reaction mechanist who has to research in varied areas as bioinorganic, coordination, organometallic and synthetic inorganic chemistry, becomes abreast with the diverse nature of his work and not become polarized towards one area of chemistry.

Existing literatures on the redox reaction of $Na_4[(FeEDTA]_2O.12H_2O$ with 2-mercaptobenzothiazole, mercaptophenol, mercaptoacetic acid and L-cysteine is adequate. Adequate knowledge of the redox parameters of the oxo-bridged $Na_4[(FeEDTA]_2O.12H_20$ with thiols is essential, consequently, the behaviour of this complex with thiols, form the bedrock of this study.

1.1 Rate Monitoring Techniques

The method selected to monitor the concentrations of reactants and products and their variations with time depends on the substances involved and the rapidity with which they change[3]. Many reactions reach thermodynamic equilibrium over periods of minutes or hours but some reactions reach equilibrium in fractions of a second. Under special conditions modern techniques are capable of studying reactions that are complete within a few femtoseconds (I fs $=10^{-15}$s). A particular technique chosen depends on how fast or how slow the reaction is[11].

Spectrophotometry, the measurement of the intensity of absorption in a particular spectral region, is widely applicable, and is especially useful when one substance (and only one) in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the spectrum. For example, the reaction

$$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)} \quad \text{----------(1.1)}$$

can be followed by measuring the absorption of visible light by bromine.

If a reaction changes the number or type of ions present in a solution, then it may be followed by monitoring the conductivity of the solution. Reactions that change the concentration of hydrogen ions may be studied by monitoring the pH of the solution with a glass electrode. Other methods of determining composition include titration, mass spectrometry, gas chromatography, and magnetic resonance. Polarimetry, the observation of the optical activity of a reaction mixture, is occasionally applicable[3].

1.1.1 Conventional Methods

These methods involve the measurement of the concentration or any physical property of one or more of the reactants or products as a function of time. For instance, in some reactions,

absorbance of any of the reactants or products could be measured and related directly to the concentration[19].

1.1.2 Monitoring Rates of Fast Reactions

Sufficient strides have been made in the development of techniques for the measurement of fast reaction rates. Such techniques are of two main types. The first employs the same principles as are used for slow reactions, the methods being modified to make them suitable for more rapid reactions. The second type is of a different character and involves special principles like temperature-jump[20].

The reasons why conventional techniques lead to difficulties for rapid reactions are as follows:

(1) The time that it usually takes to mix the reactant or to bring them to a specified temperature, may be significant in comparison with the t½ of the reaction. An appreciable error therefore will be made, since the initial time cannot be determined accurately.

(2) The time that it takes to make a measurement of concentration is significant compared with the t½.

Real-Time Analysis

In a real-time analysis the composition of a system is analyzed while the reaction is in progress, either by direct spectroscopic observation of the reaction mixture or by withdrawing a small sample and analyzing it[21].

Quenching Method

In the quenching method, the reaction is stopped after it has been allowed to proceed for a certain time, and the composition is analyzed at leisure. The quenching (of the entire

mixture or of a sample drawn from it) can be achieved either by cooling suddenly, by adding the mixture to a large amount of solvent, or by rapid neutralization of an acid reagent. This method is suitable only for reactions that are slow enough for there to be little reaction during the time it takes to quench the mixture[21].

Flow Method

In the flow method, the reactants are mixed as they flow together in a chamber. The reaction continues as the thoroughly mixed solutions flow through the outlet tube, and different points along the tube correspond to different times after the start of the reaction. Therefore, spectroscopic observation of the composition at different positions along the tube is equivalent to the observation of the composition of the reaction mixture at different times after mixing. The disadvantage of conventional flow techniques is that a large volume of reactant solution is necessary because the mixture must flow continuously through the apparatus. This disadvantage is particularly important for reactions that take place very rapidly, because to spread the reaction over an appreciable length of tube the flow must be rapid[21].

Stopped-Flow Technique

The stopped-flow technique avoids the disadvantage encountered in flow method. The two solutions are mixed very rapidly by injecting them into a mixing chamber designed to ensure that the flow is turbulent and that complete mixing occurs very rapidly. Behind the reaction chamber there is an observation cell fitted with a plunger that moves back as the liquids flood in, but which comes up to a stop after a certain volume has been admitted. The filling of that chamber corresponds to the sudden reaction of an initial sample of that reaction mixture. The reaction then continues in the thoroughly mixed solution and is monitored spectrophotometrically. Because only a small, single charge of the reaction chamber is prepared the technique is much more economical than the flow method. The suitability of the

stopped-flow technique to the study of small samples means that it is appropriate for biochemical reactions, and it has been widely used to study the kinetics of enzyme action[21].

Flash Photolysis

In flash photolysis, the gaseous or liquid sample is exposed to a brief photolytic flash of light, and then the contents of the reaction chamber are monitored spectrophotometrically. Although discharge lamps can be used for flashes of about 10^{-5}sec duration, most work is now done with lasers, which can be used to generate nanosecond flashes routinely, picoseconds flashes quite readily, and flashes as brief as a few femtoseconds in special arrangements. Both emission and absorption spectroscopy may be used to monitor the reaction, and the spectra are observed electronically or photographically at a series of times following the flash[21].

Relaxation Methods

The limitation of the stopped- flow method is the dead time during which the enzyme and substrate are mixed[22]. Relaxation method overcomes the mixing problems associated with the flow method. The term órelaxationô denoted the return of the system to equilibrium. In its application to chemical kinetics the term indicates that some externally applied influence has shifted the equilibrium position of a reaction normally very quickly, and the reaction relaxes into the new equilibrium position[23].

One of the most important relaxation techniques uses a temperature jump. The equilibrium is changed by causing a sudden change of temperature and the concentration are monitored as a function of time. One way of raising the temperature is to discharge electric current through a sample which has been made by conducting the addition of ions. With a suitable choice of condensers, temperature jump of between 5 and 10 K can be achieved[18]. The recorded data

enables the number of intermediates to be deduced and the various rate constant calculated from the relation times[22].

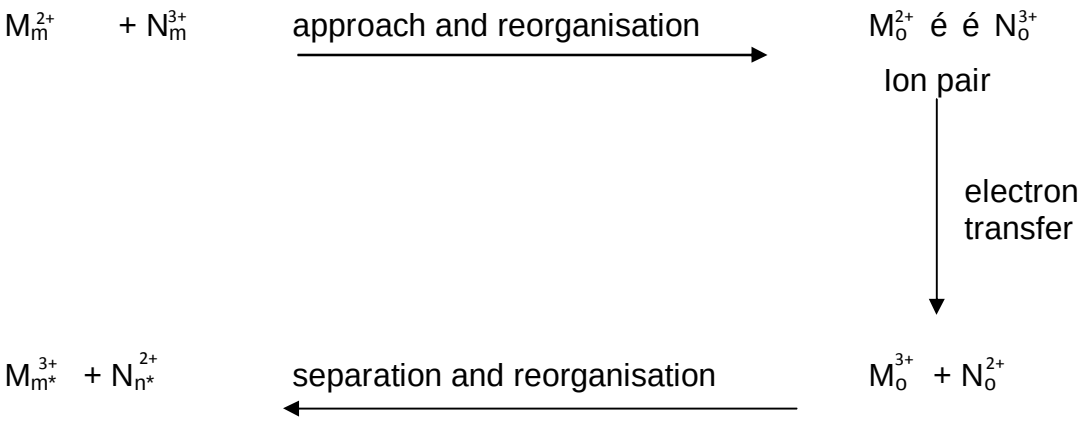
1.1.3 Resonance Techniques

Rates of reactions could be monitored using the nuclear magnetic resonance (nmr) technique. Resonance absorption line is related to the t½ of the nucleus in a given spin state. For cases where electron spin resonance is the method of choice, resonance absorption is related to the life-time of paramagnetic species in a given energy state. If the life-time of these states is shortened by say a chemical interaction, it results into line broadening of ^{1}H nmr. Line broadening has been used to measure the rate of exchange of various mono-and bidentate nitrogen and oxygen donor ligands coordinated to Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)[3].

1.2 Theoretical considerations in electron transfer processes

1.2.1 Franck-Condon Principle

Frank-Condon principle states that electronic transitions are virtually instantaneous in comparison with atomic rearrangement[24]. In other words, valence, unless they posses sufficient geometrical similarity to reduce to a minimum the energy transfer required by the simultaneous and instantaneous conversion of an ion of one valence to another[25]. Electron transitions are rapid compared with nuclear motions and electron transfer occurs without significant movement of the atoms. Since electron transfer reactions involve bond-breaking and formation, Frank-Condon principle must of necessity come into play. However, since the atomic distances between ligands and the metal ions alter the oxidation state of the metal ion, reorganization of the metal-ligand distances for the reactions and products occurs before electron transfer takes place [26]. The sequence of event is represented as follows



Where subscripts m and n = equilibrium configurations of the coordination shell for metals M^{2+} and N^{3+} respectively, subscripts o = intermediate configuration[3].

Electron transfer can only take place when ions approach each other. When the electron transfer step is very rapid, the overall rate is that at which the ions diffuse together to form an ion-pair. Reactions of this type studied by temperature-jump techniques had rates of the order of magnitude of the diffusion-limited values[27].

Franck-Condon principle presupposes that electron transfer takes place with the nuclei of the oxidant and reductant virtually stationary. The reorganization undergone by the reactants before electron transfer occurs in such a way that their transition state energies become almost identical and energy change on electron transfer is minimized.

The total change in energy involved in the process can then be represented by equation (1.3)[28].

$\Delta G^{\#} = \Delta G_t^{\#} + \Delta G_i^{\#} + \Delta G_o^{\#}$----------(1.2)

$\Delta G_t^{\#}$ = association free energy

$\Delta G_i^{\#}$ = inner-sphere reorganization energy

$\Delta G_o^{\#}$ = outer-sphere reorganization energy

1.2.2 The Electron Tunneling Hypothesis

Considerable insight into the electron transfer process in solution is given by the electron tunneling theory developed by Weiss and by Marcus, Zwolinski, and Eyring. The electron can transfer at distances considerably greater than would correspond to actual collision of the reactants[23]. The implication is that external value for the specific rate constant as a function of the distance of approach is used to determine the most stable activated complex. This maximization is necessary to find the best distance of approach for the probability of electron penetration consistent with the smallest energy of activation[29].

Theoretical considerations based on above views resulted in the relationship known as the electron transmission coefficient $k\hat{o}^{*}$ which takes the form of the transition state theory of chemical kinetics[28].

$$k = \frac{KT}{h} k^{l} \exp\left(\frac{-\text{æ}G_r^{*}}{RT} \frac{\text{æ}G_r^{*}}{RT}\right) \text{----------(1.3)}$$

kô= electron transmission coefficient

k = rate constant

K = Boltzmann constant

T = absolute temperature

G_e^{*} = activation energy

G_r^{*} = hydration energy for inner coordination shell arrangement

R = gas constant.

The value of the transmission coefficient is less than unity and increases as the exchanging partners come close together. Electrostatic repulsion ensures that activation energy also increases hence the rate of reaction tends to decrease. However, at an optimum distance a

maximum exchange rate is obtained. The electron tunneling is viewed to be involved most electron transfer reactions but might not be the rate determining step in most cases[30,31].

1.3 Electron Transfer Reactions

These are redox reactions in which two species come together and electron passes from one to the other. In some instances there is an accompanying change in the coordination shell of one or both of the reactants. Usually, the two complexes are such that, the reaction involves no chemical change. Such a reaction is called a redox (oxidation-reduction) reaction. Redox reaction or electron transfer reactions can be classified into two broad classes, namely homonuclear (isotopic) exchange reactions and chemical or cross reactions. The class into which a particular redox reaction falls is dependent on the thermodynamic parameters involved. The stability of the oxidation state of a metal and therefore the most stable oxidation state varies with the surrounding ligands[26].

Redox reactions are usually studied in aqueous system since most metal ions are inert in non-aqueous solution. The oxidation states which are well known for example Ti(III), Cr(III) and Fe(III) are so well known simply because of their stability in the presence of water. The reason why a particular oxidation state is stable may be either thermodynamic when a change in oxidation state may be associated with an unfavourable free energy change or kinetic, when the energy of activation for the intramolecular ligand-metal redox reaction may be large[26].

Oxidation of a particular species involves electron loss and reduction involves electron gain, implying that the rate at which a redox reaction occurs is qualitatively related to the redox potential. Each ion in aqueous media has its standard electrode potential, E^o, measured in volts which is determined in comparison to the standard hydrogen electrode which is assigned zero potential. The electrode potential of an ion gives an indication of its readiness to be oxidized or

reduced by another ion. Hence, ions with higher negative values of standard reduction potentials are good reducing agents while those with less negative values or that has positive values function as good oxidizing agents.

Therefore, for two ions involved in a redox reaction, the oxidant is the ion of lower negative value of reduction (electrode) potential while the ion of higher negative reduction potential acts as the reductant. Generally, systems with higher electrode potentials are reduced by systems with lower electrode potentials. This, however, assumes that the entropy terms for the redox reaction are favourable or negligible. Also the electronic configuration of a metal ion is an important factor in determining the stability of a particular oxidation state and hence governs the redox potentials**.**

1.3.1 Homonuclear or Isotopic Exchange

Isotopic exchange involve only electron transfer between different oxidation states of the same metal in a constant environment[24], for example

$Fe^{2+}_{(aq)} + F^{*}e^{3+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + F^{*}e^{2+}_{aq}$. ----------(1.4)

$Fe(phen)_3^{2+} + Fe^{*}(phen)_3^{2+} \rightarrow Fe(phen)_3^{3+} + Fe^{*}(phen)_3^{2+}$---------- (1.5)

In such a reaction the isotope distribution tend towards equilibrium as a result of transfers of isotopically different atoms or groups.

1.3.2 Heteronuclear or Cross Reaction

This class of reactions involves electron transfer between different metal ions centres. The products are chemically distinct from the reactants and the overall free energy change (ΔG^{o}) is not equal to zero. In most cases, ΔG^{o} is less than zero. The reaction can be complementary if oxidant and reductant undergo equal changes in oxidation states (stoichiometry is 1:1 as in eqn 1.15.

$Fe(CN)_6^{4+} + IrCl_6^{2+} \ddot{Y} \; Fe(CN)_6^{3+} + IrCl_6^{3+}$ ---------- (1.6)

$Co(en)_3^{3+} + Ru(NH_3)_6^{2+} \ddot{Y} \; Co(en)_3^{2+} + Ru(NH_3)_6^{3+}$ ----------(1.7)

The reaction could be well be non-complementary whereby the oxidant and reductant undergo unique changes in oxidation states (stoichiometry is not 1:1) The reaction

$Sn^{2+} + 2Fe^{3+} \ddot{Y} \; Sn^{4+} + 2Fe^{3+}$ ----------(1.8)

Is a good example of such reactions[3.]

1.4.0 Mechanisms of Redox Reactions

The kinetics of electron transfer reactions and their mechanistic significance revolves around finding answers to the following questions:

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

(ii) Whether the transfer of electrons, atoms or other species are involved.

(iii) What is the relative rate of electron transfer as compared to the rate of substitutions?

(iv) How many electrons are transferred in a single step for multivalent reactants?

(v) For reactions that are not feasible thermodynamically, what provides the driving force?

(vi) Are the products isolable and identifiable?

(vii) Can intermediates formed before electron transfer be identified?

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

Metal ions in solution are coordinated by ligands or solvent molecules which form an inner coordination shell and this in turn is surrounded by an outer sphere of more loosely bound solvents. Activated intermediates in a redox reaction may involve both inner and outer coordination spheres of the metal ions, or outer coordination spheres of the metals ions, or just the outer sphere. These two distinct types of behaviour are possible in a redox process and are

called the inner sphere (I.S) and the outer sphere (O.S) electron transfer mechanisms. Most redox reactions have been rationalized in terms of these mechanisms[23].

1.4.1 The Outer-Sphere Mechanism

In this mechanism, the redox step postulated is simply electron transfer between two reactants whose primary coordination spheres remain intact throughout. It also occur when the metal is surrounded by easily polarizable ligands such as phenanthroline and dipyridyl which tend to promote more rapid electron transfer than those involving a bridging intermediate. The reaction

$[Os^{II}\ dypy_3]^{2+} + [M_o{}^{v}\ (CN)_8]^{3-} \rightleftharpoons [Os^{III}\ dypy_3]^{3+} + [M_o{}^{IV}(CN)_8]^{4-}$----------(1.9)

with a probable activated intermediate $(dipy_2Osdipy.(OH)_2.(CN)M_o(CN)_7]$ occurs by the outer-sphere mechanism.

Also in the Fe(II)/Fe(III) redox system of the type[3]

$Fe(phen)_3{}^{2+} + Fe(phen)_3{}^{3+}$Ÿ $Fe(phen)_3{}^{3+} + Fe(phen)_3{}^{2+}$ ----------(1.10)

The two metal centers are inert and could not permit the detachment or transfer of phen from one ion to another. The coordination shells of the two reactants remain essentially intact before and after the electron transfer[32].

As a general rule, reactions of this type follow the pathways:

(a) Formation of a precursor complex: for the reaction between two metal ions M^{II} and N^{III} respectively we obtain

$M^{II}(H_2O)_6{}^{2+} + N^{III}(NH_3)_5L^{2+} \rightleftharpoons [H_2O)_6M^{II}//LN^{III}(NH_3)_5]^{4+}$----------(1.11)

(b) Activation of the precursor complex:

$[CH_2O)_6M^{II}//LN^{III}(NH_3)_5]^{4+} \rightleftharpoons [(H_2O)_6M^{II}//LN^{III}(NH_3)_5{}^{4+}]$----------(1.12)

(c) Electron transfer and formation of a successor complex:

$[(H_2O)_6M^{II}//LN^{III}(NH_3)_5{}^{4+}]^{\#} \rightleftharpoons [(H_2O)_6M^{III}//LN^{II}(NH_3)_5]^{4+}$ -------(1.13)

(d) Decomposition of successor complex to give the final products:

$$[(H_2O)_6M^{III}//LN^{II}(NH_3)_5]^{4+} \rightleftharpoons M^{III}(H_2O)_6^{3+} + N^{II}(NH_3)_5L^{+} \text{ ----------} \quad (1.14)$$

Step c serves as the rate determining step for the reaction.

1.4.2 The Inner-Sphere Mechanism

The essential feature of this mechanism is that substitution at one of the metal centres occur, to give a binuclear ligand-bridged species, previous to the transfer of an electron. The two metal cetres participating in the reaction are linked by at least one bridging ligand common to their inner coordination shells. The ligand bridge acts as conduction route for transfer of electron from one metal ion to the other. Decomposition of the activated complex, after the electron transfer, yields the products of the reaction. In most cases, the bridging ligand is transferred from its metal centre of origin to the next as can be seen by the typical inner-sphere reaction between chromium (II) and cobalt (III) [33.]

$$[Cr^{II}(H_2O)_6]^{2+} + [ClCo^{III}(NH_3)_5]^{2+} \text{ Ÿ } [(H_2O)_5\,Cl\text{-}Co(NH_3)_5^{4+}]^{\#}$$

$$\xrightarrow{H^+} [(H_2O)_5Cr^{III}CL]^{2+} + Co^{2+} + 5NH_4^{+} \text{ ----------} \quad (1.15)$$

The following steps have been identified to operate in most inner-sphere electron transfer process.

(a) Formation of collision complex

$$L_5M^{III}X^{2+} + N^{II}(H_2O)_6^{2+} \rightleftharpoons [\,L_sM^{III}X//N^{II}(H_2O)_6]^{4+} \text{ ----------} \quad (1.16)$$

(b) Formation of bridged precursor complex

$$[L_5M^{III}X//N^{II}(H_2O)_6]^{4+} \rightleftharpoons [L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5]^{4+} + H_2O \text{ ----------} \quad (1.17)$$

(c) Activation of precursor complex, electron transfer and formation of successor complex

$$[L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5^{4+}] \text{ Ÿ } [L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5^{4+}]^{\#} \text{ ----------} \quad (1.18)$$

(d) Deactivation of successor complex and formation of products

$$[L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5^{4+}]^{H} \text{ Ÿ } [L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5^{4+}]$$

$$\longrightarrow L_5M^{II}H_2O^{2+} + XN^{III}(H_2O)_5^{2+} \text{ ----------} \quad (1.19)$$

Any of the steps in this reaction could be rate determining depending on which one is the slowest step. If the rate of formation of the precursor complex or the rate of dissociation of the successor complex is slow, then we are dealing with a substitution controlled reaction. Alternatively, if the rate of electron transfer is slow, then we have a redox controlled system . Using the generalized scheme for inner-sphere electron transfer process (equs 1.25-1.29), Haim (1983) summarized the various limiting forms of the rate laws (cf table 1)[34]

$$M^{III}L_5X + N^{II}L_6{}^{I} \underset{kd}{\overset{k_d}{\underset{pc}{\rightleftharpoons}}} M^{III}L_5XN^{II}L^{I}{}_5+L^{I} \text{ ----------} \quad (1.20)$$

$$M^{III}L_5XN^{II}+L_5{}^{I} \underset{K_{-et}}{\overset{K_{et}}{\rightleftharpoons}} M^{II}L_5XN^{III}L_5{}^{I} \text{ ----------} \quad (1.21)$$

$$M^{II}L_5XN^{III}L_5{}^{I} + S \underset{K_f{}^{sc}}{\overset{k_d{}^{sc}}{\rightleftharpoons}} M^{II}L_sS + N^{III}L_5X\text{----------} \quad (1.22)$$

Where k_f = rate of formation, k_d = rate of dissociation,

k_{et} = rate of electron transfer, p^c = precursor complex,

sc = successor complex, S=successor.

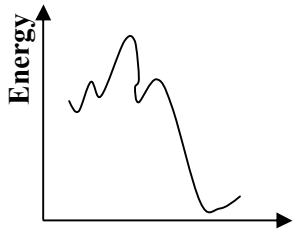
Table 1: Limiting forms of Rate Laws for Inner-Sphere Mechanisms

Rate determining step	Other conditions	Rate law
Formation of precursor complex	$k_{et} > k_d^{pc}$	k_f^{pc} [MX] [N]
	$k_d^{sc} > k_{-et}$	
Dissociation of successor complex	$k_f^{pc}/k_d^{pc} >> 1$	$k_d^{sc}[M^{II}XN^{III}]$
	$k_{et}/k_{-et} >> 1$	
Dissociation of successor complex	$k_f^{pc}/k_d^{pc} << 1$	$\frac{k_f^{pc} k_{et} k_d^{sc}}{k_d^{pc}}$ [MX] [N]
	$k_{et}/k_{-et} << 1$	K_{-et}
Dissociation of successor complex	$k_f^{pc}/k_d^{pc} >> 1$	$\frac{k_{et} k_d^{sc}}{k_{-et}}$ $[M^{III}XN^{II}]$
	$k_{et}/k_{-et} << 1$	
Electron transfer	$k_f^{pc}/k_d^{pc} << 1$	$\frac{K_f^{pc} k_{et}}{k_d^{pc}}[MX][N]$
	$K_d^{sc} > k_{-et}$	
Electron transfer	$K_f^{pc}/K_d^{pc} >> 1$	$k_{et\,[M}{}^{III}XN^{II}]$
	$K_d^{sc} > k_{-et}$	

Where k_{et} = rate of electron transfer, k_d = rate of dissociation

k_f = rate of formation, pc = precursor complex, sc = successor complex.

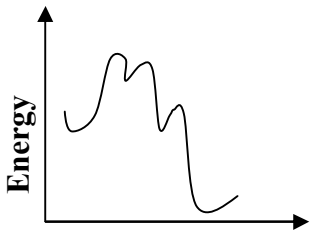
Reactions in which precursor complexes are readily formed, and their rates of transformation to successor complexes are relatively slow can be represented by the energy diagram (scheme 1) below[35]



Reaction coordinate
(Scheme I)

A typical example is the inner-sphere of trans-$Co(en)_2H_2OCl^{2+}$ by Fe^{2+}. Substitution first takes place on the labile Fe^{2+} ion, followed by electron transfer and subsequent Co-Cl bond rupture to yield $FeCl^{2+}$ and Co^{2+} as initial products[36].

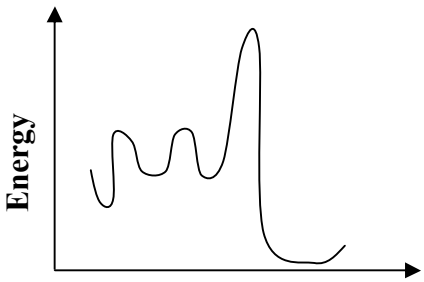
The second case is where electron transfer occurs rapidly as soon as the precursor complex is formed. The energy profile (scheme II) below represents such reactions.



Reaction coordinate
(Scheme II)

Most reductions by V^{2+} and Co^{3+} oxidation of several substances belong to this group[37].

Mechanism in which reactant and the successor complex are in equilibrium, the overall reaction rate is dependent on the rate of bond-rupture in the successor complex and could be represented by scheme III as the energy profile diagram for such systems.



Reaction coordinate
(Scheme III)

Cr^{+}-reduction of cis-$Ru(NH_3)_4Cl_2^{+}$) as well as that of cis-$Ru(NH_3)_4H_2OCl^{2+}$ and $Ru(NH_3)_5Cl^{2+}$ [38] proceed by the mechanism of scheme III.

Their data fit the rate law:

$$\frac{d[Ru^{III}]}{dt} = \frac{k_1K\ [Cr^{2+}][Ru^{III}]}{I + K[Cr^{2+}]} \text{----------} \quad 1.23$$

and consistent with the mechanisms

$Ru^{III} + Cr^{2+} \underset{}{\overset{k}{\rightleftharpoons}} (RuCr)^{n+}$ ----------1.24

$(RuCr)^{n+} \xrightarrow{k_i} Ru^{II} + CrCl^{2+}$----------1.25

Atom transfer is not essential for reactions occurring by the inner-sphere mechanism. However, systems which can be unequivocally assigned an inner-sphere mechanism are those which the oxidant and oxidized reducing agent are with substitution inert and where atom transfer occurs during the redox reaction.

1.5.0 Determination of Mechanism of Redox Reactions

The inorganic reaction mechanists first task is the diagnosis of the actual pathway by which a redox reaction occurs. In order to achieve this objective, the following criteria are usually explored.

1.5.1 k_{redox} (K_{red}) versus $k_{substitution}$ (k_{sub})

For inner-sphere reactions, substitution into the coordination shell occurs before electron transfer hence if $k_{red} >> k_{sub}$ such a reaction is likely to occur by the outer-sphere path[39]. This was observed for the electron exchange reaction between $Fe(CN)_6^{4+}$ and $F(CN)_6^{3+}$. Also, for the reaction

$Fe(phen)_3^{2+} + Fe(phen)_3^{3+}$ Ÿ $Fe(phen)_3^{3+} + Fe(phen)_3^{2+}$ ----------(1.26)

K_{sub} was determined to be 7.5 x $10^{-5}s^{-1}$ (Fe^{3+}) and 5.0 x 10^{-5} s^{-1} (Fe^{3+}), while k for exchange is 10^5mol-1dm^3 s^{-1} indicating outer-sphere mechanism[32]. For a reaction in which $k_{sub} >> k_{red}$, and in the presence of a suitable bridging ligand, inner-sphere exchange may occur.

1.5.2 Proton Coupled Electron Transfer(PCET)

Proton Coupled Electron Transfer is an electrochemical reaction mechanism in which an electron and proton are simultaneously moved in a concerted mechanism[40].

It is when a proton and electron starting in different orbitals are transferred to different end orbitals in a single concerted elementary step. Concerted PCET is thermodynamically more favourably than the first step in competing consecutive processes involving stepwise electron transfer (ET) and Proton Transfer (PT), often by Ó1 ev. PCET reactions of the form x ï H + yŸ x + H ï y can be termed hydrogen atom transfer (HAT). Another PCET class involves outer-sphere electron transfer concentrated with deprotonation by another reagent Y^{+} + XH - B Ÿ Y + X ï HB^{+}[40]----------(1.27)

These reactions play an important role in many areas of chemistry and biology. These reactions also form the basis of many types of solar fuel cells and electrochemical devices. Recent advances in the theory of PCET enable the prediction of the impact of system properties of the reaction rates. These predictions may guide the design of more efficient catalysts for energy production, including these based on artificial photosynthesis and solar energy conversion.

A similar proton couple electron transfer has been reported by the reduction of di-μ-oxo-tetrakis-(1, 10-phenanthroline) ï dimanganese (III, IV) perchlorate by Ascorbic acid in acid medium [41]. This is further supported by the fact that $Mn^{III}O_2Mn^{IV}$ has a protonable moiety and H_2A has acidic protons which are necessary conditions for the occurrence of the proton coupled electron transfer pathway. The oxidation of H_2A by Ru_2O^{4+} has been reported to be complicated by proton transfer[42]. This implies that protons are also transferred during the electron transfer reaction, so that the reduction of $Mn^{III}O_2Mn^{IV}$ most probably involves the transfer of both protons and electrons.

1.5.3 Ion-Pair Formation

Ion-pair formation involves an ionization process in which a positive fragment ion and a negative fragment ion are among the products. Ion-association is a chemical reaction whereby ions of opposite electrical charge come together in solution to form a distinct chemical entity. Ion-association are classified according to the number of ions that associate with each other and the nature of the interaction.

It is a pair of oppositely charged ions held together by coulomb attraction without formation of a covalent bond. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

According to Bjerrum, ion-pair is oppositely charged ions with their centres closer together than a distance

$$q = 8.36 \times 10^{6} Z^{+} Z^{-}/(\Sigma r T) pm \quad \text{----------} \quad (1.28)$$

are considered to constitute an ion-pair (a "Bjerrum ion pair"). (Z^{+} and Z^{-} are the charge numbers of the ions, and Σr is the relative permittivity (or dielectric constant) of the medium[43].

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of X^{+} and Y^{-} is symbolically represented as $X^{+}Y^{-}$

In chemistry, the intimate ion-pair concept introduced by Saul Winstein describes the interactions between a cation, anion and surrounding solvent molecules. In ordinary aqueous solutions of inorganic salts an ion is completely solvated and shielded from the counter-ion. In less polar solvents two ions can still be connected to some extent. In a tight or intimate or

contact ion pair there are no solvent molecules between the two ions. When salvation increases, ionic bonding decreases and a loose or solvent-shared ion pair results.

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a ñloose ion pairò, symbolically represented as X^{+}/Y^{-}. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g. by isotopic labeling) and this affords an experimental distinction between tight and loose ion pairs[43]

.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In ñsolvent-shared ion pairsò the ionic constituent of the pair are separated by only a single solvent molecule, whereas in ñsolvent-separated ion-pairsò more than one solvent molecule intervenes. However, the term ñsolvent-separated ion pairò must be used and interpreted with care since it has also widely been used as a less specific term for ñlooseòion pair.

1.6.0 Product Identification

The detection of a binuclear complex, either as a stable product or as a transient intermediate along the pathway between reactants and products, represents another piece of experimental information that is taken to be very persuasive evidence in favour of an inner sphere mechanism[31]. Until relatively recently, the binuclear complexes that were detected were successor complexes. Such complexes are expected to be produced when an inner-sphere mechanism is operative and both the reduced form of the oxidant and the oxidized form of the reductant are inert with respect to substitution[37]. Under these circumstances, neither metal centre will ñlet goò of the bridging ligand, and binuclear complex is the final product of the reaction or a relatively long-lived intermediate Table (III) Haim(1983).[34] Once the parameters

required to observe the occurrence of ligand transfer have been delineated, it is relatively simple to devise systems to test for a bridged activated complex.

An example of a system that features a binuclear successor complex and which has been studied in detail is the $IrCl_6^{2-}$ - $Cr(OH_2)_6^{2+}$ system. The reaction proceeds in two discernible stages at 2^0C[18]. The first is the very rapid disappearance of the reddish brown $IrCl_6^{2-}$ and is accompanied by the formation of a green intermediate. The second stages involve the disappearance of the green intermediate and the formation of the final products, olive-brown in colour. The reactions in Eqs 1.29 and 1.30 were postulated in account for the observations[18].

$$Cr(OH_2)_6^{2+} + IrCl_6^{2-} \longrightarrow (H_2O)_5\ Cr\text{-}Cl\text{-}IrCl_5 + H_2O \quad (1.29)$$

$$(H_2O)_5\ Cr\text{-}Cl\text{-}IrCl_5 \xrightarrow{H_2O} Cr(OH_2)^{3+} + IrCl_6^{3-} \quad (1.30)$$

On the basis of its electronic spectrum, it is evident that the binuclear complex $(H_2O)_5$ Cr-Cl-$IrCl_5$ contains chromium (III) and Ir(III) (low ï spin) and is therefore a successor complex. It is noteworthy that the products of the dissociation of the successor complex (Eq.1.30) are identical to those of the outer-sphere electron transfer reaction.

$$Cr(OH_2)_6^{2+} + IrCl_6^{2-} \text{ Ÿ } Cr(OH_2)_6^{3+} + IrCl_6^{3-} \quad (1.31)$$

Therefore, the inner-sphere mechanism is substantiated for this system on the basis of the detection of the binuclear complex, since ligand transfer does not obtain in the postulated sequence(Eqs 1.29 and 1.30). This finding is considered to be quite significant since it demonstrates that ligand transfer does not always accompany inner-sphere electron transfer, and is not, therefore, an essential feature of the mechanism. However, the system was reinvestigated, and it appeared at first that ligand transfer did accompany inner-sphere electron transfer[34] . However, there are inner-sphere reactions which are not accompanied by atom transfer, for example reductants like Fe^{2+}, Fe^{3+}, Eu^{2+} and in such reactions where easily

hydrolysable products are formed, identification of products are difficult. Cases like $Co(NH_3)_5SCN^{2+}/N^{2+}$ system where stopped flow technique has been used to identify the products can be classified[44, 45].

1.7.0 Reactivity Pattern

1.7.1 Trends of Halides – Relative stability of transition states.

The effects of halide ions on the rates of redox reaction have been investigated extensively by various workers [34.] For oxidant-halide complexes, the reactivity order $I^->Br^->Cl^->F^-$ is known as ñnormalò[46.] Redox reactions of this type include $Cr^{II}/[Co^{III}(NH_3)_5\ X\ ]^{2-,}$ $Cr^{II}/Cr^{III}\ (NH_3)_5\ X\ ]^{2+}$ [47.] The opposite trend $I^-<Br^-<Cl^-<F^-$ is known a ñinverse and has been identified in such reactions as $Eu^{II}/[Co^{III}(NH_3)_5\ X\ ]^{2+}$ and Fe^{III} reduction by $Cr(H_2O)_6^{2+}$.

For complexes of the form $Co(NH_3)_5\ X^{2+}$ (x = Cl^-, F^-, Br^- or NO_3^-) the formation of the reductant ï X bond in the transition state is of most importance and the strength of the bond follows the sequence M ï F >M ï Cl> Mï Br >Mï I (M = oxidant or reductant). If this complex is reacted with another metal ion, rates of reaction should be sensitive to the nature of X if the reaction is inner-sphere whereas for outer-sphere reaction, rates will be unaffected irrespective of the nature of X[48, 49].

1.7.2 Relative Rates of Reaction of Hydroxo and Aquo complexes

Most electron transfer reactions between aquo complexes exhibit a rate law consisting of the sum of an acid-independent term and an inverse-acid term.

$$\text{Rate} = \left(\frac{k_0 + k_1}{[H^+]}\right)[Ox][Red] \qquad (1.32)$$

Acid-independent terms are observed for the $Co(NH_3)_5OH_2^{3+}$- $Cr(OH)_6^{2+}$ and $Fe(OH_2)_6^{3+}$ - $Cr(OH_2)_6^{2+}$ reactions when the measurements are carried out utilizing sodium perchlorate to

maintain constant ionic strength[50, 51]. The inverse acid path has been rationalized on the basis of an inner-sphere hydroxide-bridge mechanism. The reaction especially for the $Co(NH_3)_5OH^{2+}$ - $Cr(OH_2)_6^{2+}$ goes through the activated binuclear complex, $[(NH_3)_5CoOHCr\ (OH_2)_5^{4+}]$. For the labile system, indirect arguments based on the relative reactivity of water and hydroxide suggests an inner-sphere pathway for the k_{-1} term. For the systems where OH^- is known to act as a bridge, the hydroxo complex is considerably more reactive than the aquo complex. For inert systems, where the inner-sphere mechanism is precluded (redox rate faster than substitution rates), the inverse acid paths are no longer operative or proceed very slowly[34.]

Based on the relative efficiency of ligands to acts as electron conductors ($I^->Cl^->F^->OH_2>NH_3>>RNH_2>CN^->OH^-$)[31] and to the reaction given above, it is suggested that when the hydroxo and the aquo complexes have similar reactivities, the outer-sphere mechanism obtains. In contrast, when the hydroxo complex is substantially more reactive than the aquo complex, then an inner-sphere mechanism for the k_1 pathway is indicated. Generally, in outer-sphere reactions the hydroxyl complex appears to react slower than the corresponding aquo species[52].

1.7.3 Effect of Added Ions

Substitution of anions into the inner-sphere of labile reactants can alter the rate of electron transfer markedly. This could be as a result of the formation of different bridging groups[53.] For an electron transfer reaction that follows the outer-sphere mechanism, the absence of bond-breaking steps makes the rate of reaction theoretically easier to determine than that of the inner-sphere reaction mechanisms.

However, for an outer-sphere reaction the reactants must be in sufficiently close proximity to create an electronic interaction which provides a basis for the delocalization of the exchanging electron. This implies that reactions operating by the outer-sphere mechanism can be catalyzed

in the presence of added ions that can increase the proximity between the oxidant and reductant thereby shortening the distance to within which the electron can be transferred by forming a bridge[54].

The reduction of Mn(II) and Fe(III) tetraphyridylporphins with Cr(II) and V(III) is altered appreciably by addition of anions[31.] The anion catalyzed path increases in the order $1^-<Br^-<Cl^-<<SCN^-$. With substitution inert complexes, such as those of Co(III), the effects are less marked with changes in the bridging group[55, 56, 57, 50.] A typical rate law for the effect of added anions is

Rate = $(k_o + k_1$ [external ion]) [oxidant] [reductant].

For a reaction involving reactants having positive charges, anion catalysis can arise from anion coordinating to one of the reactants (reductant) thereby reducing the degree of repulsion between the reactants. In that way electron transfer becomes faster. Also, for reactants carrying negative charges, added cations (metal ions) can catalyze such reaction by coordinating to one of the reactants (oxidant) thereby reducing the degree of repulsion between the redox partners. This equally enhances the rate of electron transfer since the reactants are now brought in close proximity to each other. However, for redox partners that carry opposite charges, added ions could retard the rate of reaction since coordination to any of the reactants could reduce the degree of attraction between the reactants. This will increase the distance between the redox partners and slow down the rate of electron transfer.

1.7.4 Activation Parameters

Activation parameters æH$^{\#}$ æG$^{\#}$ and æS$^{\#}$ do not seem to have strong correlation to the type of mechanism operating in a particular redox process. However their signs of magnitudes could give a clue as to which mechanism is inherent in a reaction. Negative æH$^{\#}$ indicates formation of a precursor complex as in inner-sphere mechanism[58.] However, this pattern has no general

application as regards other reactions. For example, despite the difference in mechanisms the æS$^{\#}$ for the reaction of Cr^{2+} and V^{2+} with Ru^{3+} complexes are almost the same. Measurements of the volume of activation (æV$^{\#}$) for the reduction of various complexes have been applied as diagnostic tool in reaction kinetics[59]. It has been reported that for the reaction, there are two possible routes indicated as regards the nature of intermediates.

$$[(H_3N)_5\ Co^{III}Y]^{n+} + [Fe^{II}(OH_2)_6]^{2+}$$

$$\downarrow \text{I.S} \qquad \downarrow \text{O.S}$$

$$[(H_3N)_5Co.Y.Fe(OH_2)_5]^{(n+2)+} \quad [(H_3N)_5Co(Y)\ (H_2O)\ Fe(OH_2)_5]^{(n+2)2} \qquad \text{-------} \quad (1.33)$$

The I.S pathway should be retarded with increasing pressure (æV$^{\#}$ should be positive) if it is assumed that the volume of ñfreeò H_2O is larger than that of coordinated H_2O. Obtained results support an inner-sphere mechanism[33]. However, the same trend has not been obtained in some other redox systems making the application of æV$^{\#}$ as a diagnostic tool of limited scope.

1.7.5 Marcus Theory

Marcus (1963) attempted to calculate the minimum energy ófreaction coordinateô or reaction trajectory tended for electron transfer to occur[18]. The calculation of electron transfer rates using such parameters as interatomic distances, dielectric constants, force constants, etc is difficult and unwieldy. This is because the values of these qualities cannot be known with certainty. However, for reactions occurring by the outer-sphere mechanism, the weak interaction between reactants during electron transfer make it possible that kinetic and thermodynamic parameters can be related[13]. The reaction coordinate includes contributions from all of the trapping vibrations of the system including the solvent[54]. The reaction coordinates is a complex function of the coordinates of the series of normal modes that are involved in electron trapping.

This approach to the theory of electron transfer gives the rate constant for outer-sphere electron transfer [60].

$$k_{obs} = Zk_{exp}\,[-(W_R)/RT]\exp[-(\Delta G^0)/RT] \qquad (1.34)$$

The above equation (1.43) shows the rate constant to be a product of four factors (1) z is the collision frequency between two neutral molecules in solution. It is not the diffusion limited rate constant since it also includes encounter between reactants in a solvent cage. For H_2O at 25^0C, Z = 10^{11} mol $^{-1}$ dm^3s^{-1}. (2) k is the transmission coefficient. It is related to the probability that electron transfer will occur once the interaction between the potential coordinate modes of the redox couple is reached. Most simple outer-sphere electron transfer reactions have k values close to unity (3) W_R is the free energy change associated with bringing together the reactants and is unfavourable for like charged reactants since they will repel each other but favourable for unlike charged reactants as they have mutual attraction (4) ΔG^o is the minimum free energy increase above the background thermal energy. RT, required in the vibrational and solvent trapping modes in order for electron transfer to occur with energy conservation. ΔG^o is also related to the inner-sphere (vibrational) and outer-sphere (solvent) reorganization energies for self-exchange reactions[3].

The k_{obs} value derived by above equation (1.34) by Marcus includes pre-association between reactants, a time dependence arising from the frequency with which the reactants collide and the thermal activation required for electron transfer to occur. However, quantum mechanically derived expressions for the rate of electron transfer, k_{et}, are dependent upon the interreactant separation, and the dependence on V (electron coupling term) must be included explicitly . Combination of these ideas gives that

$$k_{obs} = K_A k_{et} \qquad (1.35)$$

K_A is the association constant between reactants and using Eigen-Fuoss equation (1.36), K_A can be written for spherical reactants as

$$K_A = \frac{4kNr^3}{3000} \exp ï \left(\frac{W_R}{RT}\right) \text{----------(1.36)}$$

These equations presuppose that for an outer-sphere reaction, given the translation mobility of the reactants, electron transfer may occur over a range of distances. Therefore, electron transfer is expected to be dominated by reactants in close contact. However, equation (1.36) is only an approximation for real molecules in that it assumes both a single value for internuclear separation (r) between reactants and structureless, spherical reactants. In fact, it has been suggested for $Fe(H_2O)_6^{3+,\ 2+}$ self-exchange that a significant feature of the reaction may be the interpenetration of the coordination spheres in order to enhance electronic orbital overlap[54].

Since electron transfer is dominated in fluid solution by reactants in close contact, it will be expected that those in close contact will be quickly depleted and their statistical population be brought back to the equilibrium level by diffusion together of the reactants. As long as the time for diffusion is short compared with that for electron transfer, the equilibrium statistical distribution is maintained and equation (1.35) $k_{obs} = K_A k_{et}$) is valid which implies that the rate constant for electron transfer remains the product of K_A and k_{et}. For very rapid reactions, statistical equilibrium is not reached and the experimentally observed rate constant will include a contribution from the diffusion together of the reactants. The diffusion limited rate constant, k_D, can be introduced into the rate term as

$$\frac{1}{k_{obs}} = \frac{1}{k_D} + \frac{1}{k_{act}} \text{----------(1.37)}$$

(where $k_{act} = k_{et} \cdot K_A$)

The diffusion controlled rate constant (k_D) for spherical reactants was calculated to include the viscosity (η) of the solvent, the radii (a_D and a_A) of the reactants and the thermal energy term W

$$K_D = \frac{(2RT)(2}{3000\eta} + a_D + \frac{a_A)}{a_A} \frac{W / RT}{a_D\, e^{W/RT-1}} \quad \text{---------- (1.38)}$$

(R = gas constant and T = absolute temperature)

Experimental tests have been applied to the theories of Marcus and Hush and the extent to which these thermodynamic and kinetic parameters affect the rate of electron transfer reactions, for a series of closely related redox reactions like

$$Fe(H_2O)_6^{2+} + M(phen)_3^{3+} \text{ Ÿ } Fe(H_2O)_6^{3+} + M(phen)_3^{2+} \text{----------(1.39)}$$

(M=Fe,Ru,Os)

Charge types and molecular radii are constant, thus ensuring a constancy in intermolecular vibrations, electrons trapping and solvent effects as well as K_A. Also the similarity in molecular structures ensures that the only remaining variable is the free energy aG^o_{et} which for the series shown varies by 20.5 V. Generally, for the following redox systems (1.40) and (1.41) when compared with the ñcross reaction (1.42), the forward rate constant can be estimated from expression (1.43).

$$R_d^1 + O^1 \underset{}{\overset{k11}{\rightleftharpoons}} R_{do}^1 + O_r\,1 \text{ ----------} \quad (1.40)$$

$$R_d^2 + O^2 \underset{}{\overset{k22}{\rightleftharpoons}} R_{do}^2 + O_r\,2 \text{ ----------} \quad (1.41)$$

$$R^2 + O^1 \underset{}{\overset{k12}{\rightleftharpoons}} R_o 2 + O_r 1 \text{ ----------} \quad (1.42)$$

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad \text{----------} \quad (1.43)$$

$$\text{Where } f_{12} = \frac{(\ln K_{12})^{1/2}}{4\ln(k_{11}k_{12}/Z^2)} \quad \text{----------} \quad (1.44)$$

K_{12} is the equilibrium constant for the ñcross reactionò and can be obtained from electrode potential data. Z is the number of collisions occurring between two neutral species in solution (10^{11} $mol^{-1}dm\text{-}^3s^{-2}$), k_{11} and k_{22} are rate constants for isotopic exchange and f_{12} is frequency close to unity[3].

With the knowledge of k_{11} and k_{12} it is possible for closely related systems to obtain a value to k_{12}. Also as k_{12} approaches unity, f_{12} approaches unity then

$$k_{12} = (k_{11}\, k_{22}\, K_{12})^{1/2} \quad \text{----------} \quad (1.45)$$

The Marcus ñcross reactionò equation (1.43) above interrelates the rate constant for the net reaction (k_{12}) with the equilibrium constant (K_{12}) and self-exchange reactions (k_{11} and k_{22}). As stated above, its determination is based on the assumption that the contributions to vibrational and solvent trapping for the net reaction from the individual reactants are simply additive. The factor of one-half appear because only one of the two components of the self-exchange reaction involved in the reaction Equ (1.43) can be related to the free energy of self-exchange reaction and can be interpreted as[61].

$$æG^{\#}_{12} = 0.5æG^{\#}_{11} + 0.5æG^{\#}_{22} + 0.5æG^{o}_{12} \quad \text{----------} \quad (1.46)$$

Where $æG^{\#}$ is the free energy of activation $æG^{o}$ = free energy change and could be calculated from electrode potentials. The expressions above are applicable to outer-sphere electron transfer reactions. For a series of reactions, a plot of $æG_{12}^{\#}$ versus $æG_{12}^{o}$ gives a straight line with a slope of 0.5 if the reaction occurs by outer-sphere pathway. Another type of comparison allowable by equation (1.50) is obtained by dividing the cross-reaction constant for a common

reagent with two other reagents, k_{12}/k_{13} and comparing this relative rate value with that obtained by a similar procedure for reagent ñ4ò k_{42}/k_{43}. If the f terms are small, the two rates should be the same, For example, for a third electron exchange

$$R_d^3 + O^3 \overset{K_{33}}{\rightleftharpoons} R_{do}^3 + O_r^3 \text{ ---------- (1.47)}$$

The modified expressions (1.48) could be obtained

$$\frac{k_{12}}{k_{13}} \left(\frac{k_{11}k_{22}K_{12}}{k_{11}k_{33}K_{13}}\right)^{1/2} = \left(\frac{k_{22}K_{12}}{k_{13}K_{13}}\right)^{1/2} \text{ ----------(1.48)}$$

When the value of k_{12} is known, the value of k_{13} can be calculated.

1.8.1 Objectives of the Study

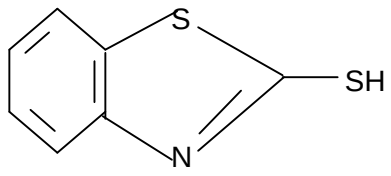
The complexes of iron and the reductants (Mercaptobenzothiazole, mercaptophenol. Mercaptoacetic acid and L-cysteine play very important role in biology, chemistry, biochemistry, chemical technology, physiology and other related areas[62,63]. Iron metalloproteins serve as agents for oxygen transport and storage while haemoglobin and myoglobin are essential for electron transfer in the cytochromes. The thiols (Mercaptobenzothiazole, merceptophenol, mercaptoacetic acid and L-cysteine) used in this work has been used in metal binding and metal-thiol complex is linked with effectiveness of the thiol in removing unwanted metal ions [64]. Hence, electron transfer of oxo-bridged iron (III) complex with the thiols will be studies in this work.

CHAPTER TWO

LITERATURE REVIEW

2.1 2-MERCAPTOBENZOTHIAZOLE (MBSH)

2-mercaptobenzothizole is designated as MBSH and has the structure



Mercaptobenzothiazole has bitter taste, slightly foul odour and soluble in dimethylformadide(DMF). It is a crystalline heterocyclic compound made by heating aniline, sulphur and carbon disulphide and used chiefly as an accelerator for the vulcanization of rubber [65]. It can be found in industries, household and safety products, health care and sports equipment, made with natural, buty rubber, nitrile or neoprene-such as boots shoes adhesives, gloves, toys, swimwear, hoses, tubing and elastic. Because mercaptobenzothiazole is used in certain types of rubber products, it can react with other substances used in manufacture of rubber such as thiourea. If oneôs skin is regularly exposed to rub, one may develop reactions to other substances in rubber such as thiuriams, carbamates and mercapto mixes[66].

Mercaptobenzothiazole is almost non-toxic to birds on an acute oral basis and is only slightly toxic to birds on a dietary basis However, it is highly toxic to freshwater fish and moderately toxic to equatic invertebrate. The sodium and zinc salts of 2-mercaptobenzothiazole are used as fungicides, micro biocides and bacteriostats. These salts are used as preservatives for adhesives. latex and oil paints, paper products, metal working cutting fluids and textile fibres, The acid of 2-mercaptobenzothizole is classified as non-quantifiable ôGroup Cô carcinogen, a possible human carcinogen[67].

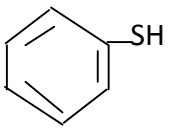
2-mercaptobenzothiazole ($C_7H_{14}NS_2H$) and its metal derivatives have been extensively used for prevention of metal corrosives and eye as anti-turnover agent. The basis of these

applications is apparently associated with the ability of mercaptobenzothiazole to form metal complexes, although little is known of the true nature of these compounds, probably because of their insolubility,

2-mercaptobenzothiazole and its complexes play vital role in the zinc oxide assisted acceleration of the vulcanization of natural rubber. $C_7H_{14}NS_2H$, or its mono-or di-alkylsulphemide derivatives, are frequently used as organic additives to zinc vulcanizing mixture, and it is believed that these react with ZnO forming complexes .It is known that $[ZnC_7H_{14}NS_2]^+$ is formed in this reaction, but this compound is extremely insoluble suggesting that if zinc complexes do actually play a role in vulcanization acceleration, then they should be solubilized in some way, even if only transiently in the overall reaction[67].

2.2 MERCAPTOPHENOL

Mercaptophenol is an organosulfur compound with the formula C_6H_5SH,

with the structure 

and sometimes abbreviated as PhSH. This foul-smelling colourless liquid is the simplest aromatic thiol. The chemical structures of mercaptophenol are analgous to phenols except the oxygen atom in the hydroxyl group (-OH) bonded to the aromatic ring is replaced by a sulfur atom. The prefix thio-implies a sulfur containing compound and when used before a root word name for a compound which would normally contain an oxygen, atom, thio-commonly means that the oxygen atom is replaced by a sulfur atom[68,69].

Mercaptophenol also describes a class of compounds formally derived from mercaptophenol itself. All have a sulfhydryl group (-SH) covalently bonded to an aromatic ring. The organosulfur ligand in the medicine merthiolate is a mercaptophenol.

Mercaptophenol can be generated by action of elemental sulfur on phenyl magnesium halide or phenyllithium followed by acification and by reduction of benzenesulfonyl chloride with zinc.

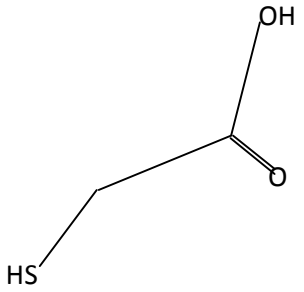
The first chemical contrast of thiols and sulfides with alcohols and ethers is acidity which is important in organic reactions. Thiolate conjugate bases are easily formed, and are excellent nucleophiles in SN2 reaction of alky halides and tosylates[70].

Mercaptophenol is a toxic flammable clear liquid boiling at 168^0C. It is insoluble in water but soluble in acetone and ether. Many chemical reactions of mercaptophenol are analogous to phenols. The substantial difference between sulfur and oxygen is that sulfur much more readily gets oxidized to higher oxidation states than oxygen. Sulfur in organic compounds is fairly stable in several oxidation states. The ring closure reaction of 0-amino thiophenol produces benzothiazole, an important industrial product. Thiophenol itself is used as an antinematodal agent. Thiophenol class compounds have the skeleton of thiophenol[71].

Thiophenol is known to be a toxic compound with LD_{50} of 46200 µg/kg when administered orally to rats. It is my interest to find good oxidants that will have the capability of reducing both the odour and toxicity of thiophenol. The results of this research I hope will go a long way in complimenting the much needed data on the reaction of thiols with lanthanides[72].

2.3 β- MERCAPTOACETIC ACID

ß-Mercaptoacetic acid also known as thioglycolic acid (tga), $HSCH_2CO_2H$, has the structure



Pure thioglycolic acid is a white crystalline substance decomposes at about 78^{o}C. It is very soluble in water, alcohols, acetone, acetates, slightly soluble in ethyl ether; sparingly soluble in hydrocarbon solvents and polymerizes at above 50^{0}C. Commercially it is available in crystal form as well as in aqueous solutions of various concentrations

It is also used in the making of tin stabilizers often used in certain polyvinyl chloride products. Tga, usually as its dianion, forms complexes with metal ions, such complexes have been used for the detection of iron, molybdenum, silver and tin and can be used in cleaning applications and removal of hardness of water. Thioglycolic acid is a useful intermediate in organic synthesis including oxidation/reduction, esterification and formation of oligomers as well as long chain polymerization. Thioglycolic acid is naturally found in sugar beets, cane sugar and unripe grape. It is known that it diminishes the lines on the skin and makes skin look young. Synthetic glycolic acid and its derivatives are used commercially in leather tanning and textile dyeing, as a flavouring agent and preservative in food processing and water treatment industries[73,74,75].

Mechanism of the oxidation of 2-mercaptoacetic acid by enH_2[(FeHEDTA)$_2$O].6H_2O in aqueous acid medium have been reported to follow outer-sphere pathway[70.] It showed rate dependence on reciprocal of [H^+] and presence of free radical intermediate was reported. However, in the reaction of tga with Na_4[(FeEDTA)$_2$O].12H_2O, it was reported to follow inner-sphere pathway. The oxidation product of these reactions(Fe_2O^{4+} with MSH) is the disulphide compound of MSSM. They resulted from the abstraction of proton from the sulphydryl group and subsequent

formation of RS^- or free radical RS*. Recombination of two of these radicals leads to formation of the disulphide as seen below for the reaction of $[RuORu]^{4+}$ with the thiols

$$RSH \rightleftharpoons RS^- + H^+ \text{ ----------(2.1)}$$

$$[Ru^{III}ORu^{III} + RS^- \rightleftharpoons [Ru^{III}ORu^{III}RS^-] \text{----------(2.2)}$$

$$[Ru^{III}ORu^{III}RS^-] \rightarrow Ru^{III}ORu^{II} + RS^* \text{----------(2.3)}$$

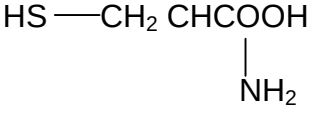
$$2RS^* \rightarrow RSSR \text{---------- (2.4)}$$

The dissociation step above is also responsible for the inverse dependence of rate on hydrogen ion concentration. Thioglycolic acid has been applied in preventing corrosion of copper [76].

The redox reaction of $[FeOFe]^{4+}$ with mercaptoacetic acid has been studied in this work. This is with a view to determine the redox parameters and compare with well established reactions of the thiols.

2.4 L-cysteine

L-cysteine (2-amino-3-mercaptopropanoic acid) hereafter designed as RSH has the structure



Its oxidation product in most of its redox reactions is the amino acid cystine (a disulphide of cysteine)[77]

cystine

L-cysteine is an amino acid that exists naturally as a protein in most living organisms. Although most cystine is found in proteins, small amounts of cysteine are also located in body fluids and in plants in non-protein form. Many people are able to obtain as much of this protein source as they need without taking any type of supplement. L-cysteine can be found in a number of foods ranging from meats to dairy and vegetable sources. L-cysteine in the form of cystine is found in many different protein sources. Chicken, turkey and pork are all good sources of cysteine. Even many varieties of processed meats contain this amino acid. Cooking does not destroy the presence of cysteine and in some cases may even help to enhance the absorption[78].

When it comes to dairy products L-cysteine as cystine can be obtained from eggs and milk. Products such as ricotta and cottage cheese are also good sources. Plant yogurt and whey protein products also produce cysteine in a natural form. Onions, garlic, and broccoli are just a few of the vegetables that contain cysteine and provide good dietary resource when there is a need to augment L-cysteine levels in the body [78.]

Cysteine like most thiol undergo redox reactions with transition metal complexes. The major oxidation product is the disulphide cystine. This is true for its reaction with trioxalatocobaltate(III) ion [79] and $[RuORU]^{4+}$ [80] .

These results indicates that the main centre of attack on cysteine is sulphur atom and not nitrogen atom as nitrogen is less electrophilic than sulphur. The mechanism of redox reactions could be either outer-sphere or inner-sphere depending on the nature of the oxidant. The inner-sphere pathway have proposed for the reduction of Molybdenum by complex Fe(III) in hydrochloric acid medium[81],while outer-sphere pathways have been proposed for the reactions of l-cysteine with periodate [3] and $[RuORU]^{4+}$ [81]

2.5 Oxo-bridged Iron(III) Complexes

Binuclear complexes of iron(III) have been prepared and characterized using infrared, uv-visible and nuclear magnetic resonance spectroscopy. Various studies on their stability in aqueous solution[66] and hydrolysis and dimerization behaviour were carried out[2,70,80]. These studies have shown the presence of dimeric species of the form $[Fe\text{-}O\text{-}Fe]^{4+}$ or $[Fe(OH)_2Fe]^{4+}$ existing in equilibrium with monomeric species of the form $FeOH^{2+}$ [6].

Infrared, uv-visible and mossabuer spectral data have shown that compounds of the form $enH_2[(FeHEDTA)_2O].6H_2O$, $Na_4[(FeEDTA)_2.12H_2O$ where actually μ-oxo-bridged dimeric iron(III) species. Their electronic data show two visible absorption bands at 530 and 475nm[6, 3, 5].

Baxendal and Bridge reported a yellow complex formed when iron(III) is mixed with 2, 2-bipyridyl[82]. From photometric studies of the complex, it was observed that the complex has the structure $[Fe(bpy)_2]$. However, complexes of iron(III) phenathroline in aqueous solution where shown to be brown high spin complexes with Fe-O-Fe bridge devoid of hydrogen ions. The binuclear complexes existed in aqueous solution as $[L_2(H_2O)FeOFe(H_2O)L_2]^{4+}$ (L = bpy or phen). Interaction with H^+ ions resulted in the rupture of the oxo-bridging leading to formation of mononuclear species. This implies the bridge oxygen protonation weakens the Fe-O-Fe bonds, then accelerating its cleavage leading to formation of $[FeL_2(H_2O)_2]^{3+}$. Hence existence of the oxo-bridged complex in acid medium is very doubtful. Stopped-flow techniques have been used to spetrophotometrically follow the concentration of dimeric Fe(III) species. The rate of cleavage of hydroxo bridged iron (III) complexes in 3M $NaClO_4$, following the equation

$$[Fe_2(OH)_2]^{4+} \rightleftharpoons 2FeOH^{2+} \text{ ----------} \quad (2.5)$$

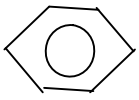
had the rate law

$$-\frac{d[Fe(OH)_2{}^{4+}]}{dt} = (k_1 + k_2 [H^+] [Fe_2(OH)_2{}^{4+}] \text{----------} \quad (2.6)$$

Where $k_1 = 0.4s^{-1}$, $k_2 = 3.1s^{-1}$

This shows that cleavage of the bridge is dependent on hydrogen ion concentration[69]

The presence of oxo-bridged iron(III) species was also implicated in the reaction of chlorate ions with $[Fe(phen)_3]^{2+}$. Although detailed mechanism of the redox reactions is uncertain, the final oxidation product was proven to be $[(phen)_2Fe\text{-}O\text{-}Fe(phen)_2]^{4+}$ [83]. Studies on the effect of temperature and ionic strength showed that dimerization at optical density 540mn gave æH# = -7.1 kcal/mol and qS° = 13.0 ev. This indicated that dimerization of Fe(III) complexes followed oxo-bridging producing Fe-O-Fe or $Fe_2(OH)_2$[80].

Apart from studies on the behavior of these complexes in aqueous acid of alkali solutions, one area of interest has been the extent of interaction; between two metal ions separated by ligand - bridge. Emphasis has been on the degree of metal-metal interaction across the bridging ligands and the consequences of such interactions on the physical and chemical properties of such system[84,85]. For transition metal systems in which metal ions or atoms are linked by bridging ligand, there could be strong, direct metal-metal bonding or strong metal-metal interactions but through the ligand bridge. Also weak metal-metal interactions can exist or there might not exist any form of metal-metal electronic interactions. For first row transition metal ion systems, weak metal-metal interactions exist but the component ions still have chemical and electronic properties similar to the properties expected for isolated monomeric complexes[64]. Magnetic studies have revealed that for complexes like $[(NH_3)_3\ RuN$  $NRu\ (NH_3)_5]^{5+}$ and $[C_5H_5Fe(C_5H_4C_5H_4)\ Fe(C_5H_5)]^{4+}$, they have localized integral oxidation state but the metal centres are non-identical[71]. If however, cases arise where strong metal-metal interactions exist, the constituent metal atoms or ions are significantly modified both chemically and electronically when compared to related monomeric complexes. Also, the chemistry of the

constituent ions will be modified if strong metal-metal interaction exists across the bridging ligand. Whereas there are not common complexes of these group of complexes, oxo-bridged complexes M-O-M because of their short bridging distance and because of the possibility of strong π-overlap show relatively strong metal-metal interaction across the ligand bridge. Oxo-bridged iron(III) complexes show marked intensity enhancement of the one-centre Fe(III) ligand field bands. Simultaneous excitation of Fe(III) pairs also give several bands[6,1.] Spin coupling via Fe-O-Fe has been indicated through magnetic studies. Also it has been shown that whereas the first row transition elements exhibit only weak metal-metal interactions, the degree of interaction is stronger for second row and third-row elements.

Interest in the reaction of Fe_2O^{4+} with thiols has increased over the years. This is because of the role played by RSH/RSSR couples in mediating redox potentials at biological sites as earlier stated. Some of these reactions are; metabisulphite ions by $[Fe_2(bpy)_4O]Cl_4$ [2], ß-mercaptoacetic acid by trioxoiodate(v)[3], thiophenol by bis(salicylideneiminato)sulphatocerium(iv)[72], catechol by Fe2(bipy)4O4+[6], and hypophosphorus acid by poly(pyridine) iron(iii) complexes[7]. There are still more like reductions of iron(III) complexes $enH_2[(FeHEDTA)_2O].6H_2O$, by thiosulphate ions[4], oxyanions[3], mercaptoethanol and mercaptoethylamine[86].

In most of these reactions stated above, oxidation of the thiols to the disulphide as the more facile and presence of thiyl radicals are common features of such reactions[11]. Most of these reactions have featured the formation of intermediates complexes having metal-thiol linkages which later decomposes in the redox step of the reaction to yield the products[72,87]. In pursuit of an in-dept knowledge of the dynamic of the various redox reactions by thiols, the oxidation of mercaptobenzothiazole, mercaptophenol, mercaptoacetic acid and l-cysteine by a Fe_2O^{4+} complex in perchloric acid medium is necessary.

CHAPTER THREE

EXPERIMENTAL

3.0 Materials and Methods

3.1 MATERIALS AND REAGENTS

3.1.1 Equipments

The following equipments were used

1. B.Bran 722 ï 2000 Spectronic 20D UV spectrophotometer ï for reading absorbances.
2. Jenway (England) 6405 UV/Vis spectrophotometer for reading absorbances, scanning and UV analysis.
3. Shimadzu FTIR Spectrophotometer used for infrared data.
4. Mettler balance (0-200 Gallenkamp) for weighing samples.
5. UV-2500 PC Spectrophotometer for UV analysis
6. Thermostated water-bath(Gallenkamp) for heating
7. pH meter (Searchtech Instruments) for measurement of pH of liquids
8. Suction pump (Associated Electrical Industries) for filteration

3.1.2 Reagents

The following reagents were used; -

1. 2-mercaptobenzothiazole (Fisher Scientific Company 98%).
2. Mercaptophenol (BDH, Analar grade 97%).
3. 2-mercaptoacetic acid (Sigma Aldrich Analar grade 99.6%).
4. L-cysteine (Fisher Scientific Company, Analar grade 98%).
5. Dimethylformadide(DMF), (BDH, Analar grade 95%).
6. Acetone(BDH Limited Poole England 99/100%).
7. Hydrochloric acid (BDH Limited Poole England 36.40%).
8. Iron(III) chloride Hexahydrate (BDH, Analar grade, 98.0%).
9. Sodium hydroxide (BDH Chemical Ltd Poole England 98.0%).

10. Sodium Acetate (M & B, Analar grade 99.8%).
11. Perchloric acid (BDH, Analar grade 99.998%).
12. Magnesium chloride Hexahdrate(BDH), Analar grade 99.995%.
13. Sodium tetraoxosulphate(VI) (BDH, Analar grade 99.8%.
14. Sodium trioxonitriate(V) (BDH Ltd Poole England Analar grade 99.96%).
15. Sodium trioxocarbonate(IV) (BDH Ltd Poole England Analar grade 99.9%).
16. Sodium tetraborate decahydrate(BDH, Analar grade 99.7%).
17. Diethyl ether(Sigma Aldrich Analar grade 99.5%).
18. Acrylamide(Fisher Scientific Company, Analar grade 99%).
19. Methanol(Sigma Aldrich Analar grade 99%).

21.Potassium hexacyanoferrate(III) (BDH Chemicals Ltd Poole England, Analar grade

22 Disodium ethyleneamminetetraacetic acid (M & B Analar grade 99.8%).

3.1.2.1 Preparation of salt $Fe(OH)_3$

1 mol dm^{-3} solution of $FeCl_3.6H_2O$ was made by dissolving about 27.03g of the salt in 100ml of distilled water. I mol dm^{-3} solution of NaOH was also prepared by dissolving 10g of the salt in 250ml of distilled water. 50ml of $FeCl_3.6H_2O$ solution and 150ml of NaOH solution were mixed in 500ml beaker. The brownish precipitate formed was collected and filtered by suction. It was finally dried in a dessicator. The melting point of $Fe(OH)_3$ prepared was 124^OC.

3.1.2.2 Synthesis of $Na_4[(FeEDTA)_2O].12H_2O$.

$Na_4[(FeEDTA)_2O].12H_2O$ hereafter represented by Fe_2O^{4+} was prepared as in literature[1].

A slurry of salt-free $Fe(OH)_3$ (0.1 mole) in 400ml of water was allowed to react with the disodium salt of ethylenediaminetetraacetic acid (0.1 mole) for 30 minutes at 80^0 ï 90^0. The resulting dark red solution had a pH of about 9.0. A crystalline red solid was recrystallized from water ï DMF mixtures [1].

The percentage yield was 89%. The reddish coloured complex decomposes between 315^{o}C. The UV and IR spectra as shown in Fig 3.1-3.3 agreed with literature[1]. The substance was stored in amber bottle in a dark cupboard for use.

3.1.2.3 Preparation of Sodium Perchlorate($NaClO_4$) solution

25g of Sodium Hydroxide(BDH) was added to 71.5cm^3 of $HClO_4$(BDH). The mixture was stirred and a neutral solution was obtained. The white crystals of sodium perchlorate formed were filtered, dried and stored in a dessicator. $NaClO_4$ prepared was dried and ground to powder and heat was applied, spark sound like that of matches was observed. The solution of the salt was prepared and poured on some weed, within five days the colour of the weed turned yellow and gradually withered. These two experiments showed that $NaClO_4$ was confirmed because it is used as weed killer and explosives[88].

3.1.2.4 Preparation of Sodium Acetate(CH_3COONa) solution

CH_3COONa was used without further purification. 0.01M CH_3COONa solutions were prepared by dissolving accurate weights of the salt in distilled water and making up the solutions in volumetric flasks. Accurate concentrations were determined gravimetrically.

3.1.2.5 Preparation of Sodium Perchlorate ($NaClO_4$) solution

0.5M $NaClO_4$ were dissolved in a distilled water to prepare approximate concentrations of the salt solution. The solutions were standardized gravimetrically.

3.1.2.6 Preparation of Magnesium Chloride (MgCl) solution

Analytical available chemical reagents were used without further purification. 0.01M solutions of magnesium chloride were prepared fresh in double-distilled water every 2 days.

3.1.2.7 Preparation of Sodium Chloride (NaCl) solution

0.01mol dm^{-3} solutions of NaCl were made by dissolving known amounts of solute in given volume of distilled water. Accurate concentrations were determined gravimetrically.

3.1.2.8 Preparation of Hydrochloric Acid (HCl) solution

A 5 mol dm^{-3} stock solution of hydrochloric acid was prepared by diluting appropriate volumes of concentrated HCl in standard flasks. The solution was standardized with standard Na_2CO_3.

3.1.2.9 Preparation of Perchloric Acid ($HClO_4$) solution

Concentrated solution of 0.01M $HClO_4$ was diluted in standard flask to prepare about 5 mol dm^{-3} stock solution. The solution was standardized volumetrically using sodium tetraborate decahydrate as primary standard and methyl red as indicator.

3.1.2.10 Preparation of Sodium Trioxonitrate(V) solution

0.01M solution of $NaNO_3$ was made by dissolving known amount of solute in a given volume of distilled water. Accurate concentrations were determined gravimetrically.

3.1.2.11 Preparation of Mercaptobenzothiazole (MBSH) solution

0.01M solution of 2-mercaptobenzathiazole was prepared by dissolving accurately weighted amount in dimethylformadide (DMF). The solution was kept in a dark cupboard. Fresh solutions were prepared every two days to ensure that fresh solution was used for various determinations.

3.1.2.12 Preparation of Meraptoacetic acid (MSH) solution

0.01M solution of ɓ-mercaptoacetic acid was prepared by diluting concentrated solutions with doubly distilled water. Fresh solution was prepared every two days to ensure that fresh solution was used.

3.1.2.13 Preparation of L-Cysteine (RSH) solution

0.01M solution of L-cysteine made by dissolving accurately weighed amounts in 0.05 moldm^{-3} HCl The solution was kept in a dark cupboard. Fresh solutions were prepared every two days to ensure that fresh solution was used for the various determinations.

3.1.2.14 Preparation of Mercaptophenol (PhSH) solution

0.01M solution of mercaptophenol was prepared by diluting accurately measured volumes of mercaptophenol with acetone.

3.1.2.15 Preparation of Sodium tetraoxosulphate(VI) (Na_2SO_4) solution

Sodium tetraoxosulphate(VI) standard salt solutions were made by dissolving 0.01M solution of solute in given volume of distilled water and the exact concentration determined by standard methods.

3.2 Methods

3.2.1 Stoichiometric Studies

Mole ratio method was used to determine the stoichiometry of the reaction by spectrophotometric titration. The following concentrations of solutions were used:

$[Fe_2O^{4+}]$ = 1.0 x10^{-4} mol.dm^{-3}, [MBSH] = 1.0x 10^{-3} ï 1.0 x 10^{-6} mol dm^{-3}, $[H^+]$ = 1.0x 10^{-4} mol dm^{-3}, I= 0.05 mol dm^{-3} ($NaClO_4$), T = 29.0 ±0.1^{0}C for mercaptobenzothiazole (MBSH) as reductant.

$[Fe_2O^{4+}]$ = 1.5 x10^{-4} mol dm^{-3}, = 7.0 x 10^{-5} ï 7.0 x10^{-4} mol dm^{-3}, $(H^+]$ = 1.0 x10^{-4} mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$), T = 29.0 $\pm$ 0.1^{o}C for mercaptophenol (C_6H_5SH) as reductant.

$[Fe_2O^{4+}]$ = 3.4 x 10^{-3} mol dm^{-3}, [MSH] = 3.5 x 10^{-5} ï 4.4 x 10^{-5} mol dm^{-3} $[H^+]$ = 1.0 x 10^{-4} mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$), = T = 29.0 $\pm$ 0.1^{0}C for mercaptoacetic acid as reductant.

$[Fe_2O^{4+}]$ = 2.0 x 10^{-4}mol dm^{-3}, [RSH] = 5.0 x10^{-4} ï 1.4 x 10^{-3} mol dm^{-3} $[H^+]$ = 1.0 x 10^{-4} mol dm^{-3}, I= 0.05 mol dm^{-3} ($NaClO_4$), T = 27.0 $\pm$ 0.1^{o}C for L-cysteine as reductant.

3.2.2 Kinetic Measurement

The rate of the reaction of Fe_2O^{4+} with thiols was monitored by measuring the decrease in absorbance of the product at 411nm using spectronic 20D spectrophotometer and Jenway (England) 6405 UV/Vis spectrophotometer.

The kinetic measurements were carried out under pseudo- first order condition with one of the reactants in at least 20 fold excess over the other reactant at a stated temperature. Ionic strength as well as the hydrogen ion concentrations of the media were maintained constant for each system unless otherwise stated.

3.2.3 Spectroscopic Investigation of Intermediate

The spectra of the partially reacted mixtures were ran and recorded at various time intervals depending on the speed of the reaction for the detection of stable intermediate. A similar run was made for reactants separately in each case. This was carried out in order to determine whether shifts in λ max or enhancement of peak resulted as the reaction progressed. A deep reddish coloured solution was formed readily which slowly faded to a colourless solution. The visible spectrum of the reddish complex did not increase.

3.2.4 Polymerization Studies

This was carried out as follows: stoichiometric amounts of the oxidant and the reductant solution in excess methanol were mixed with 2 grams of acrylamide. Control experiment was

carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[H^+]$ and temperature of 27^0C. Gel formation in the reaction mixture indicated presence of free radicals as important intermediates in the reaction[5]

3.2.5 Product Analysis

The types of products formed were determined using appropriate methods and reagents.

Test for the presence of disulphide. Test for the presence of and quantity of disulphide formed was carried out[89,90]. The thiol was reacted with a little excess of the oxidant in acid medium and ionic strength of reaction. At the completion of reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed with distilled water and dried with anhydrous Na_2SO_4 and left overnight to dry. Crystals produced, decomposed at 262^OC. The Infrared analysis of the crystal was done and absorption frequencies confirms the presence of disulphide not sulphoxide, Table 4:14 and Figure 4:25 ï 4:28

Test for the presence of Fe(II) ions: The presence of iron(II) ion was confirmed by reacting few drops of potassium hexacyanoferrate(III) with the product solution. The formation of a dark blue precipitate confirmed the presence of iron(II) ion[95].

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Stoichiometry Determination

4.1.1 Stoichiometry of Fe_2O^{4+}- mercaptobenzothiazole

The stoichiometry of the oxidation of mercaptobenzothiazole, by oxo-bridged dimer (Fe_2O^{4+}) was determined by spectrophotometric titration using mole ratio method. The concentration of the complex was kept constant (1 x 10^{-4} mol dm^{-3}) while the concentration of mercaptobenzothiazole was varied from 1x10^{-4} ï 8.0x10^{-5} mol dm^{-3} at constant [H^+] of 5.0x10^{-3} mol dm^{-3}. The reaction mixtures was allowed to go to completion until constant colour were obtained. Plot of absorbance (A_∞) versus [MBSH]/[oxidant] were made for the mixtures from which the stoichiometry was evaluated. This reaction had sharp breaks at a ratio of 1:2 (Fig 4.1). This shows that one mole of Fe_2O^{4+} is reduced for every two moles of MBSH as represented by equation (4.1).

Fe_2O^{4+} + 2MBSH Ÿ $2Fe^{2+}$ + MBSSMB + H_2O ----------(4.1)

4.1.2 The Stoichiometry of Fe_2O^{4+} - mercaptophenol.

The stoichchiometry of the reaction Fe_2O^{4+} - PhSH) was determined the mole ratio method. The concentration of the complex was kept constant (7.0 x10^{-4} mol dm^{-3}) while the concentration of mercaptophenol was varied from 7.0x10^{-5} ï 7.0x10^{-4} mol dm^{-3} at constant hydrogen ion concentration of 5.0x10^{-3} mol dm^{-3} and I = 0.05 mol dm^{-3} ($NaClO_4$). The reaction was allowed to go to completion. Plot of absorbance (A_∞) versus [PhSH]/[oxidant] were made from which the stoichiometry was evaluated. This reaction (PhSH/ Fe_2O^{4+}) had a sharp break at a ratio of 1:2 (Fig 4.2). This shows that one mole of Fe_2O^{4+} is reduced for every two moles of PhSH oxidized as represented 4.2

Fe_2O^{4+} + 2PhSH Ÿ $2Fe^{2+}$ PhSSPh + H_2O ----------(4.2)

4.1.3 Stoichiometry of Fe_2O^{4+} and mercaptoacetic acid

The stoichiometry was determined by spectrophotometric titration under the condition $[Fe_2O^{4+}]$ = $3.4x10^{-4}$ mol dm^{-3}, $[H^+]$ = $5.0x10^{-3}$ mol dm^{-3} [MSH] = $3.5x10^{-5}$ ï $4.4x10^{-5}$ mol dm^{-3}. The stoichiometry was evaluated from a plot of the absorbance versus the mole ratio (Fig 4.3). This reaction (MSH/ Fe_2O^{4+}) had a sharp break at a ratio of 1:2. This shows that one mole of Fe_2O^{4+} is reduced for every two moles of MSH oxidized as represented 4.3

$$Fe_2O^{4+} + 2MSH \text{ Ÿ } 2Fe^{2+} + MSSM + H_2O \text{ ---------- (4.3)}$$

4.1.4 The Stoichiometry of Fe_2O^{4+} - L-cysteine

The stoichiometry of Fe_2O^{4+}-L-cysteine was determined by spectrophotometric titrations under the condition $[Fe_2O^{4+}]$ = $2.0x10^{-4}$ mol dm^{-3}, [RSH] = $5.0x10^{-4}$ ï $1.4x10^{-3}$ mol dm^{-3}, $[H^+]$ = $5.0x10^{-3}$ mol dm^{-3}. The stoichiometry was evaluated from a plot of the absorbance versus the mole ratio. This reaction (RSH/ Fe_2O^{4+}) had a sharp break at a ratio of 1: 2 (Fig. 4.4). This shows that one mole of Fe_2O^{4+} is reduced for every two moles of RSH oxidized as represented by equation 4.4

$$Fe_2O^{4+} + 2RSH \text{ Ÿ } 2Fe^{2+} + RSSR + H_2O \text{ ----------(4.4)}$$

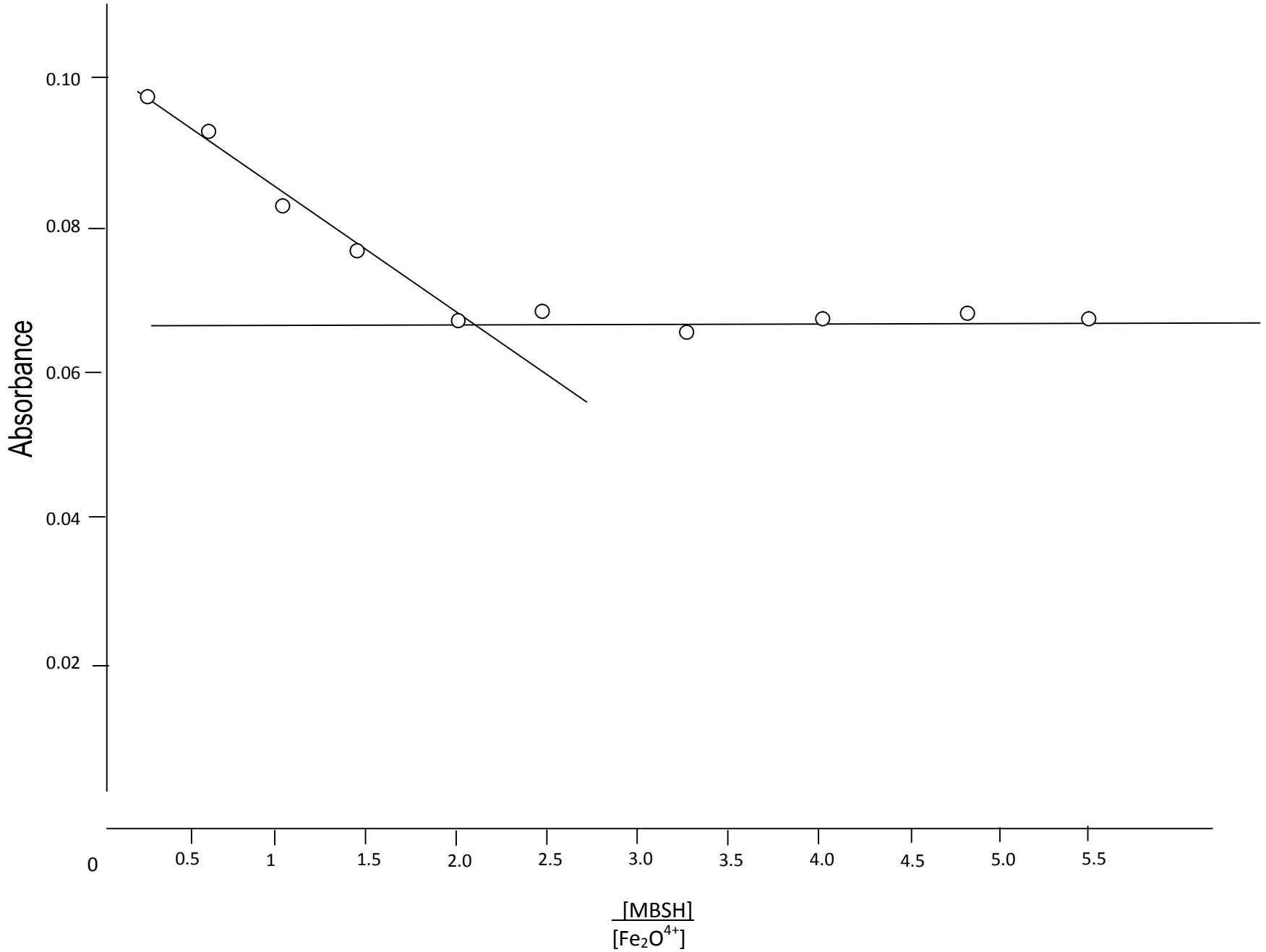


Fig. 4.1: Stoichiometry of the oxidation of MBSH by Fe_2O^{4+} at λ max 411 and T =29.0±0.1°C

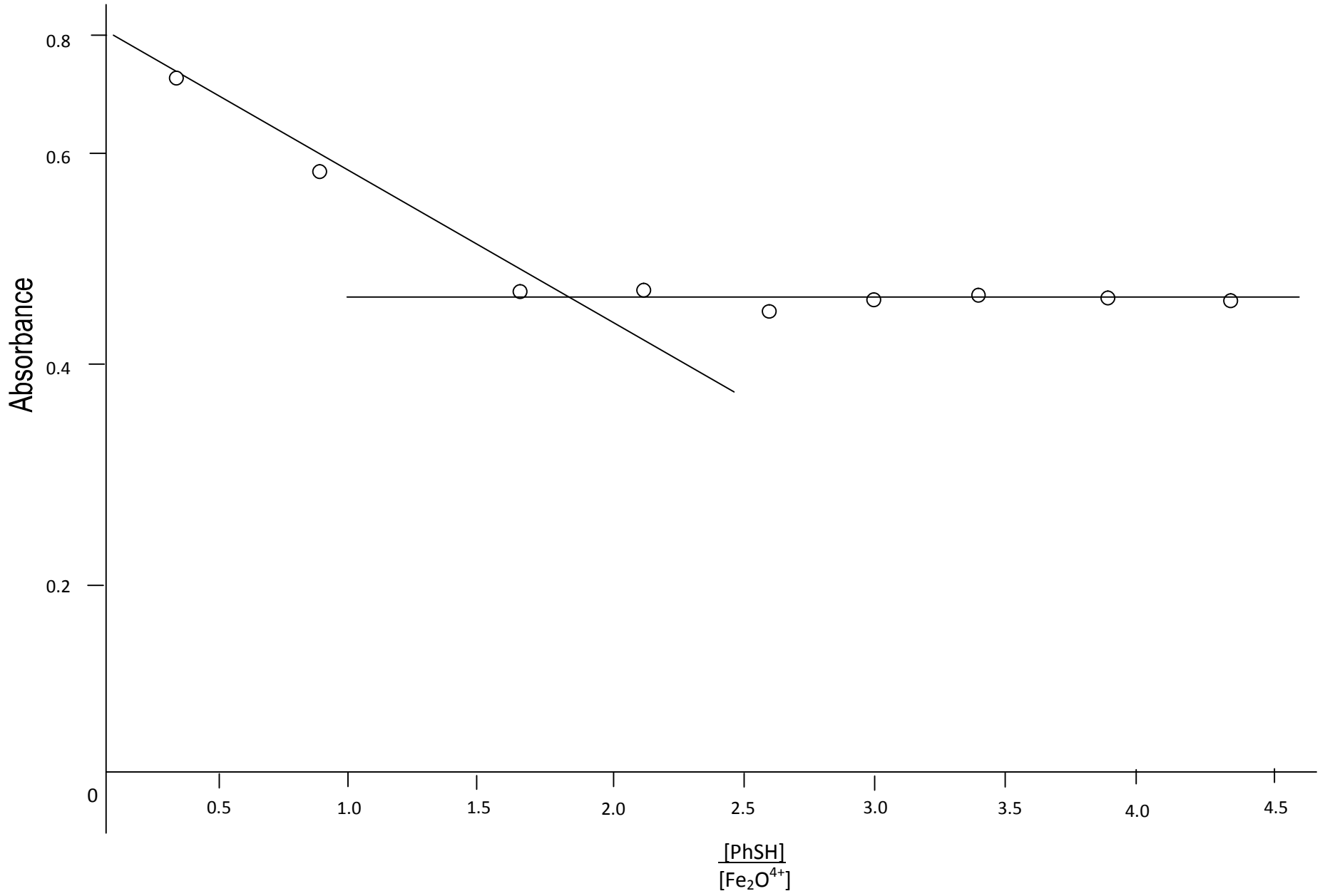
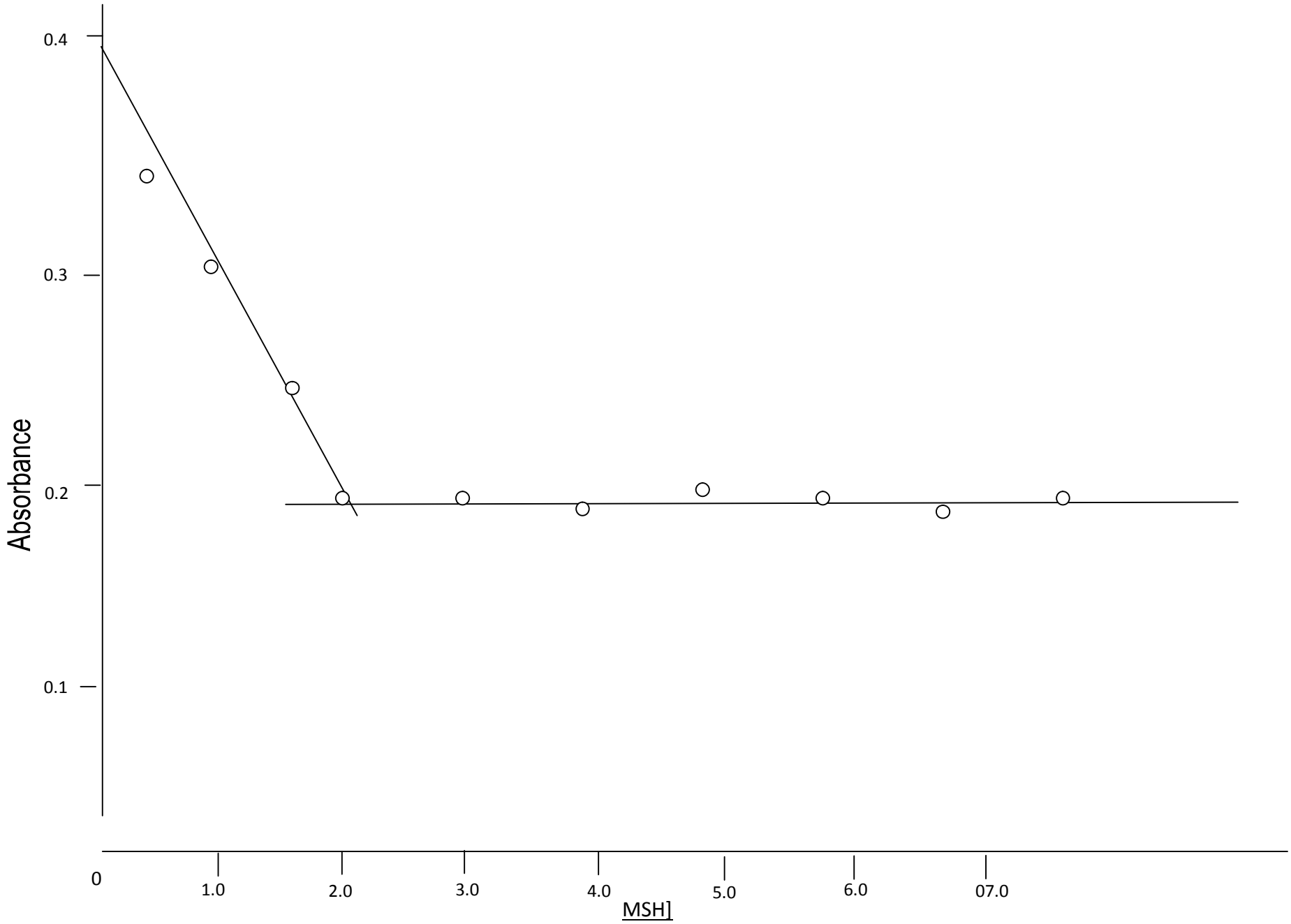
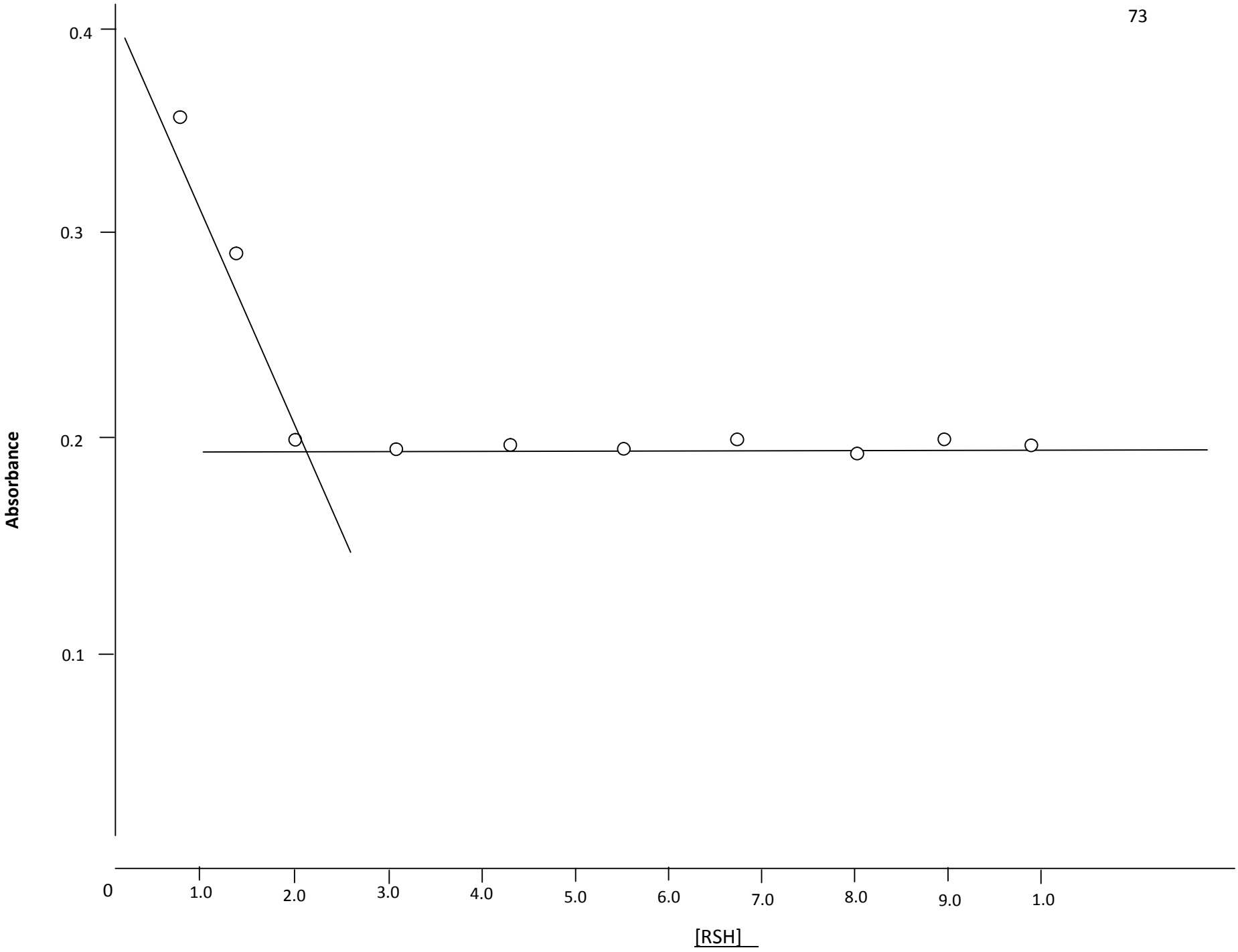

Absorbance
0.8
0.6
0.4
0.2
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
[PhSH]
[Fe2O4+]

Fig. 4.2: Stoichiometry of the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C


0.4
0.3
0.2
0.1
Absorbance
0
1.0
2.0
3.0
4.0
5.0
6.0
07.0
MSH]

$[Fe_2O^{4+}]$

Fig. 4.3: Stoichiometry of the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°


0.4
0.3
0.2
0.1
Absorbance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.0
[RSH]

$[Fe_2O^{4+}]$

Fig. 4.4: Stoichiometry of the oxidation of RSH by Fe_2O^{4+} at λ max = 411 and T =27.0±0.1°C

These stoichiometries were in accordance with what has been reported for the reaction of Fe_2O^{4+} with thiosulphate[4],reduction of di-μ-oxo-tetrakis-(1,10-phenathroline) dimanganese (III,IV) perchlorate by ascorbic acid[41]. Fe_2O^{4+} with mercaptoacetic acid[5] and mercaptoethanol[86]. The stoichiometry above shows 1:2 and 2:3 mole ratio respectively as reported for the reaction. Also the reaction of $[Fe_2(bpy)_4O]Cl_4$ with metabisulphite ions shows the stoichiometry of 1:1 (reductant/oxidant) mole ratio[2,] reaction of hypophosporus acid by poly (pyridine) iron (III) complexes showed stoichiometry of 2:1 (reductant/oxidant) mole ratio[8.]

4.2 Determination of Order of Reaction

All measurements for the order of reactions of these systems were made under pseudo -first order conditions with the concentration of thiols at least 20-fold in excess of that of the oxidant.

Pseudo - first order plots of log $(A_t - A_\infty)$ versus time following the equation (4.5)[6]

$(A_\infty - A_t) = (A_\infty - A_o)\, e\text{-}k_{obs}t$----------(4.5)

(where A_∞ and A_o are the final and initial absorbances respectively, A_t is absorbance at time t and k_{obs} is pseudo- first order rate constant) were linear to more than 80% extent of reaction. This seems to apply first order dependence of rate on $[Fe_2O^{4+}]$. Typical plots are presented as Figures (4.5 ï 4.8). Pseudo-first order rate constants k_{obs} were determined as the slopes of the plots and are presented in Tables (4.1 ï 4.4).

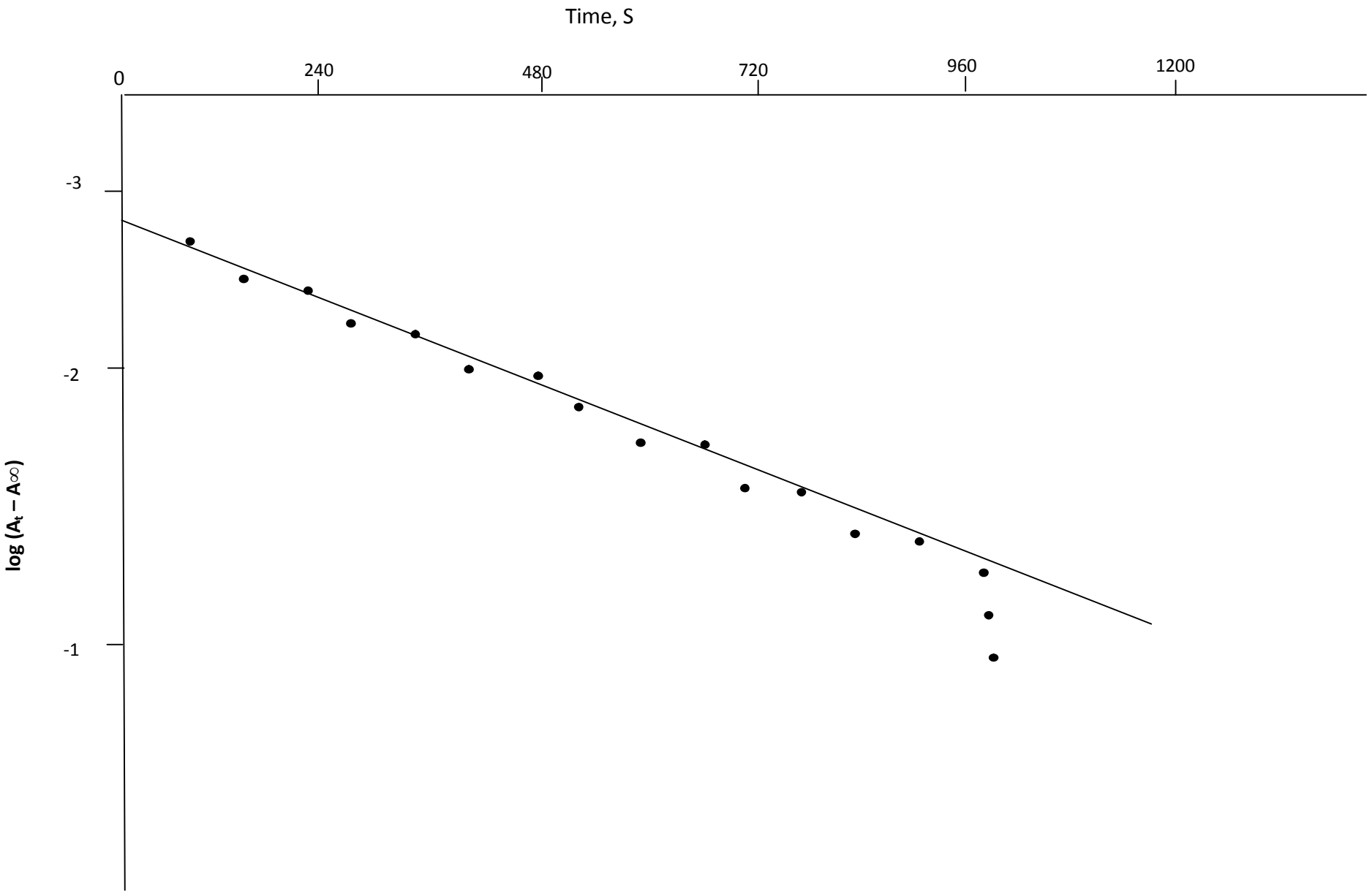


Fig. 4.5: Typical pseudo first order plot of the oxidation of MBSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

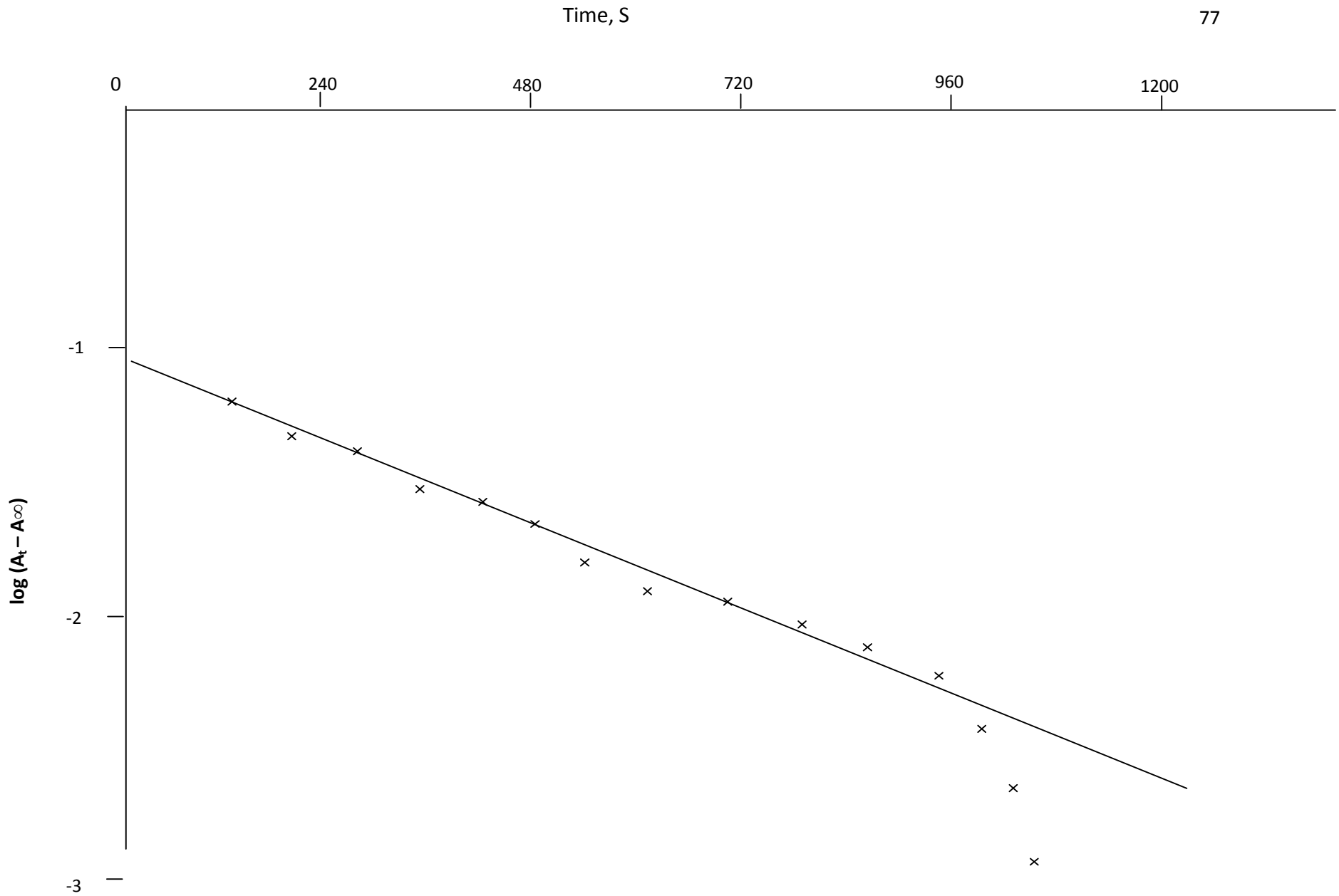


Fig. 4.6: Typical pseudo first order plot of the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

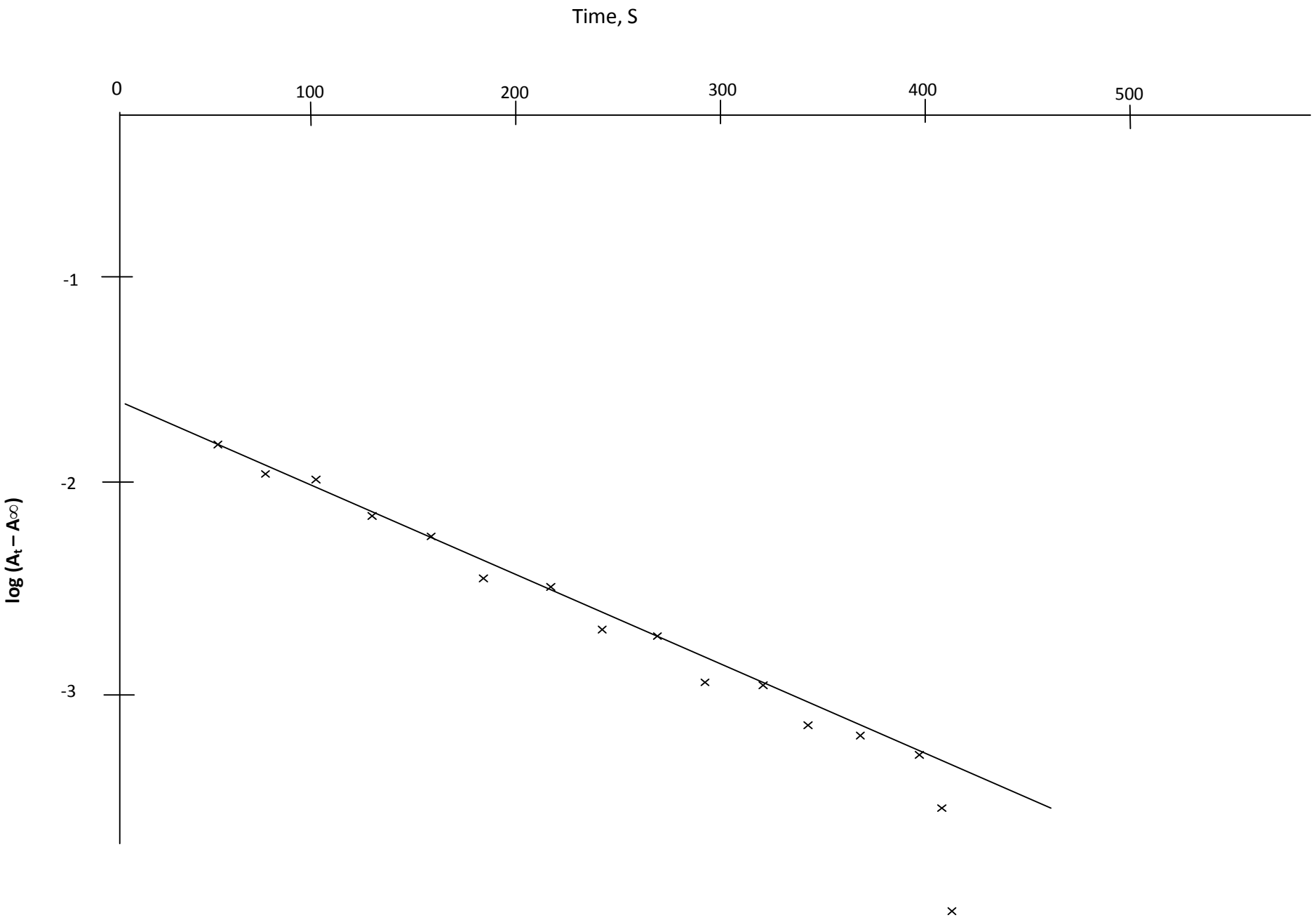

Time, S
0
100
200
300
400
500
-1
-2
-3
log (At – A∞)

Fig. 4.7: Typical pseudo first order plot of the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

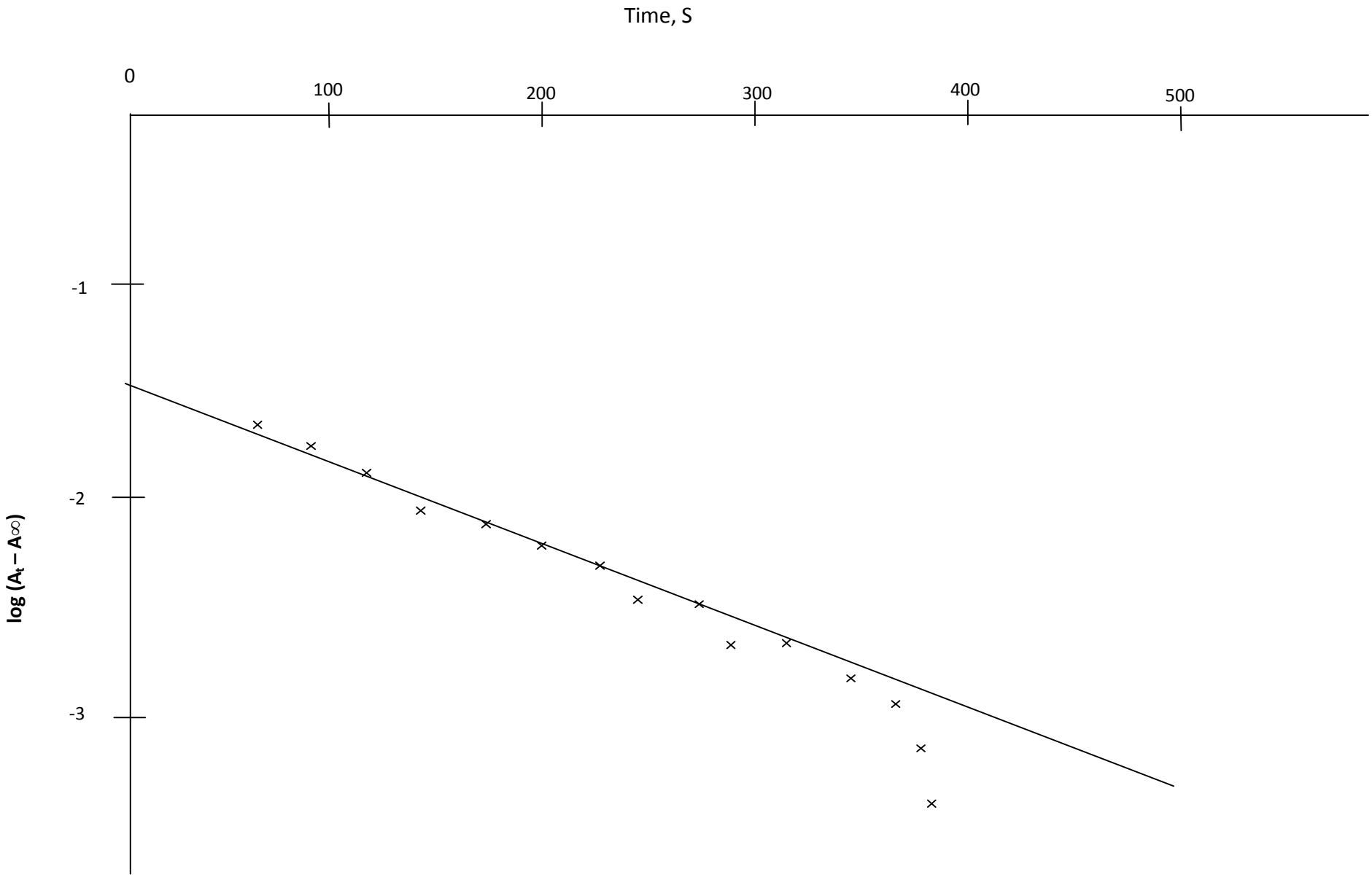


Fig. 4.8: Typical pseudo first order plot of the oxidation of RSH by Fe_2O^{4+} at λ max = 411nm and T = 27.0±0.1°C

Table 4.1: Pseudo-first order and second order rate constants for the reaction of Fe_2O^{4+} and mercaptobenzothiazole (MBSH) at Fe_2O^{4+} = 1 x10^{-4} mol dm^{-3} and λ max = 411nm

10^3[MBSH] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I, (mol dm^{-3})	10^3k_{obs} (s^{-1})	k_2, dm^3 $mol^{-1}s^{-1}$
1.0	0.0001	0.05	1.01	1.01
2.0	0.0001	0.05	1.91	0.96
3.0	0.0001	0.05	2.78	0.93
4.0	0.0001	0.05	3.80	0.95
5.0	0.0001	0.05	4.85	0.97
6.0	0.0001	0.05	5.77	0.96
1.0	0.0003	0.05	0.90	0.90
1.0	0.0005	0.05	0.86	0.86
1.0	0.001	0.05	0.72	0.72
1.0	0.0015	0.05	0.65	0.62
1.0	0.002	0.05	0.51	0.51
1.0	0.0001	0.001	0.94	0.94
1.0	0.0001	0.004	0.91	0.91
1.0	0.0001	0.006	0.96	0.96
1.0	0.0001	0.007	0.98	0.98
1.0	0.0001	0.008	0.95	0.95

Table 4.2: Pseudo-first order and second order rate constants for the reaction of Fe_2O^{4+} and mercaptophenol at Fe_2O^{4+}=1.5×10^{-4} mol dm-3, λ max = 411nm

10^3[PhSH] (mol dm^{-3})	10^{-4}[H^+] (mol dm^{-3})	I, (mol dm^{-3})	10^3k_{obs} (s^{-1})	k_2, dm^3 $mol^{-1}s^{-1}$
1.5	1.0	0.05	1.90	1.27
2.0	1.0	0.05	2.50	1.25
2.5	1.0	0.05	2.80	1.12
3.0	1.0	0.05	3.50	1.17
3.5	1.0	0.05	3.75	1.07
1.5	1.0	0.05	1.90	1.26
1.5	1.5	0.05	1.80	1.20
1.5	2.0	0.05	1.70	1.13
1.5	2.5	0.05	1.64	1.09
1.5	3.0	0.05	1.54	1.03
1.5	1.0	0.0011	1.38	0.88
1.5	1.0	0.0016	1.20	0.70
1.5	1.0	0.0021	1.26	0.84
1.5	1.0	0.0026	1.32	0.88
1.5	1.0	0.0031	1.38	0.92

Table 4.3: Pseudo-first order and second order rate constants for the reaction of Fe_2O^{4+} and Mercaptoacetic acid [MSH] =3.4×10^{-4} mol dm^{-3} λ max = 411nm.

10^3[MSH] (mol dm^{-3})	10^{-4}[H^+] (mol dm^{-3})	I, (mol dm^{-3})	10^3k_{obs} (s^{-1})	k_2, dm^3 $mol^{-1}s^{-1}$
3.4	1.0	0.05	3.29	0.97
3.9	1.0	0.05	3.84	0.98
4.4	1.0	0.05	4.76	1.10
4.9	1.0	0.05	5.11	1.04
5.4	1.0	0.05	5.56	1.03
3.4	0.3	0.05	3.88	1.14
3.4	0.8	0.05	3.56	1.04
3.4	1.3	0.05	3.00	0.78
3.4	1.8	0.05	2.25	0.66
3.4	1.0	0.001	3.07	0.90
3.4	1.0	0.0015	2.88	0.85
3.4	1.0	0.002	2.71	0.80
3.4	1.0	0.0025	2.56	0.75
3.4	1.0	0.003	2.42	0.71

Table 4:4: Pseudo-first order rate constants for the reaction of Fe_2O^{4+} and L-cysteine at Fe_2O^{4+} =2×10^{-4} mol dm^{-3} λ max = 411nm

10^3[RSH] (mol dm^{-3})	$10^{-4}H^+$] (mol dm^{-3})	I, (mol dm^{-3})	10^3k_{obs} (s^{-1})	k_2, dm^3 $mol^{-1}s^{-1}$
2.0	1.0	0.05	2.09	1.04
4.0	1.0	0.05	4.11	1.03
6.0	1.0	0.05	6.39	1.06
8.0	1.0	0.05	8.85	1.10
10.0	1.0	0.05	10.96	1.09
2.0	0.5	0.05	2.50	1.25
2.0	1.0	0.05	2.08	1.04
2.0	1.5	0.05	1.90	0.95
2.0	2.0	0.05	1.64	0.82
2.0	2.5	0.05	1.54	0.77
2.0	1.0	0.001	2.00	1.00
2.0	1.0	0.002	1.97	0.93
2.0	1.0	0.003	1.98	0.99
2.0	1.0	0.004	2.01	1.00
2.0	1.0	0.005	1.96	0.98

Plots of log k_{obs} versus log [reductant] at constant $[H^+]$ and constant ionic strength were linear with slopes of 0.98 (MBSH), 0.86 (PhSH) 0.98 (MSH), 1.2 (RSH) indicating first order dependence of the rates of reaction on [MBSH], [PhSH], [MSH] and [RSH] respectively as shown in Figures (4.10 ï 4.12). The reaction is second order overall in the four systems. Second order rate constants were determined as the ratio of k_{obs} to [reductant] and it varies from 1.01 ï 0.68 for Fe_2O^{4+}-MBSH, the values of k_2 ($dm^3\ mol^{-1}\ s^{-1}$) was 0.9 ± 0.1 (Table 4.1). It also varies from 1.27 ï 0.95 for Fe_2O^4 ï PhSH, the values of k_2 ($dm^3\ mol^{-1}\ s^{-1}$) was 1.1 ± 0.4 (Table 4.2) and fairly constant for Fe_2O^4 ï MSH and Fe_2O^4 ï RSH have the value 1.0 ± 0.1 and 1.2 ± 0.2 respectively (Table 4.43 ï 4.44)

$$-d[Fe_2O^{4+}]/dt = k_{obs}[Fe_2O^{4+}] = k_2[TSH][Fe_2O^{4+}] \quad (4.6)$$

where TSH = MBSH, PhSH, MSH and RSH.

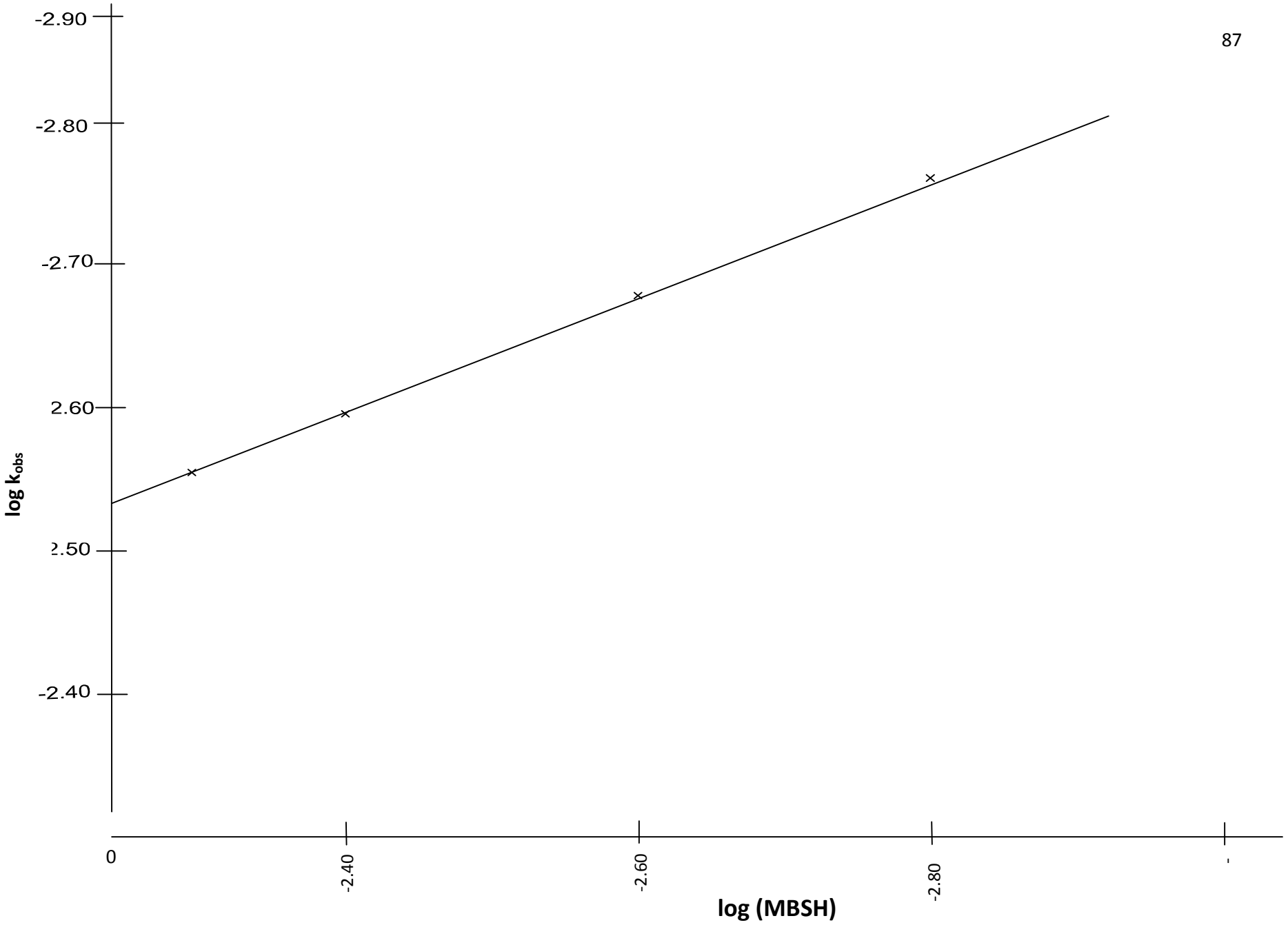


Fig. 4.9: Plot of log k_{obs} versus log [MBSH] for the oxidation of MBSH by Fe_2O^{4+} at λ max = 411nm and T=29.0± 0.1°C

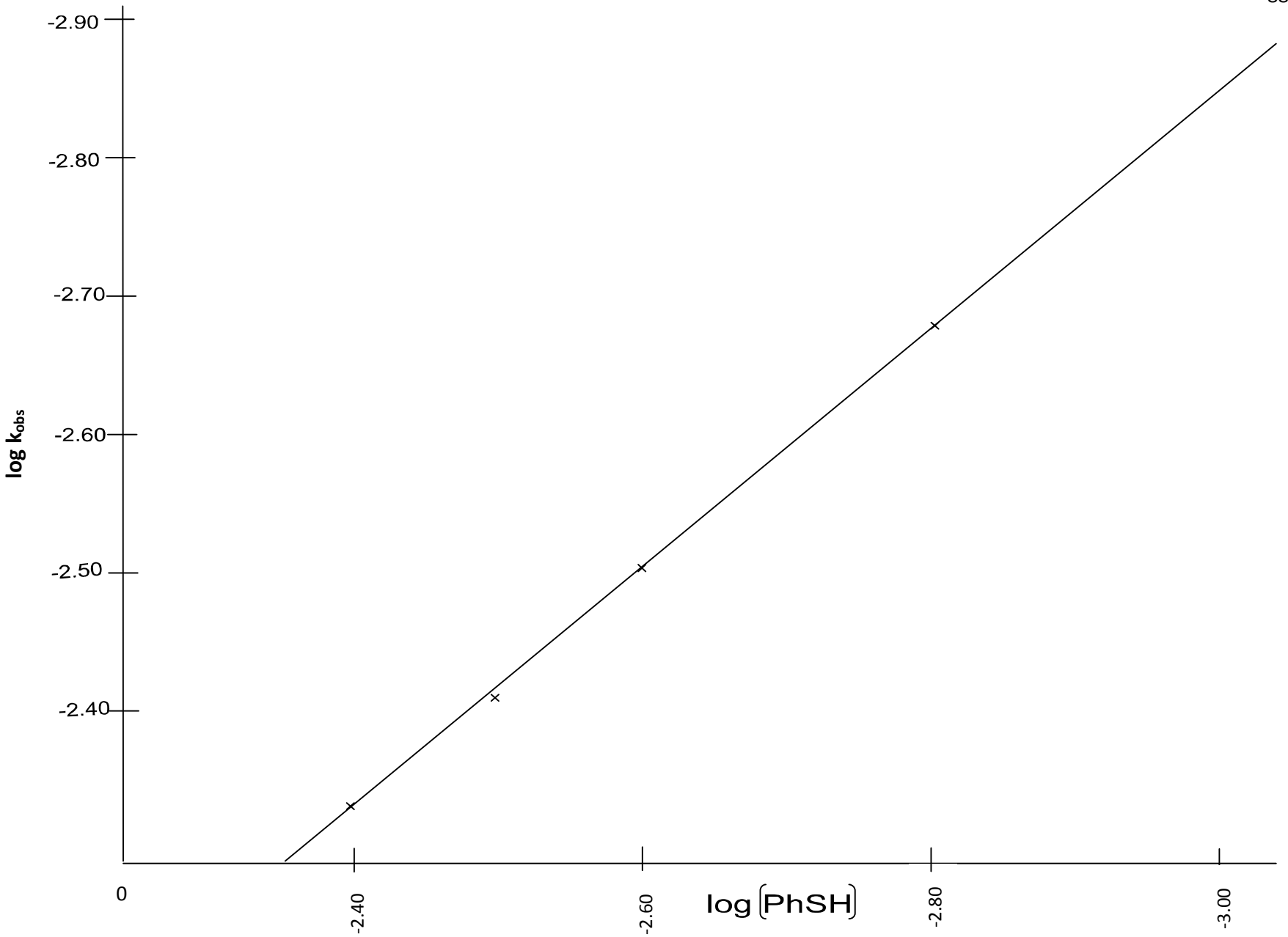


Fig. 4.10: Plot of log k_{obs} versus log[PhSH]for the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C

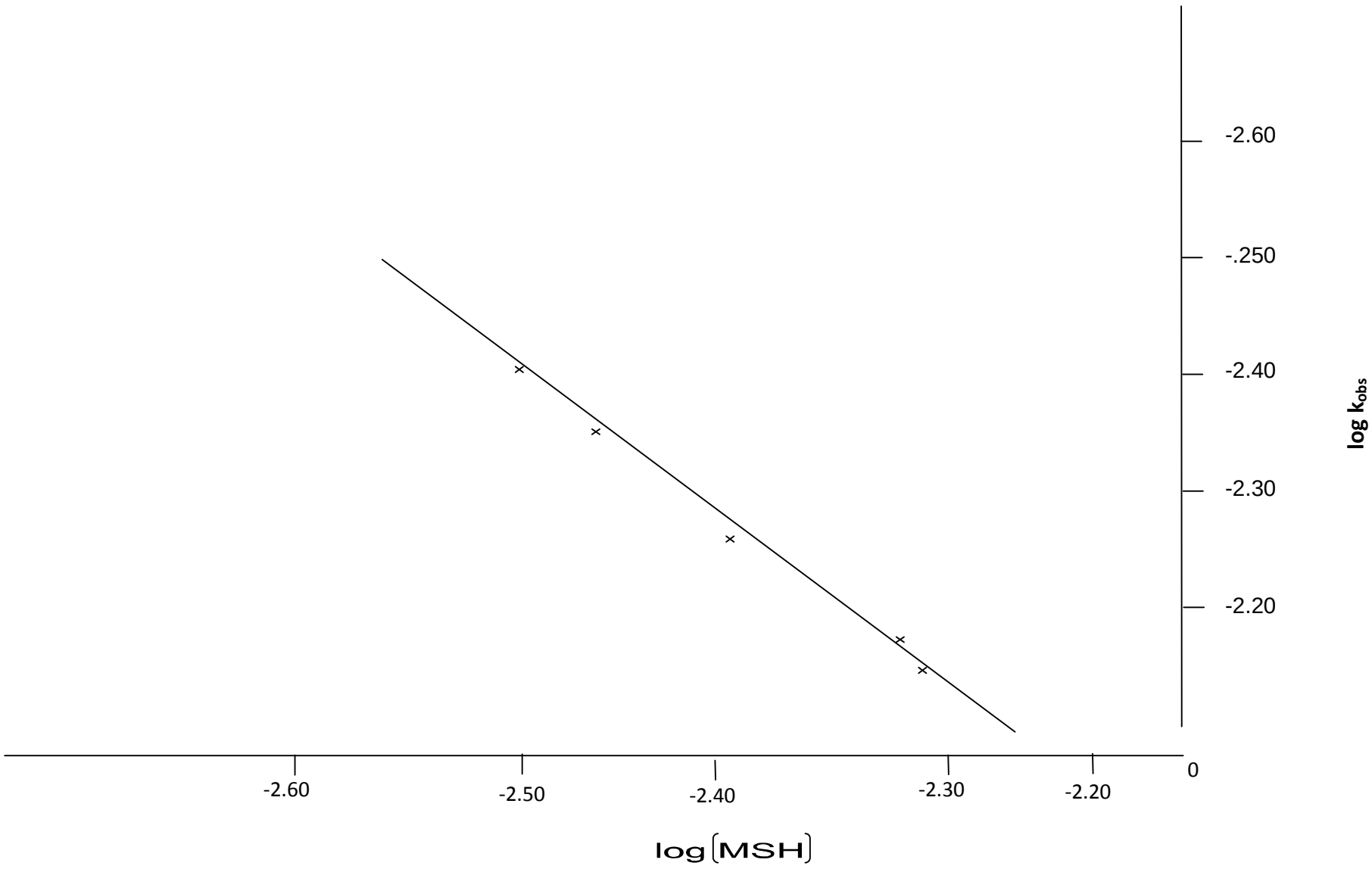


Fig. 4.11: Plot of log k_{obs} versus log [MSH] for the oxidation of MSH by **Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C**

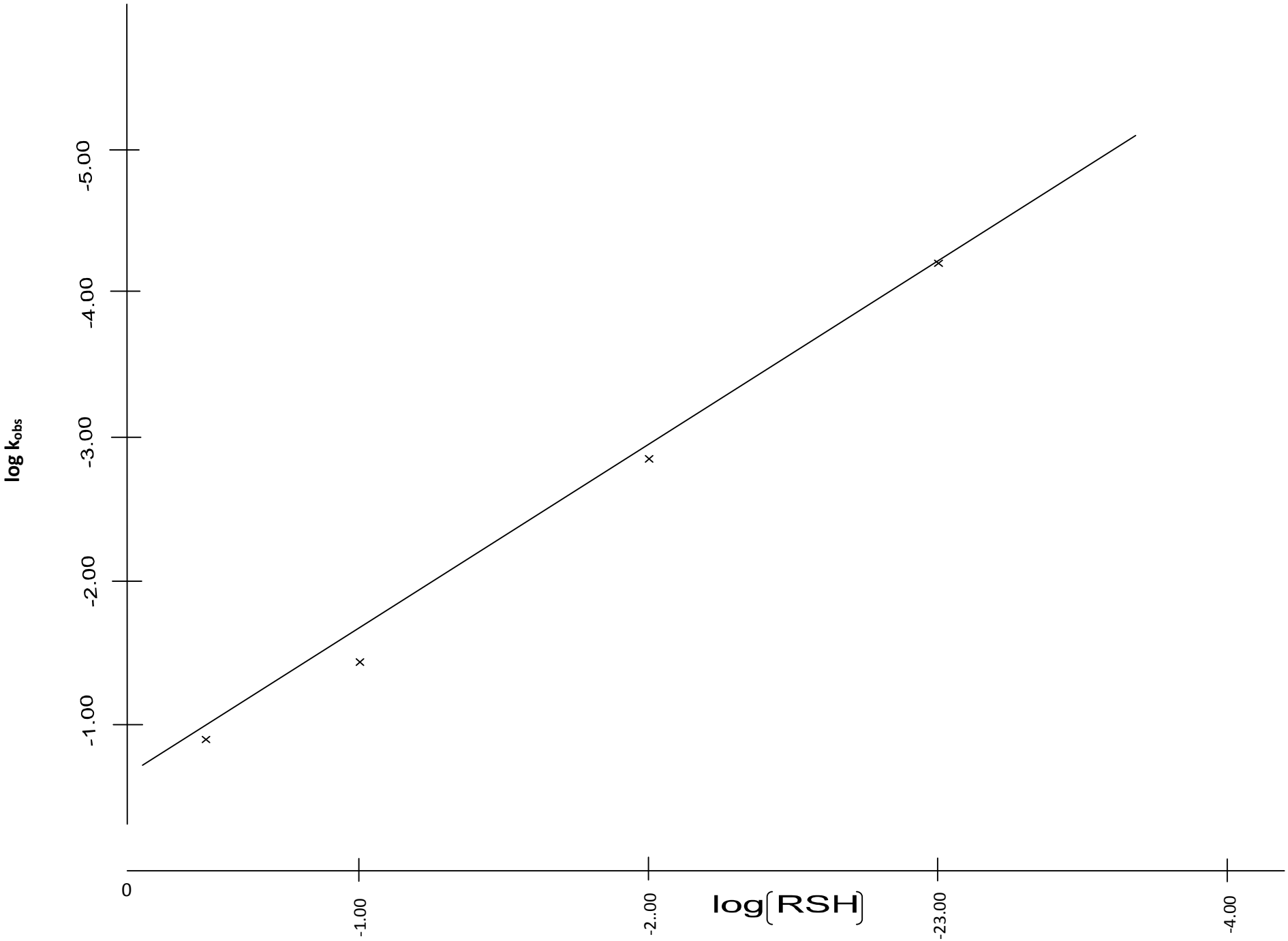

log k_{obs}
-1.00
-2.00
-3.00
-4.00
-5.00
0
-1.00
-2..00
log[RSH]
-23.00
-4.00

Fig. 4.12: Plot of log k_{obs} versus log [RSH] for the oxidation of RSH by **Fe_2O^{4+} at λ max = 411nm and T = 27.0±0.1°C**

The rate law at constant [H^+] for the reactions of the reductants mercaptobenzothiazole, mercaptophenol, mercaptoacetic acid and l-cysteine with oxo-bridged dimer Fe_2O^{4+} as represented in equation (4.6)

Similarly first-order dependence of rate of reaction on the reductant concentrations had been reported[5]. For example, oxidation of ß-mercaptoacetic acid by trioxoiodate(v) in aqueous acid medium was found to be first-order due to the plots of log($A_ß$-A_t) were linear for at least three half-lives of the reaction .This indicates first-order dependence of the rate of reaction on [RSH]. Least square fit of a plot of log k_{obs} versus log [RSH] was linear with a slope of 0.92 indicating first-order in [IO_3^-] making it second-order overall, the k_2 values is fairly constant[5]. Also in the reduction of iron(III) complex $enH_2[(FeHEDTA)_2O.6H_2O$ by thiosulphate ions in acid medium**,** a plot of pseudo-first order rate constants versus [$S_2O_3^{2-}$] was linear with a gradient of 1.02 implying also first order dependence of rate of reaction on concentration. Also the values of the second order rate constants (k_2), given by $k_2=k_{obs}/[S_2O_3^{2-}]$ were fairly constant. This indicates that the reaction is first order in [Fe_2O^{4+}] and an over all second order reaction[7]. First order dependence has been reported for reactions of thiols with Fe_2O^{4+} (oxo-bridged complex)[6.] Reactions of mercaptoethanol (GSH) and mercaptoethylamine (LSH) and Fe_2O^{4+} had been shown to occur by overall second order dependence[86.]

In a similar fashion, the reaction of catechol and $Fe_2(bipy)_4O^{4+}$ in aqueous hydrochloric acid medium plot of log (A_t ï A_∞) against time was linear of about 80% extent of reaction indicating first-order rate constants[6]. Reaction of mononuclear Fe(III) complexes with thiols have been reported to exhibit first order dependence of rate on both oxidant and reductant with disulphides and Fe(II) as products [6.]

4.3 Effect of Acid

Influence of acid on the rate of reaction was investigated in the range of [$HClO_4$] = 3.10^{-4} ï $2.0x10^{-3}$ mol dm^{-3} for mercaptobenzothiazole, 1.0 $x10^{-3}$ ï 3.0 $x10^{-3}$ mol dm^{-3}, for mercaptophenol, 3 x 10^{-3} ï $1x10^{-4}$ mol dm^{-3} for mercaptoacetic acid and 5 x 10^{-5} to 2.5 x 10^{-4} mol dm^{-3} for l-cysteine using $NaClO_4$ while concentration of oxidant and reductants were kept constant at temperature 29.0 ± 1.0^0C and λmax = 411nm. The results showed inverse dependence on the concentration of hydrogen ion as

shown in Tables (4.1ï 4.4). The plots of k_H versus $[H^+]$ were linear with intercept for the four systems shown in Figures (4.13 ï 4.16) following equation (4.7).

$k_2 = a + b\,[H^+]^{-1}$ ----------(4.7)

The overall rate equation for oxo-bridged dimer Fe_2O^{4+} - reductant systems can be represented by the equation (4.8).

$$-\frac{d[Fe_2O^{4+}]}{dt} = (a + b[H^+]^{-1})\,[Fe_2O^{4+}]\,[\text{reductant}]$$ ----------(4.8)

For the Fe_2O^{4+} - mercaptobenzothiazole system, a = 1.47 $dm^3\,mol^{-1}s^{-1}$ and b = 2.9 x 10^1 $dm^6\,mol^{-2}\ s^{-1}$ at I = 0.05 mol dm^{-3} ($NaClO_4$), and T = 29.0 $\pm$ 0.1^0C.

For the Fe_2O^{4+} - mercaptophenol system, a = 1.9x10^{-2} $dm^3\ mol^{-1}s^{-1}$and b = 4.9x10^1 $dm^6\ mol^{-2}s^{-1}$at T = 29.0 $\pm$ 0.1^0C.

For the Fe_2O^{4+} - mercaptoacetic acid system, a = 1.5x 10^1 $dm^3\,mol^{-1}\ s^{-1}$ and b = 1.7 x10^2 $dm^6\,mol^{-2}\ s^{-1}$ as shown in Figures (4.13 ï 4.15).

For the Fe_2O^{4+} - L-cysteine system, a=2.80 $dm^3\,mol^{-1}$ s-1 and b = 2.35 $dm^6\,mol^{-2}\,s^{-1}$, Figures (4.16)

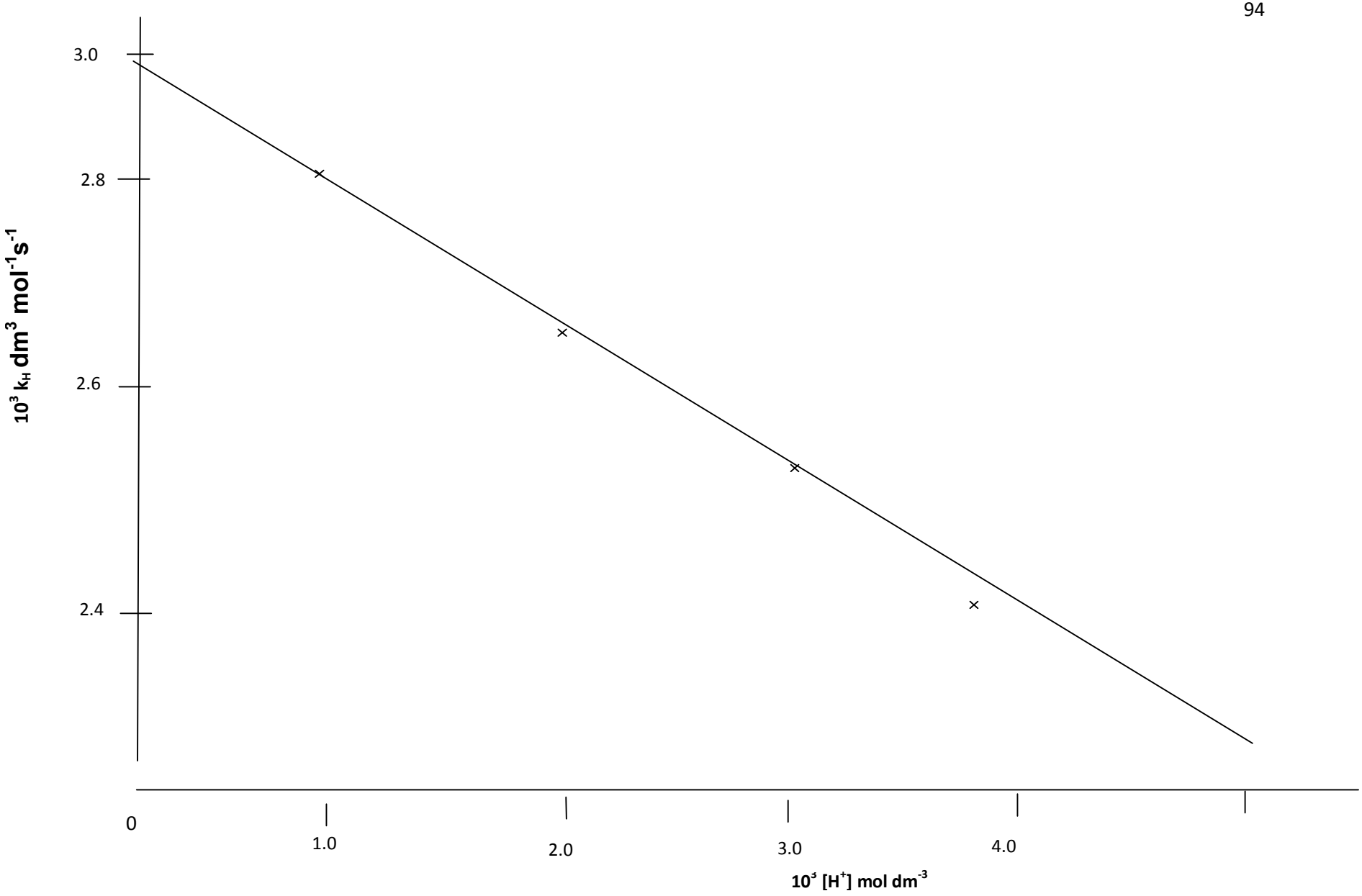
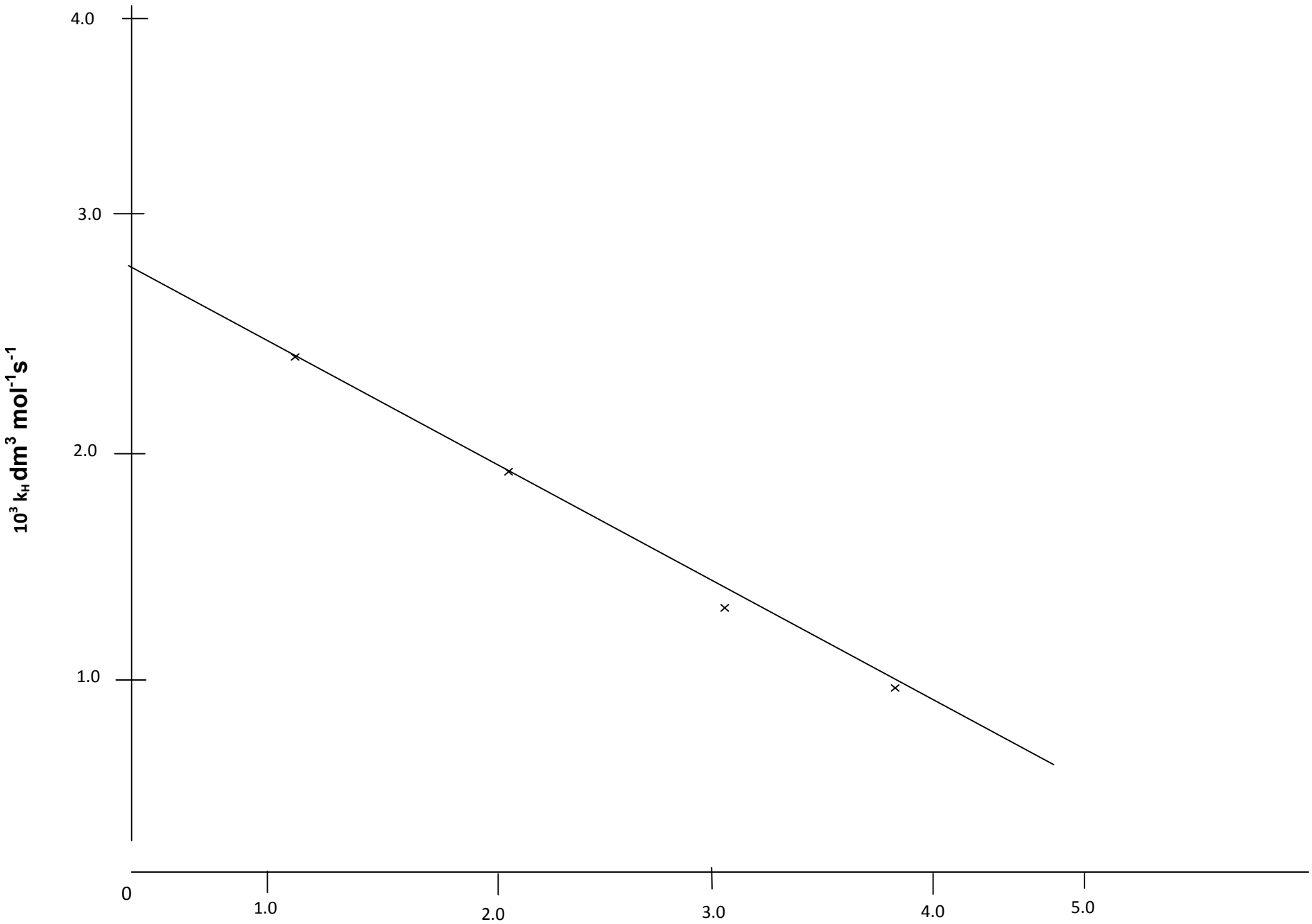


Fig. 4.13: Plot of k_H versus $[H^+]$ of the oxidation of MBSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C


4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
$10^3 k_H dm^3 mol^{-1} s^{-1}$

10^3 [H^+] mol dm^{-3}

Fig. 4.14: Plot of k_H versus [H^+] of the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm and T = 27.0±0.1°C

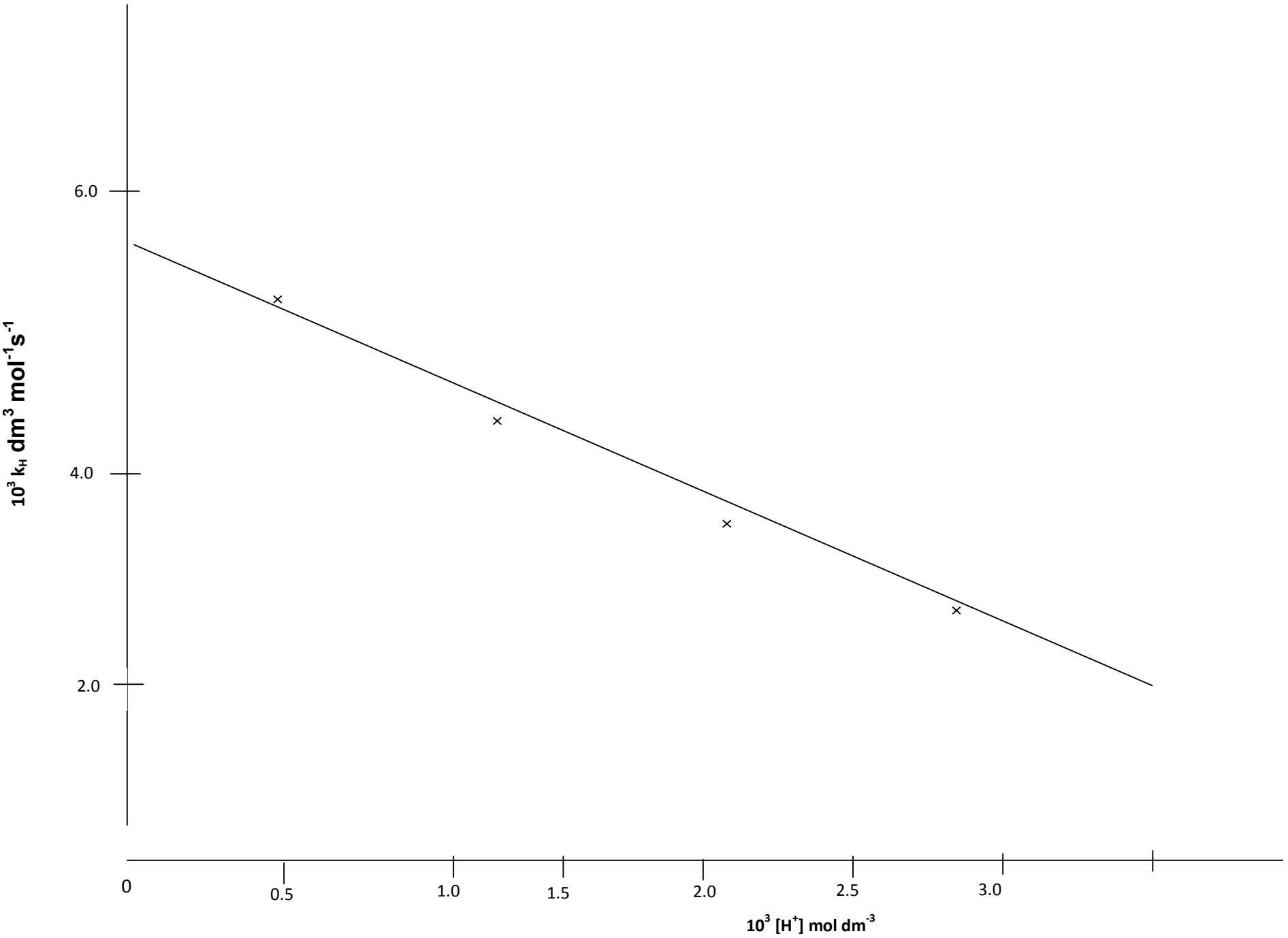

6.0
4.0
2.0
$10^3 k_H$ dm^3 mol^{-1}s^{-1}
0
0.5
1.0
1.5
2.0
2.5
3.0
10^3 [H$^+$] mol dm^{-3}

Fig. 4.15: Plot of k_H versus $[H^+]$ of the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C

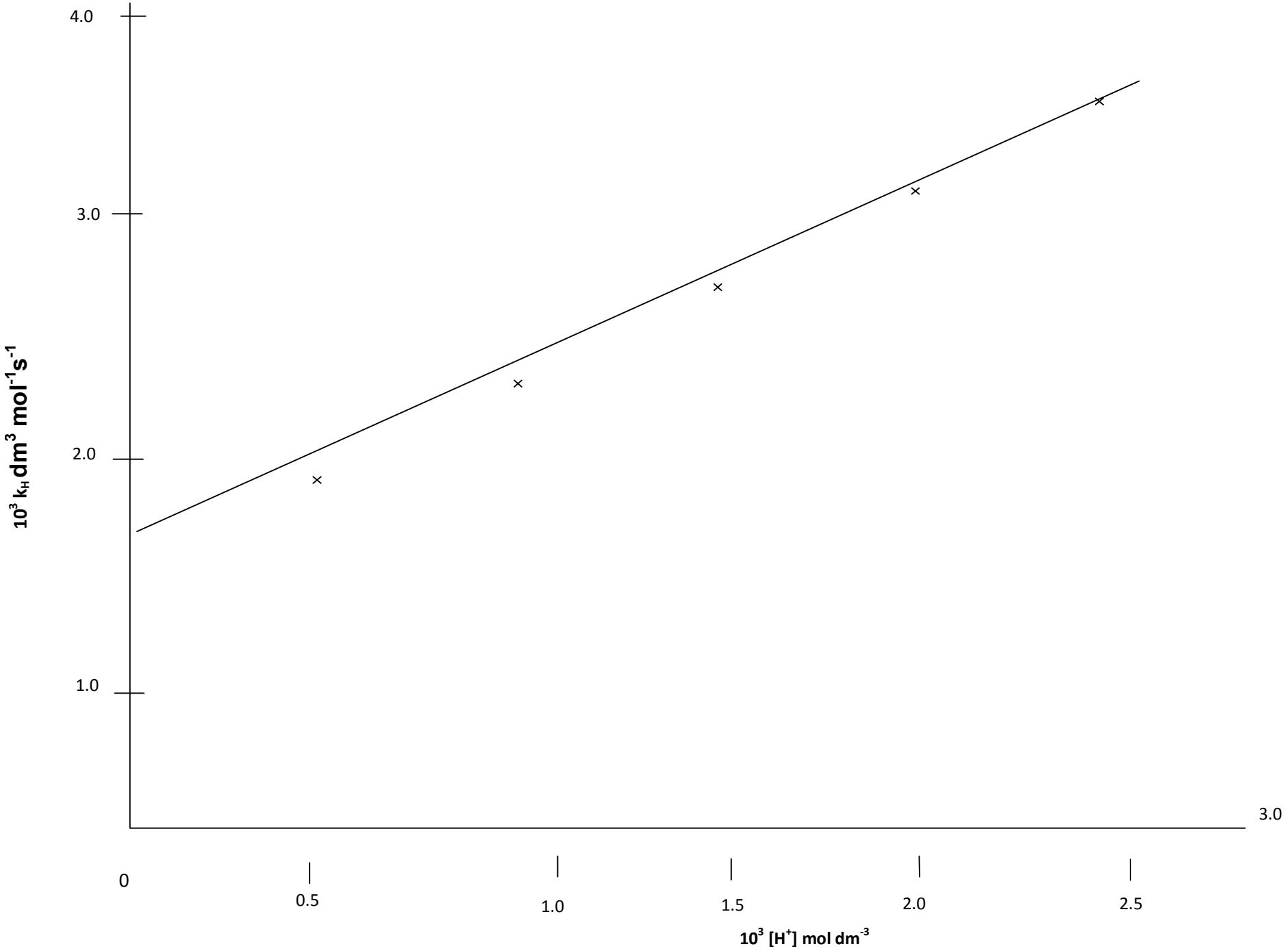

4.0
3.0
2.0
1.0
$10^3 k_H dm^3 mol^{-1}s^{-1}$
3.0
0
0.5
1.0
1.5
2.0
2.5
10^3 [H^+] mol dm^{-3}

Fig. 4.16: Plot of k_H versus $[H^+]$ of the oxidation of RSH by Fe_2O^{4+} at λ max = 411nm and T =27.0±0.1|

Inverse acid dependence is a common feature of reactions of thiols with metal ion[92,93] . It has been specifically reported that reduction of Fe_2O^{4+} by mercaptoacetic acid, reduction of Ru_2O^{4+} by LSH showed inverse acid dependence[5]. Decrease in rate of reaction with increase in $[H^+]$ had been explained in terms of the deprotonation of the sulphyhydryl (-SH) groups in the thiols prior to electron transfer[3]. This is structural requirement for electron transfer as the reductant must first ionize before electron transfer takes place. The inverse acid dependence also suggests the relative unimportance of the process.

$$[Fe - O ï Fe]^{4+} + H^+ \rightleftharpoons Fe_2OH^{5+} \text{ ----------(4.9)}$$

The instability of the Fe ï O ï Fe bridge in acid solution has been reported[9,3,69.] Protonation of the oxo-bridged oxygen leads to cleavage and formation of mononuclear species, contribution from this process is supposed to result in direct acid dependence. The inverse acid dependence observed for these reactions shows that contribution from the process is very minimal.

In this study, it was discovered that at greater than $1x10^{-4}$ $[H^+]$ mol dm^{-3}, Fe_2O^{4+} was unstable and cleavage of the oxo-bridge resulted with the colour of the complex changing from red to colourless.

4.4 Effect of Ionic Strength

Changes in the ionic strength of the reaction medium had a negative effect on the rate of reaction of Fe_2O^{4+} ï mercaptobenzothiazole, mercaptoacetic acid, l-cysteine and constant for mercaptophenol.

Ionic strength was varied between $1.3x10^{-3}$ ï $1.7x10^{-3}$ mol dm^{-3} for Fe_2O^{4+} - merceptobenzothiazole, $1.1x10^{-3}$ ï $3.1x10^{-3}$ mol dm^{-3} for Fe_2O^{4+} - mercaptophenol, $1.0x10^{-3}$ ï $3.0x10^{-3}$ mol dm^{-3} for Fe_2O^{4+} - mercaptoacetic acid and $1.0x10^{-3}$ ï $5.0x10^{-3}$ mol dm^{-3} for Fe_2O^{4+} - L-cysteine, all using $NaClO_4$. The reaction was monitored at T = 28^0C, $[H^+] = 1x10^{-4}$ mol dm^{-3}, [oxidant] and [reductant] was constant. The

rate of reaction decreased as the ionic strength increase for the three systems except PhSH. The results are presented in Tables (4.1 ï 4.4).

For reactions of ions in aqueous media the rate of reaction is directly dependent on the square root of the ionic strength of the media according to equation (4.10) [94].

$\log k_2 = \log k_1 + 2ƀ Z_A Z_B I^{½}$ ----------(4.10)

k_2 = rate constant for the reaction

k_1 = hypothetical rate constant in a medium of infinite dielectric constant.

Z_AZ_B = change on reactants A and B respectively

I = ionic strength of the media

ƀ = 0.5 at 25^{o}C

If ionic strength is varied, the various values of k_2 obtained could be plotted as log k_2 against $\sqrt{1}$, and a straight line is obtained with intercept of log k_1 and slope of Z_AZ_B (product of charges at the rate determining step)[19]. Also a plot of log $\left(\frac{k_2}{k_1}\right)$versus $\sqrt{1}$ gives a straight line which passes through the origin and also with a slope of Z_AZ_B. For reactions where the rate of reaction increases with increase in ionic strength (positive salt effect) or where rate of reaction decreases with increase in ionic strength (negative salt effect) the equation adequately accounts for such phenomenon. Plots that give negative slope show that at the rate determining step anion-cation interaction is the most likely. On the other hand, where a positive slope is obtained, cation-cation or anion-anion interaction subsists. The magnitude of the slopes gives an idea of the product of the charges[95]. Positive salt effect is anion-anion or cation-cation interaction whereas negative salt effect is the result of anion-anion interaction. Non-dependence of rate of reaction on ionic strength will likely be due to no charge on one of the reactants or on both reactants.

Variation of ionic strength between oxo-bridged dimer (Fe_2O^{4+} and thiols using $NaClO_4$, result in decrease in rate as ionic strength increased as shown in Table 4.1 ï 4.4. This is suggestive of interaction between cation and anion[91,96,97].

4.5 Effect of Dielectric Constant

Influence of dielectric constant D on rate of reactions between oxo-bridged dimer Fe_2O^{4+} and mercaptobenzothiazole, mercaptophenol, mercaptoacetic acid and l-cysteine respectively was investigated at constant concentrations of oxidant and reductant. While the temperature, acidity and ionic strength of the medium were kept constant, the dielectric constant of the medium was varied using appropriate solvents.

Reduction of Fe_2O^{4+} by mercaptobenzothiazole using dimethylformamide(DMF)- and water at $[H^+]$ = 1.10^{-4} mol dm^{-3}, I= 0.05 mol dm^{-3} ($NaClO_4$) and T = 29.0 $\pm$ 0.1^0C showed a decrease in rate as dielectric constant increased (Table 4.5).

Reaction of Fe_2O^{4+} by mercaptophenol using acetone and water at $[H^+]$ = $1x10^{-4}$ mol dm^{-3}, I= 0.05 mol dm^{-3} ($NaClO_4$) and T = 29.0 $\pm$ 0.1^0C showed decrease in rate as dielectric constant increased (Table 4.6).

Reduction of Fe_2O^{4+} by mercaptoacetic acid using acetone and water at the concentration of hydrogen ion at $1x10^{-4}$ mol dm^{-3} at ionic strength of 0.05 mol dm^{-3} using $NaClO_4$ and Temperature of 29.0 $\pm$ 0.1^0C. The result showed decrease in rate as dielectric constant increased (Table 4.7).

The reaction of Fe_2O^{4+} by L-cysteine at ionic strength of 0.05 mol dm^{-3} ($NaClO_4$), $[H^+]$ = 1x10^{-4} mol dm^{-3} and T = 28.0 $\pm$ 0.1^{0}C showed a decrease in rate as dielectric constant increased using acetone and water as shown in Table (4.8).

Table 4.5: Dependence of rate constant on anions, cation and dielectric constant for the reaction of Fe_2O^{4+} and MBSH at $[Fe_2O^{4+}]$ = 1x10^{-4} mol dm^{-3} [MBSH] = 1x 10^{-3} -6×10^{-3} mol dm^3, $[H^+]$ = 1x10^{-4} mol dm^{-3}, I($NaClO_4$) = 0.05 mol dm^{-3}, ə-max = 411nm.

X	10^3[X]	10^3 k_{obs}	k_2 dm^{-3}
CH_3COO^-	mol dm^{-3}	s^{-1}	$mol^{-1}s^{-1}$
	1.3	0.98	0.98
	1.4	0.97	0.97
	1.5	0.96	0.96
	1.6	0.94	0.94
	1.7	0.90	0.90
NO_3^-	1.2	0.99	0.99
	1.4	0.97	0.97
	1.6	0.95	0.95
	1.8	0.87	0.87
Mg^{2+}	1.0	0.87	0.87
	1.5	0.96	0.96
	2.0	0.95	0.95
	2.6	0.97	0.97
	3.0	0.96	0.96
D			
63		0.97	0.97
70		0.89	0.89
71		0.84	0.84
78		0.82	0.82
82		0.78	0.78

Table 4.6: Dependence of rate constant on anions, cation and dielectric constant for the reaction of Fe_2O^{4+} and PhSH at $[Fe_2O^{4+}] = 1.5x10^{-4}$ mol dm^{-3}, [PhSH] = 1.5 x 10^{-3} - 3.5×10^{-3} mol dm^{-3}, $[H^+] = 1x10^{-4}$ mol dm^{-3} ,I ($NaClO_4$) =0,05 mol dm-^{3}, λ max = 411nm .

X	10^3[X]	10^3 k_{obs}	k_2 dm^{-3}
CH_3COO^-	mol dm^{-3}	s^{-1}	$mol^{-1}s^{-1}$
	1.3	0.98	0.65
	1.4	0.97	0.64
	1.5	0.98	0.65
	1.6	0.96	0.64
	1.7	0.97	0.64
Cl^-	1.1	0.99	0.66
	2.1	0.97	0.64
	3.1	0.98	0.65
	4.1	0.99	0.66
	5.1	0.98	0.65
Mg^{2+}	0.5	0.87	0.44
	1.0	0.88	0.58
	1.5	0.89	0.59
	2.0	0.86	0.57
	2.5	0.88	0.58
D			
58		1.89	1.26
65		1.60	1.07
66		1.40	0.93
68		1.23	0.82
73		1.09	0.73

Table 4.7: Dependence of rate constant on anions, cation and dielectric constant for the reaction of Fe_2O^{4+} and MSH at $[Fe_2O^{4+}] = 3.4x10^{-4}$ mol dm^{-3}, [MSH] = 3.4 $x10^{-3}$ - 5.4×10^{-3} mol dm^{-3}, $[H^+] = 1x10^{-4}$ mol dm^{-3}, I ($NaClO_4$) = 0.05 mol dm^{-3}, λ max = 411nm.

X	10^3[X]	10^3k_{obs}	k_2 dm^{-3}
Cl^-	mol dm^{-3}	s^{-1}	$mol^{-1}s^{-1}$
	1.0	3.07	0.90
	1.5	2.71	0.79
	2.0	2.42	0.71
	2.5	2.19	0.64
	3.0	2.00	0.59
NO_3^-	2.0	2.95	0.87
	2.5	2.62	0.77
	3.0	2.35	0.69
	3.5	2.13	0.63
	4.0	1.95	0.57
K^+	0.20	32.0	0.94
	0.25	28.0	0.82
	0.30	25.0	0.74
	0.35	22.6	0.66
	0.40	20.5	0.60
D			
69		3.03	0.89
70		2.68	0.79
71		2.40	0.71
72		2.17	0.64
73		1.98	0.58

Table 4.8: Dependence of rate constant on anions, cation and dielectric constant the reaction of Fe_2O^{4+} and L-cysteine (RSH) at $[Fe_2O^{4+}] = 2x10^{-4}$ mol dm^{-3}, [RSH] = 2.0 x 10^{-3} -1×10^{-2} mol dm^{-3}, $[H^+] = 1x10^{-4}$ mol dm^{-3}, I, ($NaClO_4$)= 0.05 mol dm^{-3}, λ max = 411nm.

X	10^3[X]	10^3 k_{obs}	k_2 dm^{-3}
SO_4^{2-}	mol dm^{-3}	s^{-1}	$mol^{-1}s^{-1}$
	1.0	2.03	1.01
	1.2	1.97	0.99
	1.4	1.92	0.96
	1.6	1.98	0.99
	1.8	1.89	0.95
NO_3^-	2.0	1.97	0.99
	2.5	1.84	0.92
	3.0	1.98	0.99
	3.5	1.86	0.93
	4.0	1.98	0.99
K^+	1.0	1.92	0.96
	2.0	1.87	0.94
	3.0	1.98	0.99
	4.0	1.96	0.98
	5.0	2.01	1.00
D			
58		1.87	0.94
65		1.93	0.97
66		2.08	1.04
68		1.98	0.99
73		1.98	0.99

Variation of D using dimethylformadide ï water mixture for mercaptobenzothiazole, acetone ï water mixture for mercaptophenol, mercaptoacetic acid and l-cysteine showed drecreas in rate (Table (4.5) ï (4.8). This indicates that the reaction occurred between cation or anion or free radcial. It also implies that the rate determining step is likely to involve Fe_2O^{4+} and MBSH or MBS^{o} rather than MBS^{-} for mercaptobenzothiazole, Fe_2O^{4+} and PhSH or PhS^{o} rather than PhS^{-} for mercaptophenol, Fe_2O^{4+} and MSH or MS^{o} rather than MS^{-} for mercaptoacetic acid and Fe_2O^{4+} and RSH or RS^{o} rather than RS^{-} for l-cysteine. These are consistent with a reaction involving ion-pairs with outer-sphere character.

Also non- effect on rate observed on varying dielectric constant is consistent with formation of ion-pair to electron transfer processes[98]. The reaction of thiols (mercaptobenzothiazole, mercaptophenol, mercaptoacetic acid and l-cysteine) with Fe_2O^{4+} have involved formation of ion-pair hence the reaction is likely to follow outer-sphere mechanism.

The type of acid dependence in these thiols with the complex is very much associated with a deprotonation step that occurs in most redox reactions of complex as a structural requirement of electron transfer for the reductants.

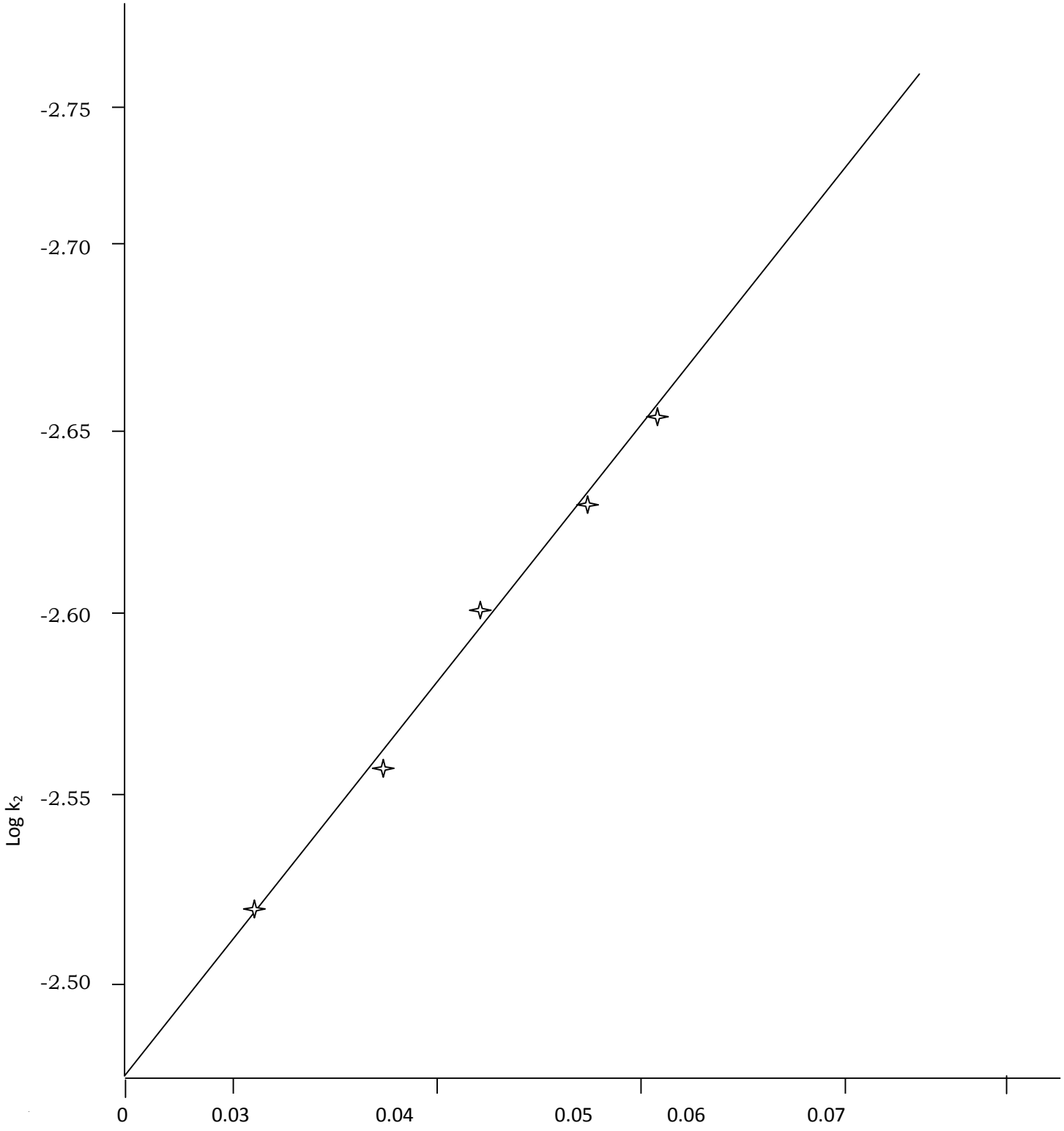


Fig 4.17: Plot of log k_2 versus $\sqrt{1}$ for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =29.0±0.1°C

4.6 Effect of Added Cations and Anions

The effect of added cations and anions was investigated at constant [oxidant] and [reductant], constant $[H^+]$ and ionic strength ($NaClO_4$). The rate of reaction was studied by varying the concentrations of X, where X can be magnesium ion (Mg^{2+}), potassium ion (K^+), acetate ion (CH_3COO^-) tetraoxosulphate (vi) ion (SO_4^{2-}), trioxonitrate(v) ion (NO_3^-) and chloride ion (Cl^-).

For the reduction of Fe_2O^{4+} by mercaptobenzothiazole concentration were varied from 1.3 x 10^{-3} ï 1.7x10^{-3} mol dm^{-3} for acetate ion, 1.0x10^{-3} - 1.8 x10^{-3} mol dm^{-3} for trioxonitrate (v) ion and 1.0×10^{-3} - 3.0×10^{-3} mol dm^{-3} for magnesium ion. The rate constant showed no catalysis of either CH_3COO^-, NO_3^- and Mg^{2+} ions.

For Fe_2O^{4+} - mercaptophenol the concentration were varied from 1.0 x10^{-3} ï 5.0x10^{-3} mol dm^{-3} for acetate ion, 1.1x10^{-3} ï 5.1x10^{-3} mol dm^{-3} for chloride ion and 5.0x10^{-4} ï 2.5 x10^{-3} mol dm^{-3} for magnesium ion. The rate constant showed no catalysis of the CH_3COO^-, Cl^- and Mg^{2+}.

For the reduction of Fe_2O^{4+} by l-cysteine concentration were varied from 1.0x10^{-3} ï 1.8x10^{-3} mol dm^{-3} for tetraoxosulphate(vi) ion, 2.0 x 10^{-3} ï 4.0x10^{-3} mol dm^{-3} for trioxonitrate (v) ion, and potassium ion,1.0×10^{-3} -5.0×10^{-3} mol dm^{-3}.

There was no change in catalysis of tetraoxosulphate (vi) ion or trioxonitrate (v) ion. The results are presented in Table (4,5,4.6,4.8).

Lack of catalysis of Fe_2O^{4+} - MBSH, PhSH and RSH was associated with reactions operating by the inner-sphere electron transfer route.

The effect of catalysis of Fe_2O^{4+} - mercaptoacetic acid was studied from the range of 1.0 $x10^{-3}$ ï 3.0 x 10^{-3} mol dm^{-3} for chloride ion, $2.0x10^{-3}$ ï $1.5x10^{-3}$ for trioxonitrate (v) ion, and $2.0x10^{-3}$ ï $4.0x10^{-3}$ for potassium ion. It was observed that there was decrease in catalysis of anions and cations (Table 4.7).

Decrease of catalysis as observed in the above reaction explained in terms of ion-pair complexes with outer-sphere character. The same observation had been made for the reaction of 2-mercaptoacetic acid and Fe_2O^{4+} [5] and reaction of Fe_2O^{4+} by thiosulphate ions in acid solution.[4]

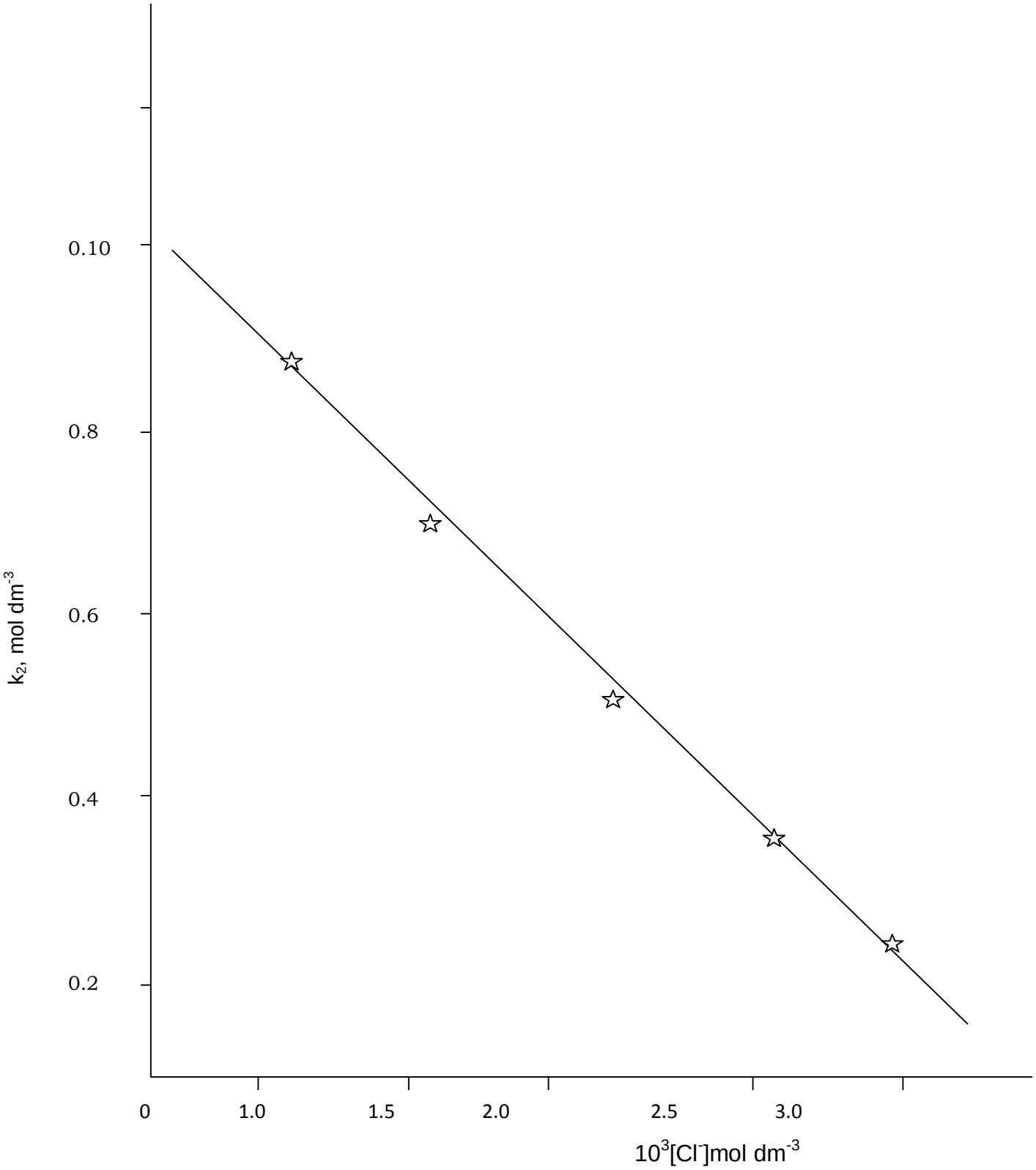


Fig 4.18: Dependence of k_2 on $[Cl^-]$ for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =28.0±0.1°C

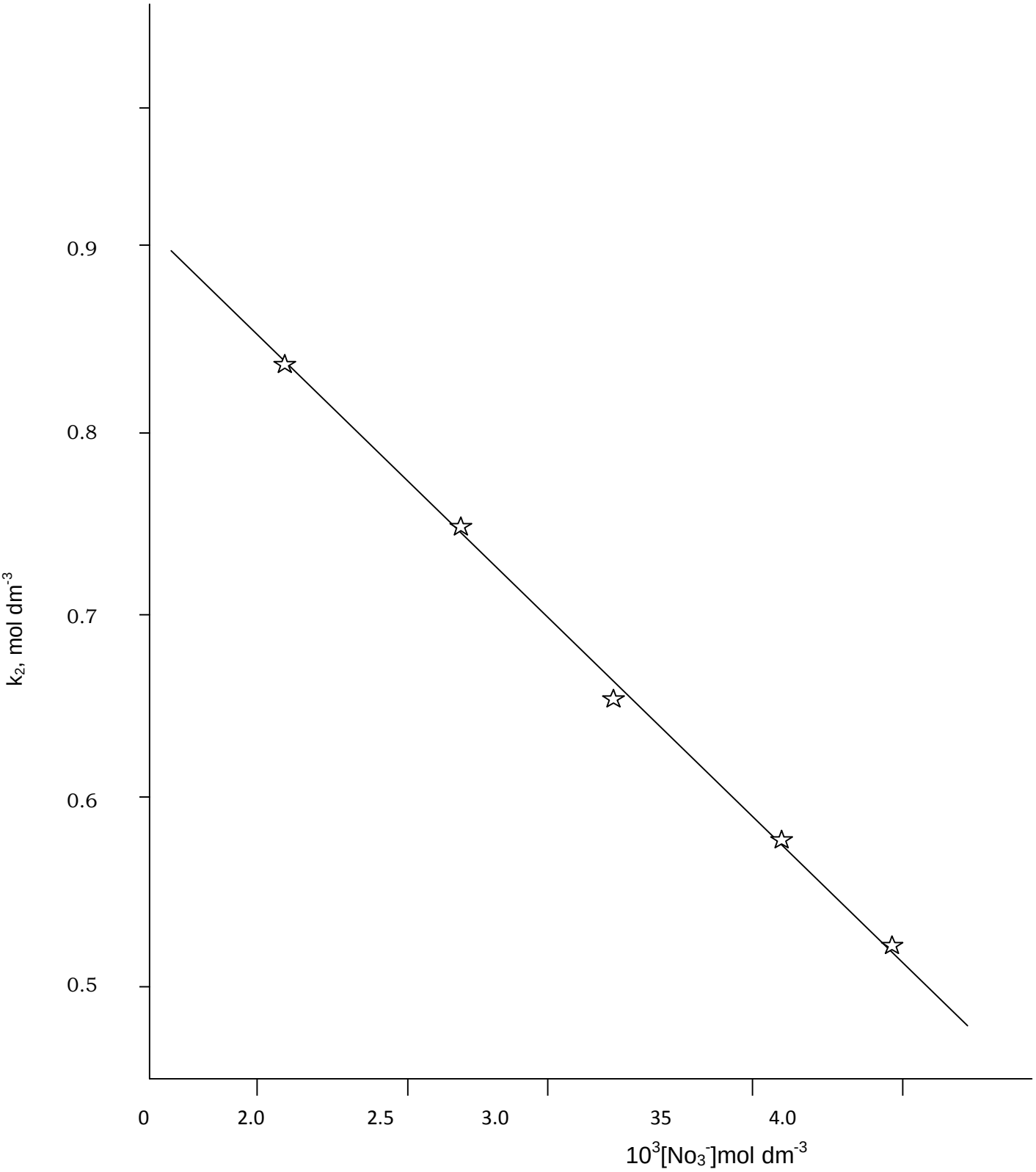


Fig 4.19: Dependence of k_2 on $[No_3^-]$ for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =28.0±0.1^oC

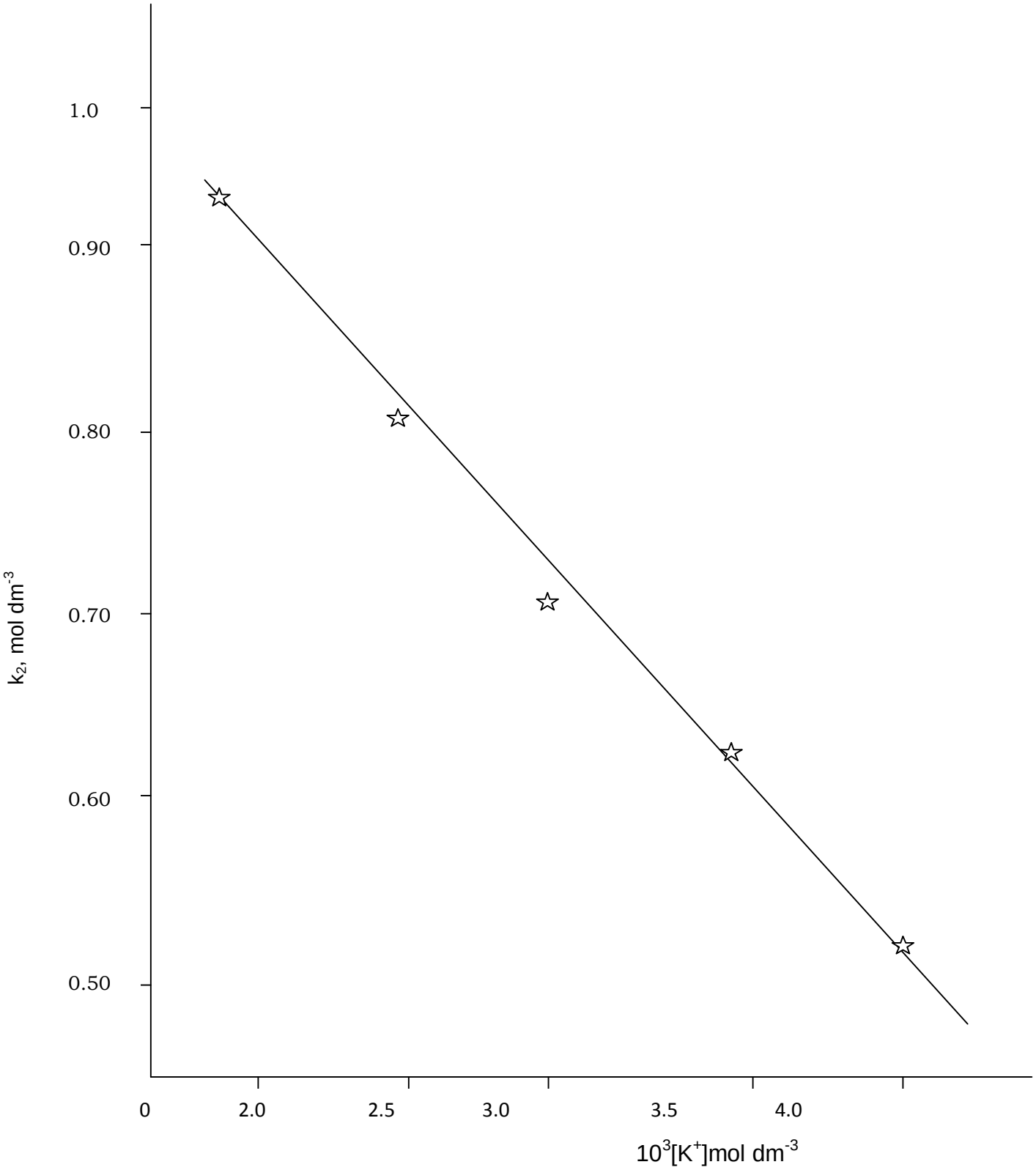


Fig 4.20: Dependence of k_2 on $[K^+]$ for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T =28.0±0.1^oC

4.7 Temperature Dependence

The effect of temperature on the rate of reduction of Fe_2O^{4+} by merceptobenzothiazole, mercaptophenol, merceptoacetic acid and l-cysteine were determined at 30°C,35°C,40°C, 45°C and 50°C.

From Arhenius equation and thermodynamics[99]

$$\log \frac{k_{obs}}{T} = \frac{\log k}{h} + \frac{\Delta S^{\#}}{2.303R} - \frac{\Delta H^{\#}}{2.303RT} \quad \text{----------(4.11)}$$

Where k_{obs} = Temperature dependence rate constant

k = Boltzmann's constant

h = Planks constant

$\Delta S^{\#}$ = Entropy of activation

$\Delta H^{\#}$ = Enthalpy of activation

R = Universal gas constant

T = Temperature

From the plots of log k_{obs}/T versus 1/T, the activation parameter were determined from the slopes and intercepts as in Table (4.9 – 4.13). The plots are as shown in Figures 4.17 – 4.20

TABLE 4.9: Temperature dependence of rate constants for the reaction of Fe_2O^{4+} - Mercaptobenothiazole at Fe_2O^{4+} =1x10^{-4} mol dm^{-3}, [MBSH] = 1 x 10^{-3} -6 ×10^{-3} mol dm^{-3} ,(H^+) = 1 x 10^{-4} mol dm^{-3} I = 0.05 mol dm^{-3} ($NaClO_4$) ə-max = 411nm.

Temp ^{O}C	Temp (k)	$10^3 k_{obs}$ (s^{-1})	log (k_{obs}) $_k$, $^{S-1}$ T	10^3 1 (K^{-1}) T
30	303	1.39	-5.34	3.30
35	308	2.88	-5.03	3.25
40	313	3.84	-4.91	3.19
45	318	4.61	-4.84	3.14
50	323	5.76	-4.75	3.10

TABLE 4.10: Temperature dependence of rate constants for the reaction of Fe_2O^{4+} - Mercaptophenol at Fe_2O^{4+} =1.5×10^{-4} mol dm^{-3}, [PhSH] = 1.5 x 10^{-3} -3.5 ×10^{-3}mol dm^{-3}, (H^+) = 1 x 10^{-4} mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$) ə-max = 411nm.

Temp ^{O}C	Temp, K	$10^3 k_{obs}$ (s^{-1})	log $\frac{(k_{obs})_k}{T}$,	$10^3 \frac{1}{T}$ (k^{-1})
30	303	2.03	-2.69	3.31
35	308	2.23	-2.65	3.25
40	313	2.40	-2.62	3.19
45	318	2.47	-2.61	3.14
50	323	2.88	-2.54	3.10

TABLE 4.11: Temperature dependence of rate constants for the reaction of Fe_2O^{4+} - Mercaptoacetic acid at Fe_2O^{4+} =3.4x10^{-4} mol dm^{-3}, [MSH] = 3.4 x 10^{-3} -5.4 × 10^{-3} mol dm^{-3} (H^+) = 1 x 10^{-4} mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$), ə-max = 411nm.

Temp ^{O}C	Temp (k)	$10^3 k_{obs}$ (s^{-1})	$\log \frac{(k_{obs})_k}{T}$, S^{-1}	$10^3 \frac{1}{T}$ (K^{-1})
30	303	2.30	-5.12	3.30
35	308	2.88	-5.03	3.25
40	313	3.54	-4.95	3.19
45	318	3.84	-4.92	3.14
50	323	4.15	-4.89	3.10

TABLE 4.12: Temperature dependence of rate constants for the reaction of Fe_2O^{4+} - L- cysteine at Fe_2O^{4+} =2x10^{-4} mol dm^{-3}, [RSH] = 2 x 10^{-3} -1×10^{-2} mol dm^{-3}, (H^+) = 1 x 10^{-4} mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$), ə-max = 411nm.

Temp ^{O}C	Temp (k)	$10^3 k_{obs}$ (s^{-1})	$\log \frac{(k_{obs})_k}{T}$, $^{S-1}$	$10^3 \frac{1}{T}$ (K^{-1})
30	303	2.37	-5.11	3.31
35	308	2.30	-5.13	3.25
40	313	2.15	-5.16	3.19
45	318	1.97	-5.21	3.14
50	323	1.70	-5.28	3.10

TABLE 4.13: Thermodynamic parameters for the reactions of Fe_2O^{4+} - MBSH, PhSH, MSH and RSH

Reductants	$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	$\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$)
MBSH	114.88	-218.16
PhSH	96.74	-310.5
MSH	88.25	-200.2
RSH	79.78	-308.6

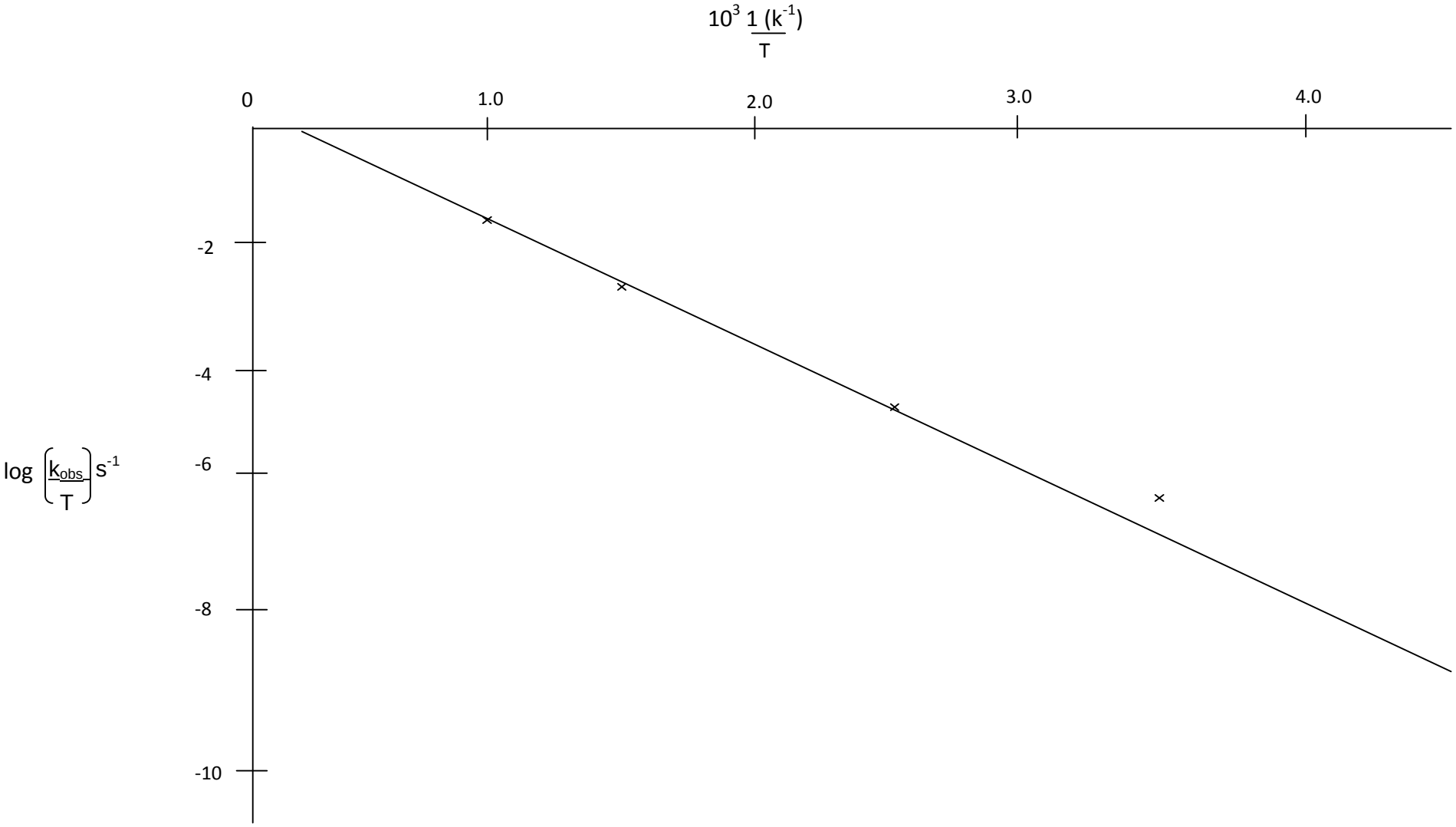


Fig. 4.21: Dependence of log $\frac{k_{obs}}{T}$ versus $\frac{1}{T}$ for the oxidation of MBSH by Fe_2O^{4+} at λ max = 411nm

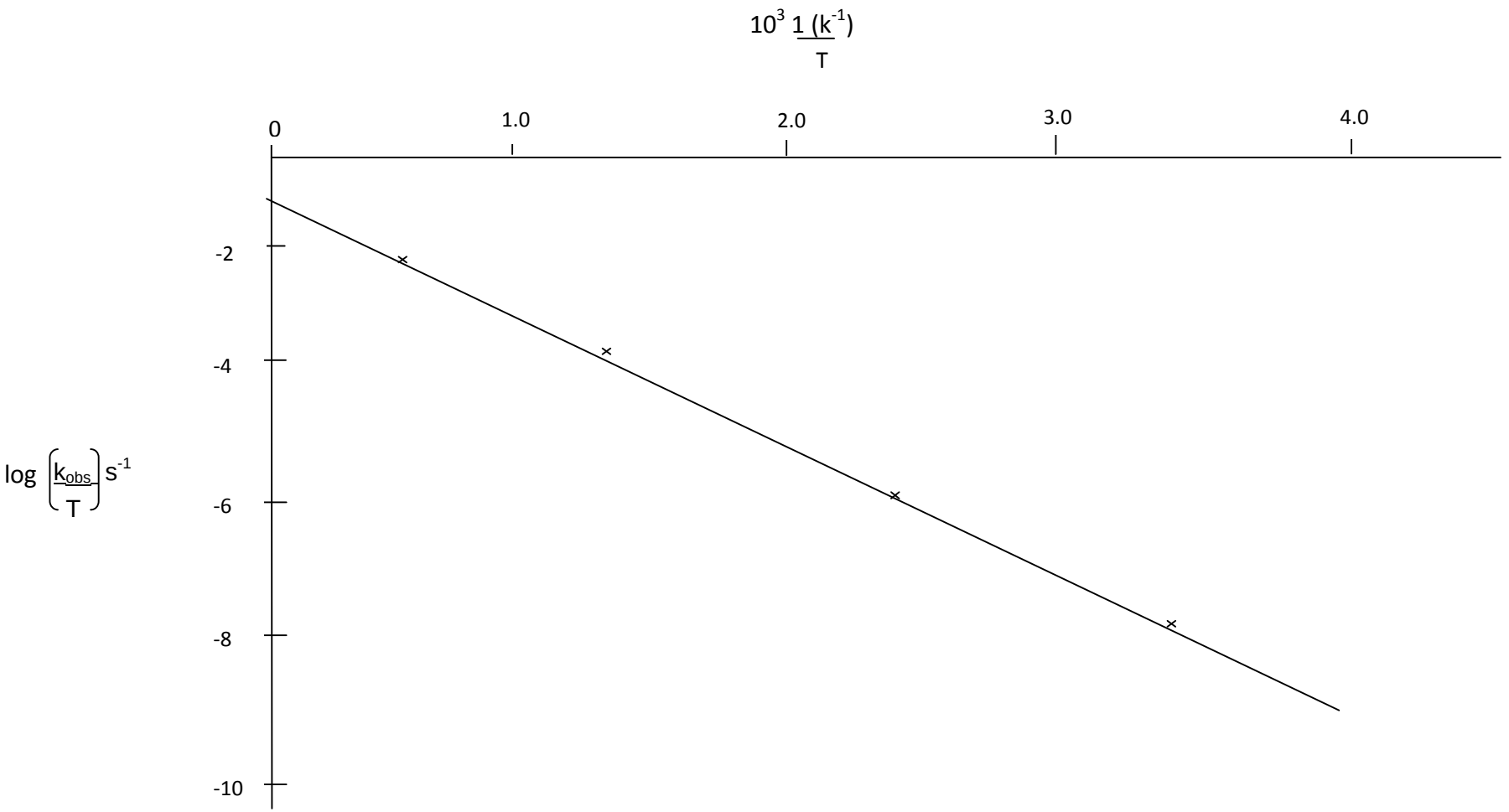


Fig. 4.22: Dependence of log $\frac{k_{obs}}{T}$ versus $\frac{1}{T}$ for the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm

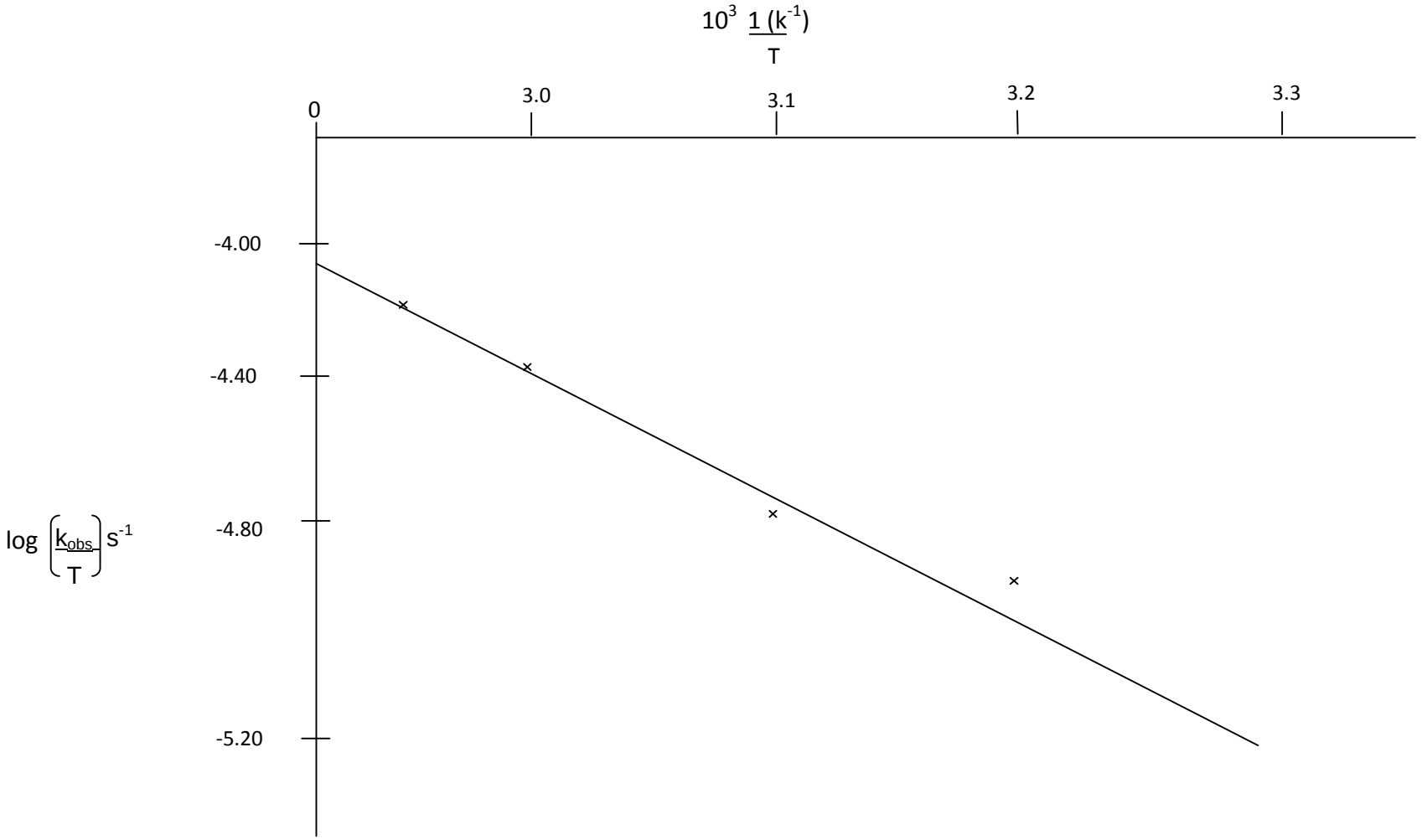


Fig. 4.23: Dependence of log $\frac{k_{obs}}{T}$ versus $\frac{1}{T}$ for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm

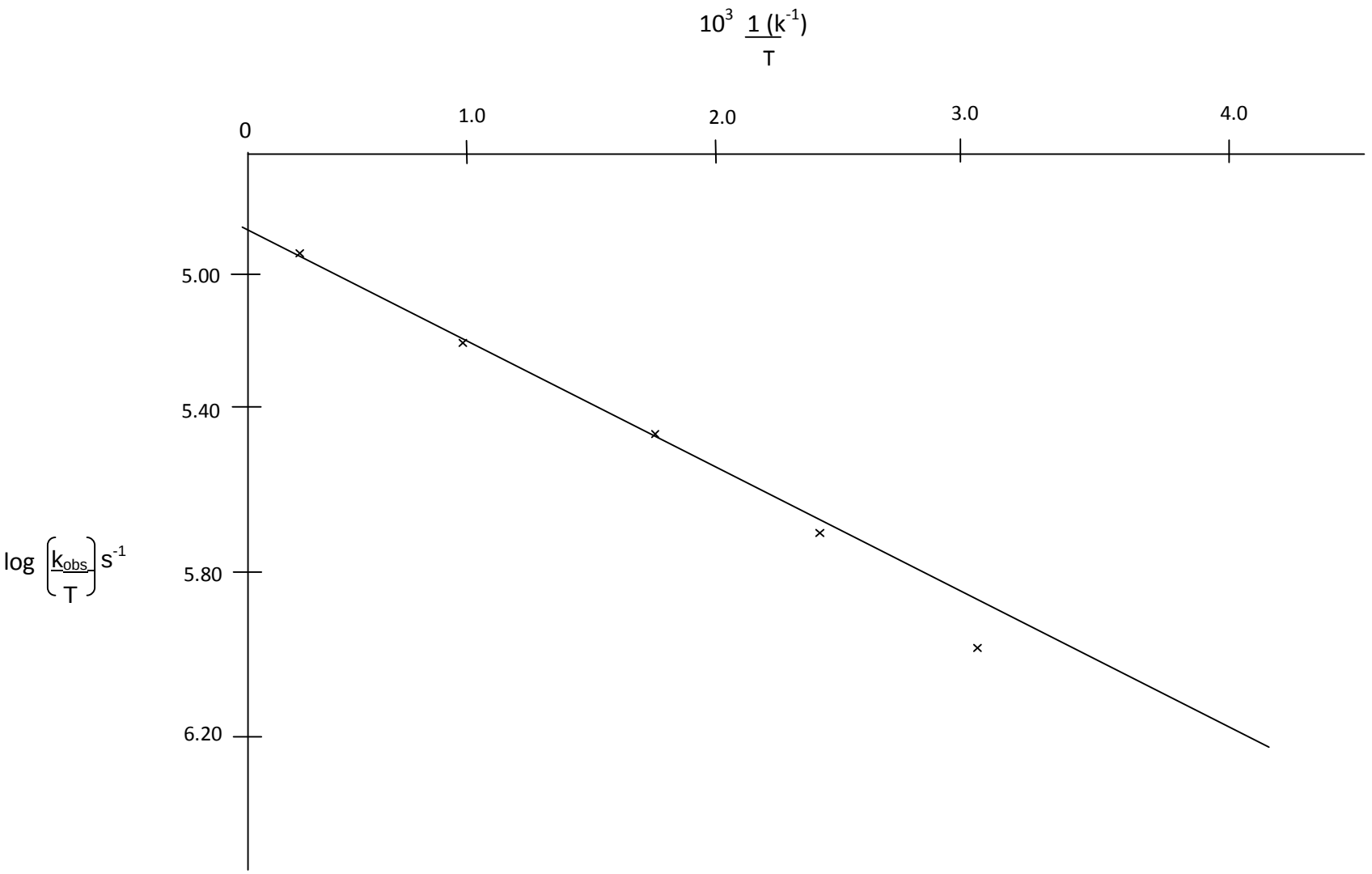


Fig. 4.24: Dependence of $\log \frac{k_{obs}}{T}$ versus $\frac{1}{T}$ for the oxidation of RSH by Fe_2O^{4+} at λ max = 411nm

The variation of rate constant with temperature showed appreciable number of æH# and æS# which means that reaction can occur without any external force. The activated energy of the Fe_2O^{4+}- MBSH, PhSH, MSH and RSH shows negative change in entropy which confirms the formation of binuclear complexes at the activated complex as presented in Table (4.10). The values of the activation energies obtained indicated also that Fe_2O^{4+} is a faster oxidant of thiols.

Similar activation energies results have been obtained from the reaction of sugar in alkaline potassium permanganate and chromic acid medium[100]. The results show that nucleophlic alkoxide anions are readily produced in solution than chromic esters in the oxidation of sugars in alkaline potassium permanganate and chromic acid respectively. Activation result was shown in reaction of ethanol and propanol by chromium (vi)[99,] and reaction of vanadium(v) extraction from hydrochloric acid solution with tri-n-butyl phosphate[101]. The observed activation energy is 5.438kjmol^{-1} which undoubtedly infers a rate limiting diffusion process. This is tantamount to saying that no matter how fast stirring had been done, diffusional effects were paramount.

4.8 Test for the formation of intermediate complex and products

4.8.1 Spectroscopic Test

The electronic spectra of the reaction mixture of Fe_2O^{4+} and four reductants was further run after two, four and six minutes at the æ-max between 300nm and 650nm. After mixing, reddish coloured solution was formed which slowly faded to a colourless solution. The reactions did not shift in æ-max with enhanced peak when the absorbance of Fe_2O^{4+}-MBSH, PhSH, MSH and RSH was run.

4.8.2 Michaelis – Menten Plots

For the enzymatic action of the form

$$\frac{d[product]}{dt} = k_{obs}\,[E^{O}] \qquad (4.12)$$

$$\text{With } k_{obs} = \frac{k_{1[s]}}{k_m + [s]} \qquad (4.13)$$

Michaelis ï Menten observed that if equation (4.13) can be rearranged to

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \left(\frac{km}{k_1}\right)[S]^{-1} \text{---------- (4.14)}$$

Where k_{obs} is the rate constant for the overall reaction and E^o is total enzyme concentration, k_m represents Michaelis-Menten rate constant. k_1 represents rate constant for the break-up of an active intermediate into products while S is the substrate. For a normal redox reaction S represents the reductant. Equation (4.14) shows that a plot of $1/k_{obs}$ against 1/[S] gives $1/k_1$ as intercept. If however, a linear plot which passes through the origin is obtained, it shows the value of $1/k_1$ to be zero. This means no equilibrium constant for the intermediate in the reaction[3].

Michaelis ï Menten plots of $1/k_{obs}$ versus 1/[reductant] figures 4.21, 4.22 and 4.24 as applied by Kumar et al [102] for the Fe_2O^{4+} - MBSH, PhSH and RSH were linear with positive slope and intercepts. This points to formation of inner-sphere pathway mechanism.

For Fe_2O^{4+} - MSH, the Michaelis-Menten plot of $1/k_{obs}$ versus 1/[MSH] linear with negligible intercepts (Figure 4.23) indicating the absence of pre-association step. This evidence is also not in favour of inner-sphere pathway. The outer-sphere pathway is therefore postulated for the reaction.

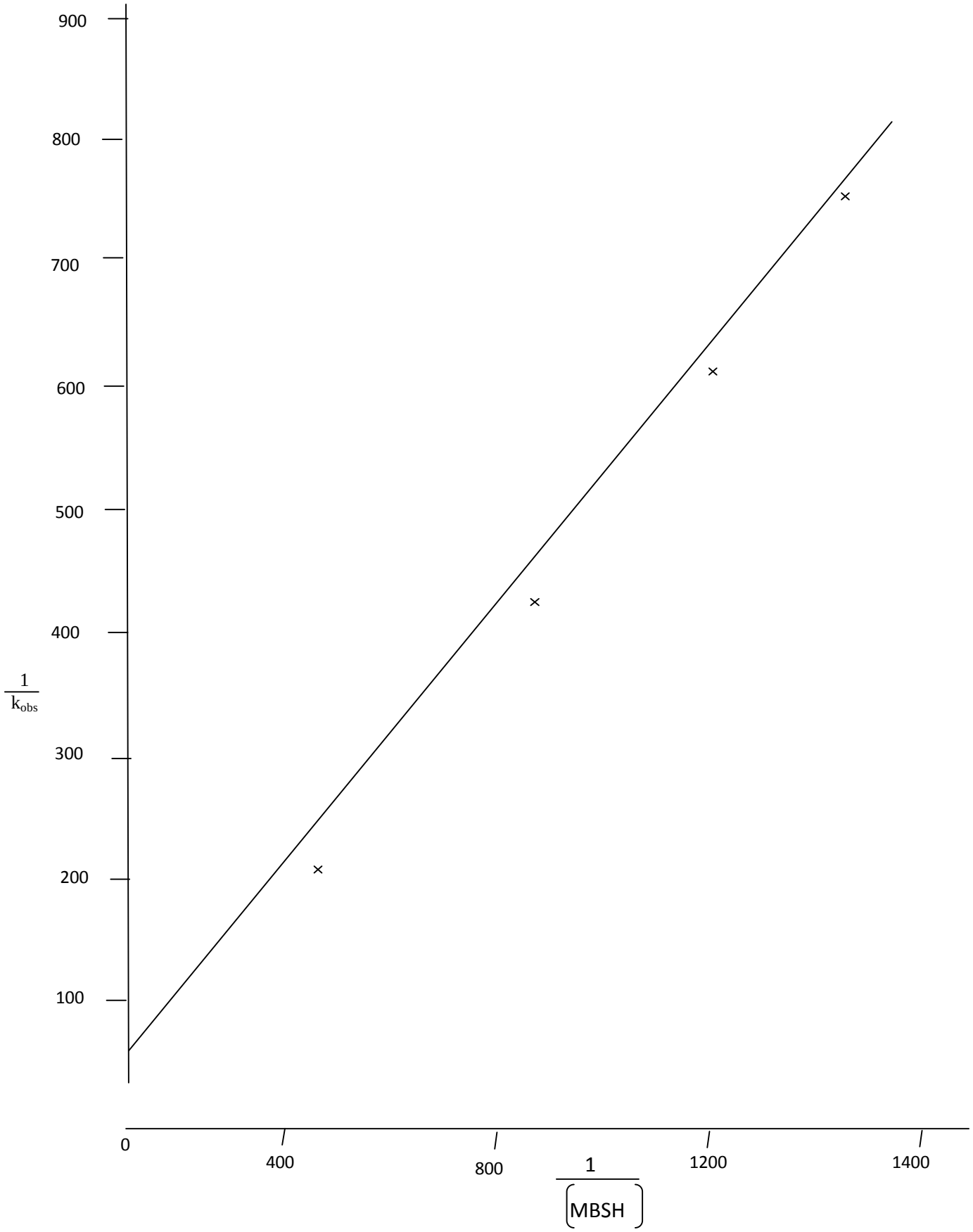


Fig. 4.25: Michaelis-Menten plot for the oxidation of MBSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

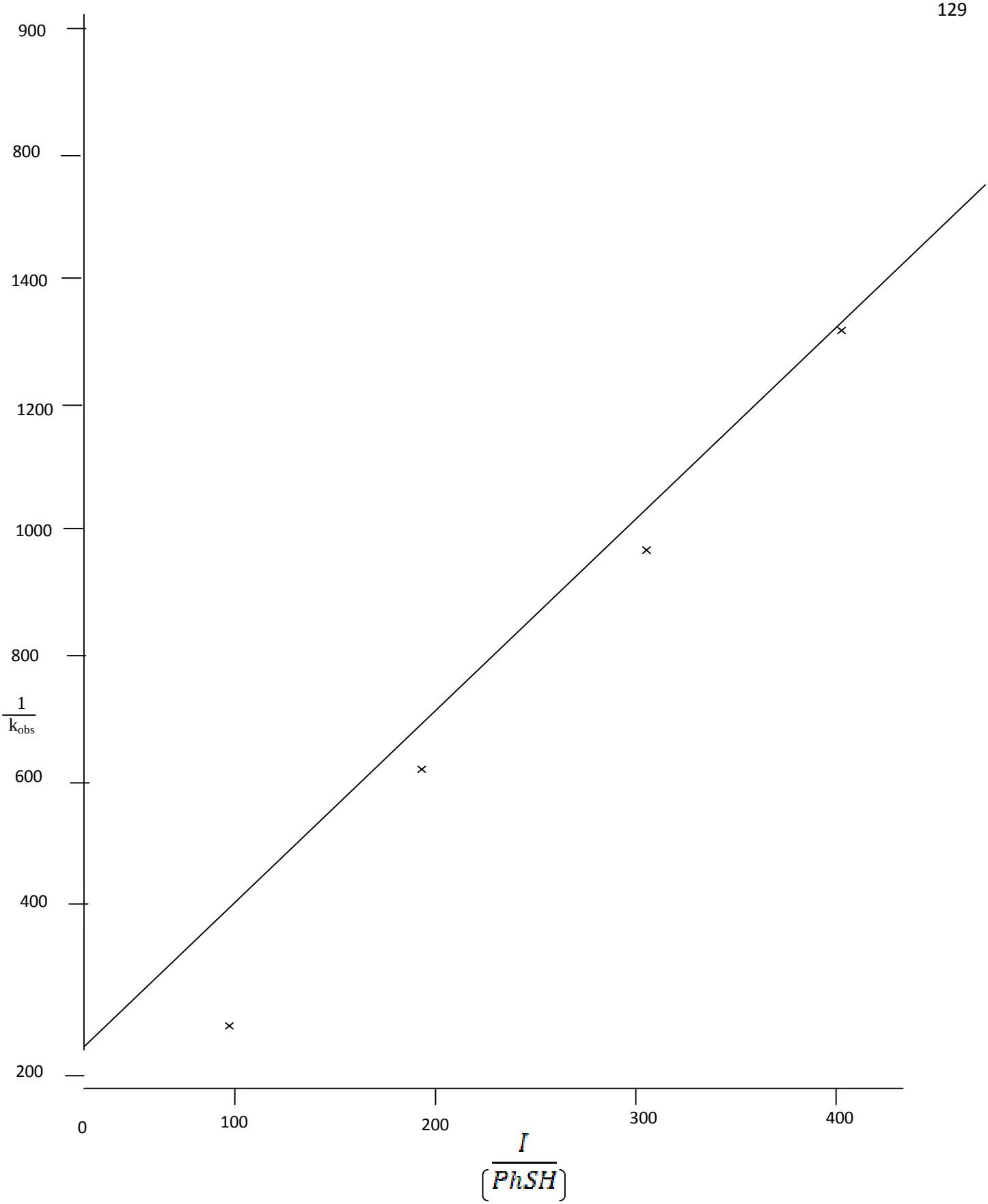


Fig. 4.26: Michaelis-Menten plot for the oxidation of PhSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

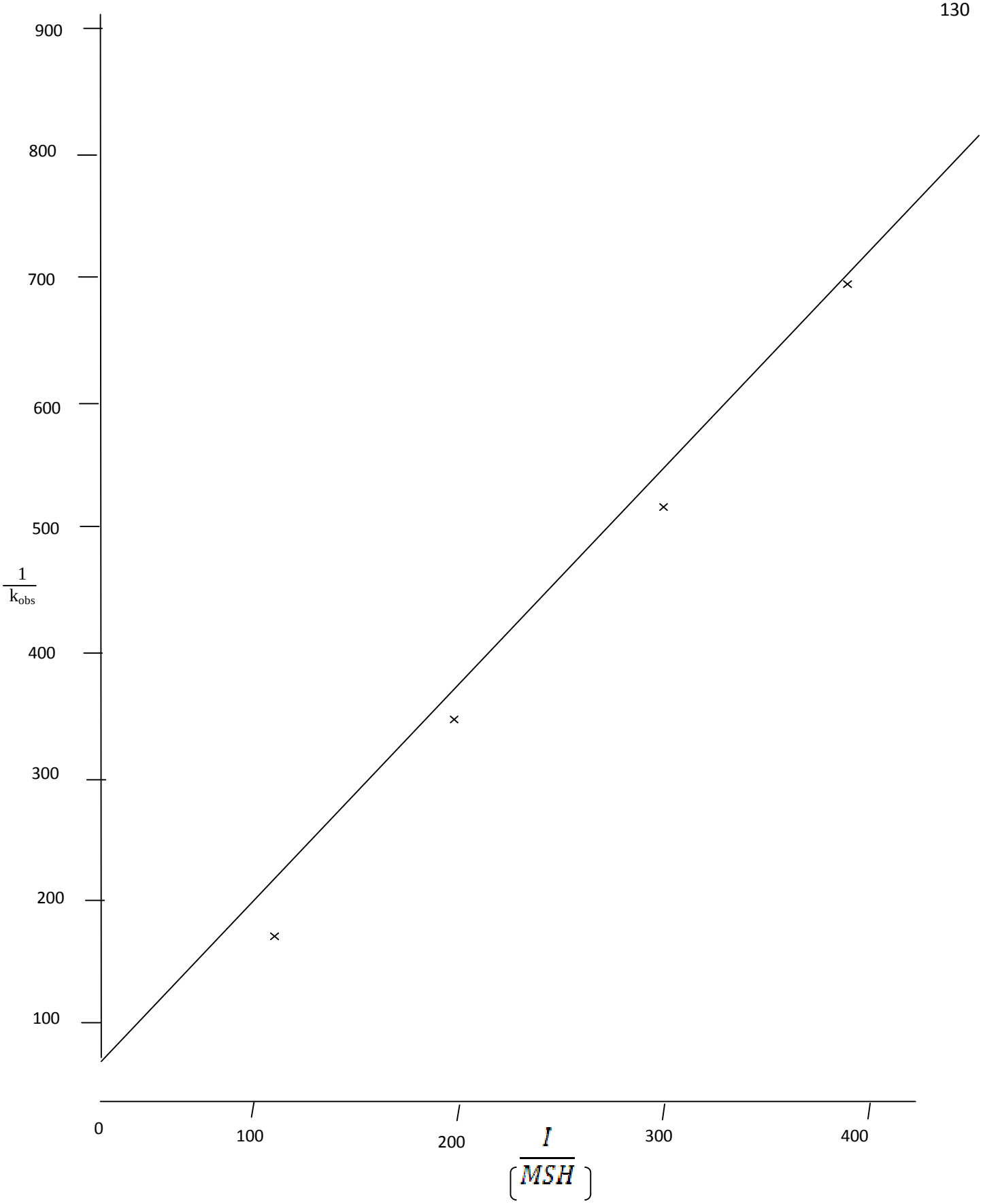


Fig. 4.27: Michaelis-Menten plot for the oxidation of MSH by Fe_2O^{4+} at λ max = 411nm and T = 29.0±0.1°C

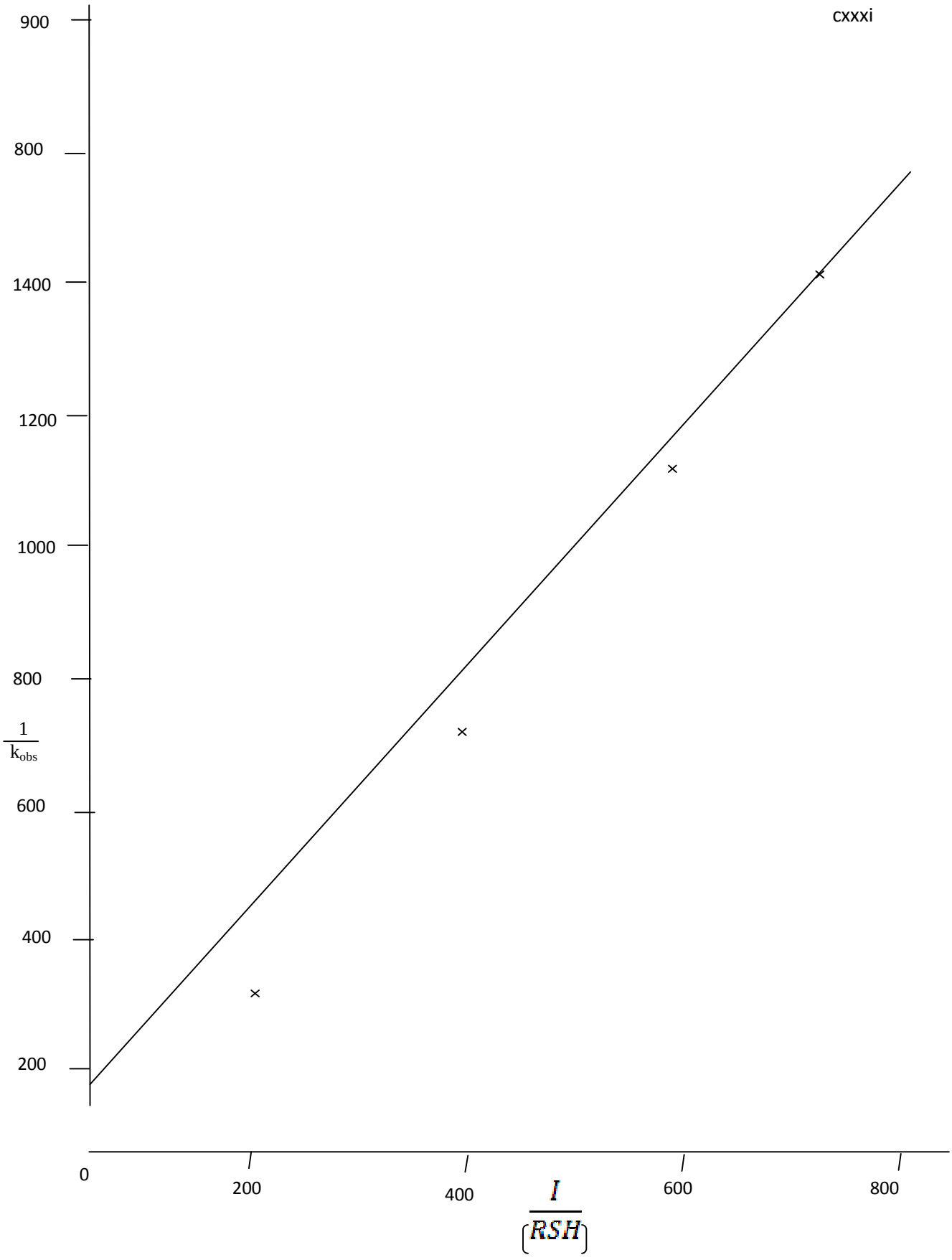


Fig. 4.28: Michaelis-Menten plot for the oxidation of RSH by Fe_2O^{4+} at λ max = 411nm and T =27.0±0.1°C

4.9 Product Analysis

The product of the reaction between Fe_2O^{4+} - MBSH, PhSH, MSH and RSH and oxidants were found to be disulphides. These results were obtained by reacting thiols with a little excess of oxidants in acid and ionic strength medium, which was washed six times with diethyl ether and dried with anhydrous Na_2SO_4. The crystal formed was analyzed in IR spectrophotometer as shown in Table 4.14 derived from Figure (4:25-4.28).

The formation of disulphides MBSSMB, MSSM, PhSSPh and RSSR as the only organic products[103] in the four reactions was confirmed using the method of McAuley and Gowalk[97,98] as reported earlier, Disulphide formation had been observed in the reaction of enH_2 $[(FeHEDTA)_2O.6H_2O$ by thiosulphate ions in acid medium[12],reaction of 2-mercaptoactic acid with enH_2 $[(FeHEDTA)_2O.6H_2O$[3], reaction of $[Fe_2(bpy)_4O]Cl_4$ with metabisulphide ion, Fe(III) dimer was reduced to Fe^{2+}. Also disulphide has been identified as the predominant product in the oxidation of thiols possessing the ï SH group[97,98,103, 104.]

The product of the reduction of the complex under kinetic conditions was confirmed to be Fe(II) by the spectral characteristics of the product solution[106,107]. Also test of the completely reacted mixtures of the three reactions with $K_4Fe(CN)_6$, $K_3Fe(CN)_6$ and KSCN separately gave pale blue, deep blue and pale red colours respectively, signifying the presence of Fe(II). This was not the case when the oxo-bridged Fe(II) complex was tested with the same reagents. This suggests Fe(II) as being one of the products in the reactions. It also confirms the reduction of Fe(III) dimer to Fe(II) by MBSH, PhSH, MSH and RSH.

UV AND IR ANALYSIS

$Na_4[(FeEDTA)_2O].12H_2O$ denoted as Fe_2O^{4+} was prepared and described as in literature[1]. The reddish coloured crystalline compound was characterized by its maximum absorption peak at 456.50 and 410.50nm.The antiasymmetric Fe-O-Fe stretch (1042.50.1022.50.971.00, 939.00, 902.00, 874.50, 862.00, 856 .50) in the infrared region recorded with UV-2500 PC series spectrometer point to the formation of the complex.

Fe_2O^{4+} -MBSH

According to Robert et al[103], disulphides (SS) absorbed between 500 and 400cm^{-1} and this bands have shifted to 394.46cm^{-1}due to bonding of thiols with the complex. Table 4:14

The v(C-N) and v(C=N) frequency showed its characteristic at 1299.1cm^{-1}.Aromatic frequency band at 1598cm^{-1} and v(C=N) 655.82 $cm^{-1}$was observed

Fe_2O^{4+}-PhSH.

403.14 cm^{-1} and 462.93 cm^{-1} showed the frequency characteristics of disulphides v(SS) as in Table 4:14, while 1567.21cm^{-1} exhibits the frequency of aromatic benzene substituted. The v(C-S) frequency of 677.4cm^{-1} remains the same.

Fe_2O^{4+}-MSH

The disulphide frequency absorption of 400cm^{-1} to 500cm^{-1} did not change in this table 4:14, according to Robert et al because of the presence of 419.53cm^{-1}. The characteristic frequency of v(C=O) appear at 1642.44cm^{-1}. Considering 3449.9 cm^{-1} is responsible for the characteristic frequency of v(OH)

Fe_2O^{4+}-RSH

The disulphide frequency characteristic here according to Robert et al is 430.14cm^{-1} band. The frequency characteristics of v(C-OH) frequency of 2903.68cm^{-1} remains the same and v(C=O) frequency of 1621.22cm^{-1}.

Table 4.14

Summary of Infra red spectral data of Fe_2O^{4+} - MBSH, PhSH, MSH and RSH

Sample	$\overline{3}$ cm $^{-1}$	Assignment
Fe_2O^{4+} - MBSH	394.46	V (SS)
	1598.08	V (C = N)
	655.82	V (C = S)
	1299.1	V (C = N)
		V (C = N)
Fe_2O^{4+} - PhSH	403.14	V (SS)
	462.93	V (SS)
	677.04	V (C ï S)
	1567.21	-Benzene substituted
	731.05	Benzene substituted.
Fe_2O^{4+} - MSH	419.53	V (SS)
	1642.44	V (C = O)
	3449.8	V (OH)
Fe_2O^{4+} - RSH	430.14	V (SS)
	3344.68	V (C ï NH_2)
	2903.93	V (C ï OH)
	1621.22	V (C = O)

4.10 Free Radical Test

The presence of free radicals was indicated by gel formation on the addition of acrylamide to the reaction mixtures of Fe_2O^{4+} - MBSH, PhSH, MSH and RSH in the presence of methanol. This shows that free radicals are important intermediate in these reactions as in reaction of some tris(diimine) iron(III) and tris(substituted diimine iron(II) complexes by aqueous acidic bromine solution[108]. Earlier reports had indicated the involvement of free radicals in thiols reactions

4.11 Stability of Fe_2O^{4+}

The absorbance of aqueous solution of Fe_2O^{4+} was monitored over a period of one week. No significant change in absorbance was observed. Stability of the complex in acidic media was monitored by adding varying concentrations of HCl, HNO_3, H_2SO_4 and $HClO_4$ to aqueous solution of Fe_2O^{4+}. There was no significant change in absorbance of the solution at low acid concentrations (10^{-5} ï 10^{-3} mol dm^{-3}). However, at $[H^+]$ Ó 10^{-3} the absorbance of the solution decreased drastically and the reddish colour of the complex changed to colourless at 0.1 mol dm^{-3} acid concentration in all the four acids.

In consideration of the kinetic data, stoichiometry, effect of acid, effect of ionic strength and the fact that the λ max of the complex did not change significantly during the course of the reaction, the following scheme has been proposed for the reaction of Fe_2O^{4+}, with MBSH, PhSH, MSH and RSH.

Fe_2O^{4+} - MBSH, PhSH and RSH

$TSH \underset{}{\overset{K}{\rightleftharpoons}} TS^- + H^+$ ----------(4.15)

$Fe_2O^{4+} + TS^- \underset{}{\overset{k_1 \text{ fast}}{\rightleftharpoons}} [Fe_2O^{4+} - ST]^{3+}$----------(4.16)

$[Fe_2O^{4+} - ST]^{3+} \underset{}{\overset{k_2 \text{ slow}}{\rightleftharpoons}} Fe_2O^{3+} + TS^*$----------(4.17)

$Fe_2O^{3+} + TSH \underset{}{\overset{H^+ \; k_3}{\rightleftharpoons}} TS^* + 2Fe^{2+} + H_2O$----------

(4.18)

$TS^* + TS^* \xrightarrow{k_4} TSST$ ----------(4.19)

Rate = $k_2 [Fe_2O - ST]^{3+} + k_3 [Fe_2O^{3+}] [TSH] [H^+]$----------
(4.20)

Applying steady state approximation

$[Fe_2O - ST]^{3+} = k_1 [Fe_2O^{4+}][TS^-] - k_2[Fe_2O ï ST]^{3+}$----------(4.21)

:. $[Fe_2O ï ST]^{3+} = k_1[Fe_2O^{4+}][TS^-]$----------(4.22)

Also $[TS^-] = K\frac{[TSH]}{[H+]}$----------(4.23)

Substituting equ. (4.21) into equ. (4.22) gives

$[Fe_2O - ST]^{3+} = \frac{Kk_1 [Fe_2O^{4+}][TSH]}{[H^+]}$ ----------(4.24)

$[Fe_2O^{3+}] = k_2 [Fe_2O - ST]^{3+} + k_3 [Fe_2O^{3+}] [TSH] [H^+] = 0$ ----------(4.25)

:. $[Fe_2O^{3+}] = \frac{k_2 [Fe_2O - ST]^{3+}}{k_3 [TSH] [H^+]}$ ----------(4.26)

Substituting equ. (4.24) into equ. (4.26) gives

$\frac{k_2 Kk_1 [Fe_2O^{4+}][TSH]}{[H^+] k_3 [TSH] [H^+]} = \frac{k_2 Kk_1 [Fe_2O^{4+}]}{k_3 [H^+]}$

=> Rate = $\frac{k_2 Kk_1 [Fe_2O^{4+}][TSH]}{[H^+]} + \frac{k_2 Kk_1 [Fe_2O^{4+}][TSH]}{[H^+]}$

$$\text{Rate} = \frac{2\,k_2\,Kk_1[Fe_2O^{4+}][TSH]}{[H^+]}$$

Where TSH can be MBSH, PhSH and RSH

Fe_2O^{4+} - MSH

$$MSH \xrightarrow{K} MS^- + H^+ \text{----------(4.27)}$$

$$MS^- + Fe_2O^{4+} \underset{}{\overset{k_1}{\rightleftharpoons}} Fe_2O^{3+} + MS^* \text{----------(4.28)}$$

$$Fe_2O^{3+} + MSH \underset{}{\overset{k_2}{\rightleftharpoons}} 2Fe^{2+} + MS^* + OH^- \text{----------(4.29)}$$

$$MS^* + MS^* \xrightarrow{k_3} MSSM \text{----------(4.30)}$$

$$OH^- + H^+ \xrightarrow{k_4} H_2O \text{----------(4. 31)}$$

$$\text{Rate} = k_1\,[MS^-]\,[Fe_2O^{4+}] \text{----------(4.32)}$$

$$[MS^-] = K\,\frac{[MSH]}{[H^+]} \text{----------(4.33)}$$

Substituting equ (4.30) into (4.32) gives

$$\text{Rate} = k_1K[Fe_2O^{4+}]\,[MSH][H]^{-1} \text{----------(4.34)}$$

4.12 Comparison of Fe_2O^{4+} - Reductant Systems

In all the reactions, Fe_2O^{4+} was reduced to Fe(II). The reactions of Fe_2O^{4+} with thiols, mercaptobenzothiazole (MBSH),mercaptophenol(PhSH) mercaptoacetic acid, (MSH) and L-cysteine (RSH) occurred by 1:2 (oxidant/reducant) stoichiometry . All the reactions showed evidence of free radical intermediate.

The order of reactivity is k_2(MBSH)>k_2>(PhSH)>k_2(MSH)>k_2(RSH). This reaction will be better understood if the redox potential of the oxo-bridged complex is determined and compared with those of the reductants.

The reactions of MBSH, PhSH, MSH and RSH showed inverse acid dependence which has been attributed to the structural requirement of reactions of thiol in aqueous solution. Rate law for the reactions is given below

$$-\frac{d[Fe_2O^{4+}]}{Dt} = (a + b[H^+]^{-1})[Fe_2O^{4+}][\text{Reductant}] \quad \text{----------(4.35)}$$

Rates of reaction of MBSH, PhSH, MSH and RSH were unaffected by variation of ionic strength and dielectric constant.

The reaction Fe_2O^{4+} - mercaptobenzothaizole, mercaptophenol and l-cysteine showed no catalysis by the added anion and cations which points to inner-sphere mechanism. The decrease of catalysis in Fe_2O^{4+} - MSH is pointing to outer-sphere reaction mechanism.

4.13 CONCLUSION

A key point of interest is whether the reactions of Fe_2O^{4+} - MBSH, PhSH, MSH and RSH occur via the inner or outer-sphere mechanism. The mechanism can be assessed by considering the following points.

- The presence of free radicals was indicated by gel formation on the addition of acrylamide to the reaction mixture in the presence of methanol. This shows that free radicals are important intermediates in these reactions.
- The presence of spectrometric evidence for precursor complex on scanning the reaction mixture as the reaction progressed show no shift in ə-max.

- Addition of varying concentrations of CH_3COO^-, Cl^-, NO_3^- SO_4^{2-},$K^+$and Mg^{2+} to Fe_2O^{4+} -MBSH, PhSH and MSH showed no catalysis. This result indicates the remoteness of the operation of outer-sphere pathway in the reaction. However on addition of these anions and cations of Fe_2O^{4+} - MSH showed decrease in rate of reaction. This indicates the operation of outer-sphere mechanism.
- Michaelis-Menten's plot of $1/k_{obs}$ versus 1/[reductant] for Fe_2O^{4+} - MBSH, PhSH and RSH was linear with significant intercept indicating absence of pre-association step. But Michaelis-Menten plot of $1/k_{obs}$ versus 1/[reductant] for Fe_2O^{4+} -MSH was linear with insignificant intercept.

From the above reasoning it can be inferred that the spectroscopic and kinetic evidence are in support of inner-sphere mechanism for Fe_2O^{4+} - MBSH, PhSH and RSH and outer-sphere mechanism for Fe_2O^{4+} - MSH [6].

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