KINETICS AND MECHANISM OF OXIDATION OF ROSANILINE MONOCHLORIDE BY SOME OXY-ANIONS IN AQUEOUS MEDIA

By

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DECLARATION

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

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CERTIFICATION

This thesis titled, "Kinetics and Mechanisms of oxidation of rosaniline monochloride by some oxy-anions in aqueous media", by Onu Ameh David, meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to scientific and literary presentation.

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DEDICATION

In an environment where immediate gain is exalted above long term benefit, it requires a person of foresight and gut to embrace a long term investment such as Education.

This work is dedicated to all, who from such background extol long term benefit and sacrifice immediate ones for it.

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ABSTRACT

The kinetics and mechanisms of oxidation - reduction reactions of rosaniline monochloride with some oxy-anions ($S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^-, ClO_2^-) have been studied in aqueous media at 30 °C I = 0.25 M (LiCl), $[H^+]$ = 3 x 10^{-4} M (HCl) for $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^-, and $[H^+]$ = 1 x 10^{-3} M (HNO_3), I = 0.5 M ($NaNO_3$) for ClO_2^-. One mole of the rosaniline is consumed by one mole of $S_2O_5^{2-}$ and the same stoichiometry is assumed for the other reactions.

The reaction is first order in both [oxidant] and [reductant] for $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^-, system respectively. In the chlorite (ClO_2^-) ion system the reaction is first order in the [oxidant] and half order in $[ClO_2^-]$.

The rates of the redox reactions showed dependence on acid concentrations.

The reactions conforms to the following rate equations:

$-\frac{d[ROS]}{dt} = (b + a[H^+]^{-2})[ROS][R]$ where R = $[S_2O_5^{2-}]$ and $[ClO_2^-]^{1/2}$ for the reactions involving $S_2O_5^{2-}$ and ClO_2^- and

$-\frac{d[ROS]}{dt} = a[H^+]^{-1}[ROS][S_2O_4^{2-}]$ for the $S_2O_4^{2-}$ reaction and

$-\frac{-d[ROS]}{dt} = a[H^+][ROS][NO_2^-]$ For the reaction involving NO_2^-

At $[H^+]$ = 3 x 10^{-4} M,
k_2 ($S_2O_5^{2-}$) = (6.24 ± 0.53) x 10^{-1} $M^{-1}s^{-1}$

k_2 ($S_2O_4^{2-}$) = (10.42 ± 1.10) x 10^{-1} $M^{-1}s^{-1}$

k_2 (NO_2^-) = (7.81 ± 1.58)x10^{-1} $M^{-1}s^{-1}$

and at $[H^+] = 1 \times 10^{-3}M$

$k_{3/2}(ClO_2^-) = (4.16 \pm 0.26) \times 10^{-3} M^{-1/2} s^{-1}$

The rate of the reaction displayed negative salt effect for the rosaniline - $S_2O_5^{2-}$, rosaniline - $S_2O_4^{2-}$, rosaniline - ClO_2^- systems and positive salt effect for rosaniline - NO_2^- system and was sensitive to changes in the dielectric constant of the medium for the reactions involving NO_2^- and ClO_2^- ions.

Added anions and cations were found to catalyze the reactions for all the systems.

Both the results of spectroscopic investigations and Michealis - Menten analysis show evidence of intermediate complex formation for rosaniline - $S_2O_4^{2-}$ system and none for rosaniline-$S_2O_5^{2-}$, rosaniline - NO_2^- and rosaniline-ClO_2^- systems.

On the basis of the experimental results obtained the outersphere mechanism is proposed for the rosaniline - $S_2O_5^{2-}$, rosaniline - NO_2^- and rosaniline-ClO_2^- reaction respectively and the inner-sphere mechanism for rosaniline - $S_2O_4^{2-}$ system.

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ABBREVIATIONS

Abbreviation		Name
aq	-	Aqueous
B.D.H.	-	British Drug House
Calcd.	-	Calculated
Equ.	-	Equilibrium
G.P.R.	-	General Purpose Reagent
K	-	Equilibrium Constant
k	-	Rate constant
M & B	-	May and Baker
Obs.	-	Observed
Phen	-	1,10 - Phenanthroline
ROS	-	Rosaniline monochloride

CHAPTER ONE

1.0 INTRODUCTION

Redox reactions are of two types, homonuclear exchange reactions, heteronuclear or cross electron transfer reactions.

(a) HOMONUCLEAR EXCHANGE REACTIONS

In these type of redox reactions, electron transfer does not lead to a net chemical change and the rate constants for the forward and reverse reactions are equal, so $K_{eqm} = 1$ and $\Delta G = O$. They are studied by isotopic labelling, for example,

$$*Co(NH_3)_6^{3+} + Co(NH_3)_6^{2+} \rightarrow *Co(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \quad \text{.....(1)}$$

(Stranks, 1960)

(b) HETERONUCLEAR OR CROSS REDOX REACTION

In these reactions $\Delta G < O$, and $\Delta H \neq O$. Products of such reactions are chemically distinct from the reactants, for example,

$$Mn(IV) + 4Mn(II) \rightarrow 5Mn(III) \quad \text{.....(2)}$$

$$Ti^{III} + NH_3OH + 2H^+ \rightarrow Ti^{IV} + NH_4^+ + H_2O \quad \text{.....(3)}$$

Kinetic studies of electron transfer reactions in solution are of considerable importance in chemistry (Basolo and Pearson 1967; Tobe 1972; Burgess 1978; and Wilkins, 1974).

Various reactions in inorganic and biological systems involve the transfer of electrons at one stage or the other during the reaction. Adequate knowledge of these redox processes

is an aid to the understanding, development and effective control of a wide area of science and technology. To understand the detailed mechanism involved will require the measurements of the reaction rates and their dependencies on parameters such as added anions, cations, temperature etc.

A wide range of experimental techniques have been used to study redox reactions. (Sykes 1966, 1967, Rosseinskey, 1972; Wilkins 1974, Haque, 1971; Burgess 1978).

The range of these techniques now vary from conventional spectrophotometric methods for slow redox reactions to continuous and stopped-flow methods for fast reactions. These methods have been exhaustively reviewed (Stranks, 1960; Caldin, 1974; Wilkins, 1974). These methods are however briefly summarised below:

1.1.0 RATE MONITORING TECHNIQUES

1.1.1 Conventional Methods

These methods which include photometric, spectrometric, polarometric and radiometric techniques, apply to slow redox reactions with $t_{½}$ approximately 10 seconds. The methods involve measuring as a function of time the concentration of one or more of the reactants or products or any physical property such as absorbance which is directly related to the concentration.

1.1.2 Fast Reaction Techniques

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

(a) Flow Methods

Different flow techniques exist, depending on the treatment given to the reaction mixture (Caldin, 1964). Common flow methods are discussed below.

(i) Continuous-Flow Method

The reaction mixture flows continuously along an observation tube while conventional monitoring is made either at different points along the observation tube with the flow maintained at constant rate or at a fixed point on the tube with varied flow rate. In either cases a series of values for the extent of reaction is obtained at different times. These values constitute the kinetic data required.

(ii) Stopped-Flow Methods

The solutions are forced together through a mixing device and as the mixed solution flow along the tube, it is abruptly stopped so that the solution come to rest within a few milliseconds. The rate of the flow along the observation tube is such that when the solution is stopped a segment within 1cm of mixing device has been mixed for only 1 - 2 milliseconds.

Any reaction taking place in this segment of solution is then monitored and the signal relayed to an oscilloscope.

(iii) Quenched-Flow Method

In quenched flow, the reaction solution is quenched after a pre-determined time and the quenched solution is analyzed by any conventional method.

(b) Relaxation Methods

These methods are usually applied to reversible reactions with half-lives ($t_{\frac{1}{2}}$) as short as 10^{-9} s (Eigen and De Maeyer, 1963). The observed equilibrium is perturbed by rapid variation of a physical parameter such as temperature, pressure or electric field intensity and the time taken to readjust to a new equilibrium is monitored, which is then related to the rate constants of the forward and reverse reactions. The dependence of a particular equilibrium on a chosen external physical parameter largely determines the method of perturbation used for such an equilibrium and hence these methods are referred to as "temperature-jump", "pressure jump" or "electric jump" methods (Wilkinson, 1980).

(c) Resonance Techniques

Both Nuclear Magnetic Resonance (n.m.r) and Electron Spin Resonance (e.s.r) techniques have been used to study complex formation (Pearson and Pulson, 1959; Pearson and Buch, 1962) and aquation of metal ions (Connick and Poulson, 1959) in solution. In n.m.r. technique, the resonance absorption line is related to the life-time of the nucleus in a given spin state, while in e.s.r. it is related to the life-time of paramagnetic species in a given energy state.

Any reduction of life-time of these state by a chemical interaction, results in line broadening. On addition of increasing amount of a reagent, measurement of the corresponding increase in width of the line due to the second reagent can be made. For example, H.n.m.r. line broadening has been used to measure the rate of exchange of several mono and bi-dentate nitrogen and oxygen donor ligands co-ordinated to Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} (Caldin, 1964, Burgess, 1978).

1.2.0 THEORETICAL CONSIDERATION IN ELECTRON-TRANSFER PROCESSES

1.2.1 Frank-Condon Principle

The actual redox process must satisfy the Frank-Condon Principle (restriction) which states that electron transfer takes place in a much shorter time (10^{-15} s) than the time (10^{-13} s) required for the nuclei to move hence electron transfer occur without appreciable movement of the nuclei (Sutin, 1966). This means that the position of the nuclei remains virtually frozen during the process of electron transfer (Platzman and Frank, 1954; Sutin, 1966).

This gives rise to two important consequences on electron-transfer process.

(a) The reactant activated complex must be identical with the products activated complex. Consequently the energy of the activated complex as described by nuclear coordinates must be two fold degenerate. If this is not so, then there exists a possibility, where the energy of the product activated complex was higher than the reactants' activated complex, this could lead to devising a way of capturing this energy to defeat the first law of thermodynamics.

(b) The second consequence of the "Frank-Condon Restriction" is that no angular momentum can be transferred to or from the transition state during the act of electron transfer and a restriction is also imposed on the change in spin angular momentum.

1.2.2 Electron Tunnelling Theory

The electron tunnelling theory developed by several workers (Weiss, 1954, Marcus, 1966, Zwolinski and Eyring, 1956) throws considerable insight on the electron transfer

process in solution. The electronic energy in the reactants and products is not as high as would ordinarily be expected from classical point of view. Under this condition electron transfer process is viewed as a tunnelling process in which the electron passes through the potential energy barrier rather than over it (Basolo and Pearson, 1967). The outcome of the tunnelling process is that electron can be moved to a longer distance beyond the distance of actual collision of reactants. The potential energy barrier leakage is illustrated in Figure 1.0. U_1 and U_2 refer to ground states of electron in cations 1 and 2 respectively.

d = width of barrier at height of penetration

w = kinetic energy of the electron

U_o = height of the barrier.

This has led to attempt to calculate the efficiency of electron transition (Marcus *et. al.*, 1954). Their result is expressed in the equation:

$$k = \frac{\hbar T}{h} K^1 \exp - \frac{\Delta G_r^{\neq}}{RT} - \frac{\Delta G_e^{\neq}}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

K^1 = Electron transmission co-efficient

k = Rate constant

$\hbar$ = Boltzman Constant

T = Absolute temperature

$\Delta G_e^{\neq}$ = Activation energy

$\Delta G_r^{\neq}$ = Hydration energy for inner coordination shell arrangement.

As the exchanging partners come close together transmission coefficient increases while electrostatic repulsion resulting in increase in activation energy decreases the rate.

Taube (1959) and Lewis (1980) were of the view that electron tunnelling is probably involved in most electron transfer processes.

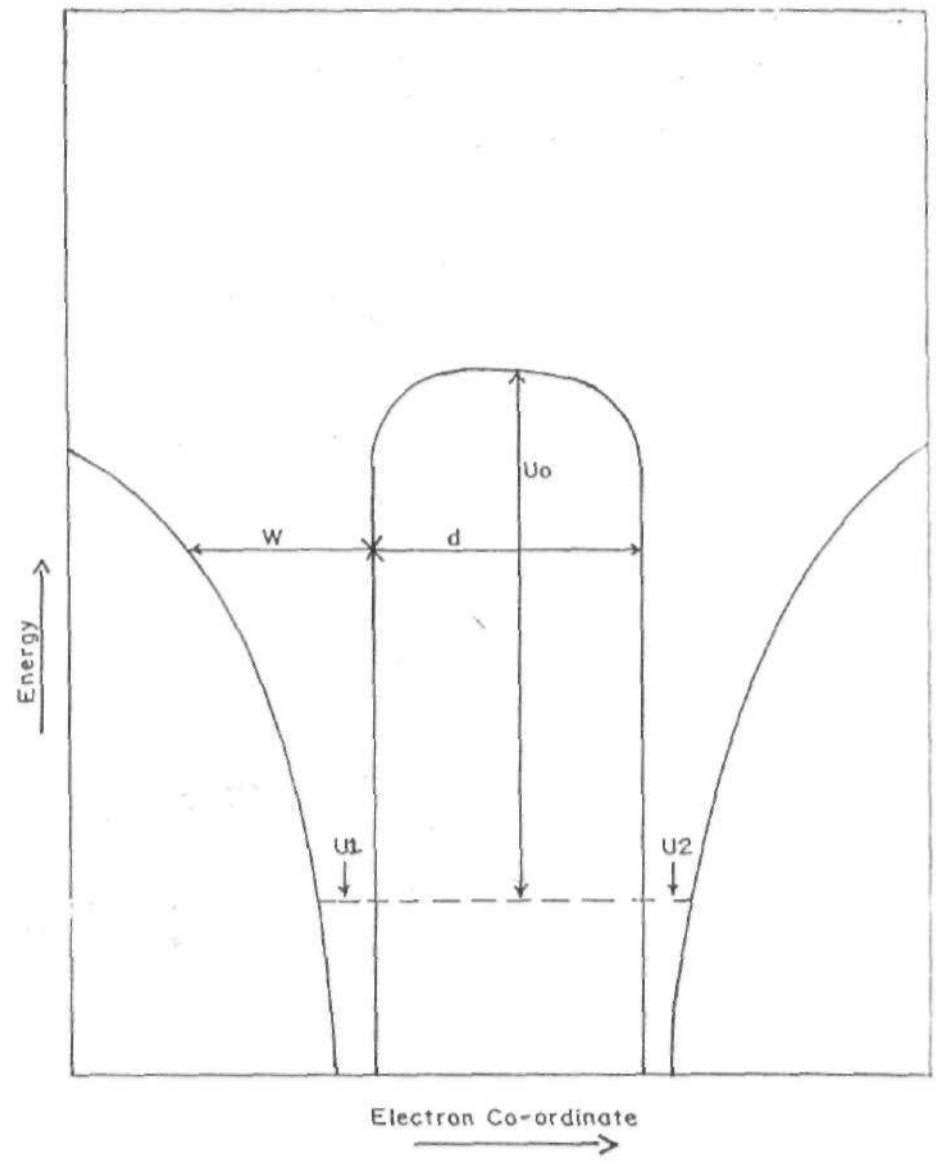


Fig. 1·0 Electron transfer by penetration of a potential energy barrier

1.3.0 POINTS OF MECHANISTIC INTEREST IN REDOX REACTIONS

When undertaking the study of the mechanism of redox reactions, the points of mechanistic interest are:

(i) The stoichiometry of the reaction and the nature (composition) of the activated complex.

(ii) Whether the reaction is accompanied by electron or atoms transfer. If atoms are transferred, which ones are?

(iii) The number of electrons transferred in each single step for a multi step reaction.

(iv) The comparison of the rate of electron transfer with the rate of substitution of the reactant.

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

(vi) The significance of acid-base catalysis when observed.

(vii) Identification or determination of the closeness of approach of the reactants in the activated complex prior to electron transfer.

(viii) Identification and isolation of the products formed.

Attempt to address the above points of mechanistic interests have led Taube and his co-workers to establish two outstanding mechanisms for redox reactions. (Taube, 1959, Taube, Myers and Rich, 1953). The two mechanism are the inner-sphere and the outer-sphere mechanisms.

1.3.1 Mechanisms of Electron Transfer Reactions

1.3.2. The Outer-Sphere Mechanism

This mechanism occurs when either or both the oxidant and the reductant are inert to substitution during the time required for oxidation-reduction to take place. The activated complex is designated "the outer-sphere activated complex". In the outer-sphere activated complex, the co-ordination sphere of the reaction partners remain intact (although not undisturbed), and the electron given up by the reducing agent must go from the primary bond system of one complex to that of the other.

A typical example of an outer-sphere mechanism is given below:

$$W^{IV}(CN)_8^{4-} + Fe^{III}(CN)_6^{3-} \rightarrow W^{V}(CN)_8^{3-} + Fe^{II}(CN)_6^{4-} \quad \text{.....(5)}$$

The mechanism is thought to occur in four stages typical of the outer sphere mechanism as shown:

Stage 1 Formation of Precursor Complex.

$$W(CN)_8^{4-} + Fe(CN)_6^{3-} \rightarrow [(CN)_7W^{IV}CN//CNFe^{III}(CN)_5]^{7-} \quad \text{.....(6)}$$

Stage 2 Activation of the precursor complex

$$[(CN)_7W^{IV}CN//CNFe^{III}(CN)_5]^{7-} \rightarrow [(CN)_7W^{IV}CN//CNFe^{III}(CN)_5]^{7-*} \quad \text{.....(7)}$$

State 3 Electron transfer and formation of the successor complex (slowest or rate determining step).

$$[(CN)_7W^{IV}CN//CNFe^{III}(CN)_5]^{7-*} \rightarrow [(CN)_7W^{V}CN//CNFe^{II}(CN)_5]^{7-} \quad \text{.....(8)}$$

Stage 4 Decomposition of successor complex to give final products

$$[(CN)_7W^{V}CN//CNFe^{II}(CN)_5]^{7-} \rightarrow W(CN)_8^{3-} + Fe(CN)_6^{4-} \quad \text{.....(9)}$$

The above stages can be represented graphically

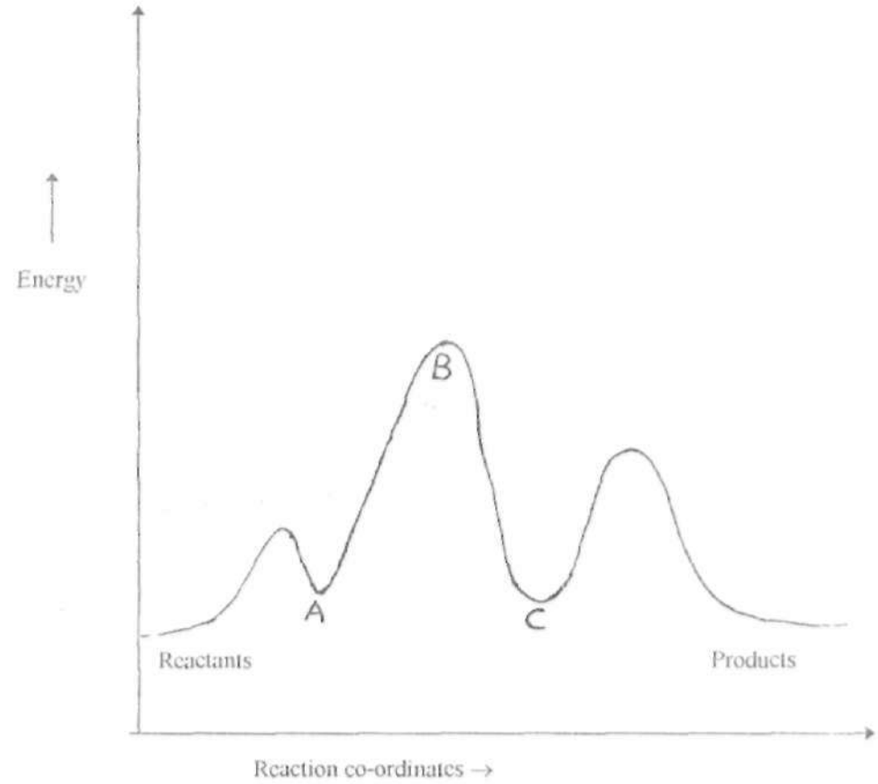


Figure 1.1:Energy profile diagram for a redox reaction which occurs by the outer-sphere mechanism.

A is the formation of precursor complex. This corresponds to stage 1 of the reacting scheme.

B is the electron transfer and formation of successor complex, which corresponds to stage three of the reaction scheme.

C is the decomposition of successor complex to give final products, which corresponds to stage four of the reaction scheme.

1.3.3 The Inner-Sphere Mechanism

The main feature of this mechanism is that substitution takes place at one of the metal centres to give a bridged binuclear complex prior to electron transfer.

The two reactants are linked together by at least one bridging ligand common to their co-ordination shells. Electron transfer occurs through this ligand which is usually but not always transferred from one reactant to another.

The detailed elementary stages for the inner sphere mechanism was independently proposed by Sutin (1968), Bennet (1972) and Linck (1972).

Stage 1 Formation of the encounter or Collision Complex

$$L_5M^{III}X^{m+} + M^{II}(H_2O)_6^{n+} \rightarrow \underset{\text{Collision complex}}{[L_5M^{III}XM^{II}(H_2O)_6]^{(m+n)+}} \quad \text{.....(10)}$$

Stage 2 Formation of a bridged precursor complex

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_6]^{(m+n)+} \rightarrow H_2O + [L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{(m+n)+} \quad \text{.....(11)}$$

Stage 3 Activation of the precursor complex

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{(m+n)+} \rightarrow [L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{(m+n)+*} \quad \text{.....(12)}$$

Stage 4 Formation of successor complex and electron transfer

$$[L_5M^{III}\text{-}X\text{-}M^{II}(H_2O)_5]^{(m+n)+*} \rightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+n)+*} \quad \text{.....(13)}$$

Stage 5 Deactivation of the successor complex

$$[L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+n)+*} \rightarrow [L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+n)+} \quad \text{.....(14)}$$

Stage 6 Decompostion of the successor complex

$$[L_5M^{II}\text{-}X\text{-}M^{III}(H_2O)_5]^{(m+n)+} \rightarrow L_5M^{II}(H_2O)^{m+} + M^{III}(H_2O)_5X^{n+} \quad \text{.....(15)}$$

Any of the reaction steps could be the rate determining step, but in practice only three (3) special cases have been noted i.e. one in which,

(a) Formation of the precursor complex is the rate determining step. This is mostly found in substitution controlled redox reactions.

(b) electron transfer within the bridged complex is the rate determining step. This is the most commonly observed case in inner sphere mechanisms.

(c) the decomposition of the successor complex is the rate determining step. An example is given by equation (16).

$$Co(CN)_6^{3-} + Fe(CN)_6^{3-} \longrightarrow [(CN)_5Co^{III}CNFe(CN)_6]^{6-} \quad \text{.....(16)}$$

The successor complex has been identified as a solid.

1.4.0 DIAGNOSIS OF REDOX REACTIONS MECHANISM

The following criteria among others are used in assigning the outer-sphere and the inner-sphere mechanism to redox reactions.

1.4.1 Rate of redox process versus rate of substitution (k_{redox} Vs $k_{subs.}$)

In the inner-sphere mechanism, substitution into the inner coordination shell of one of the reactant ions precedes electron transfer. Therefore the comparison of the rate of redox process versus rate of substitution into the inner coordination shell of the more labile of the reactant ions can be used to assign mechanism to redox reactions.

When $k_{redox} >> k_{sub}$, the outer-sphere mechanism is said to be operating, while if $k_{redox} << k_{sub}$, the inner-sphere mechanism is implicated.

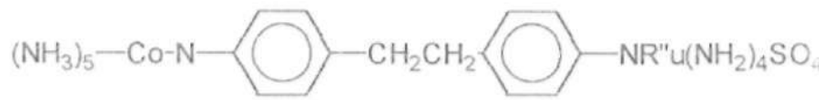
If $k_{redox} = k_{sub}$, both the inner-sphere and the outer-sphere mechanism are operating simultaneously.

1.4.2 Identification of the Binuclear Intermediate

The presence of a binuclear intermediate is an evidence in support of an inner-sphere mechanism. An example is the reaction VO^{2+} with Cr^{2+} an intermediate $VOCr^{4+}$ was characterized (Espenson, 1965). Its rate of decomposition showed hydrogen ion dependence. The identification of the binuclear intermediate in the inner-sphere mechanism is however possible if the reduced oxidant and the oxidized reductant are relatively inert and the rate of decomposition of the intermediate is slower than the rate of electron transfer.

In some cases, where the binuclear intermediate has transient nature, their presence can be inferred indirectly from kinetic data or from empirical rate law. An example, of such indirectly identified binuclear intermediate include $CrOHV^{5+}$ (Espenson, 1965) and [OHTi x $Co(NH_3)_5^{5+}$] (Orhanovic, and Earley, 1975).

Although the detection of a bridged specie suggests that a reaction may occur by the inner-sphere mechanism, it is not however, a sufficient condition for diagonizing the inner-sphere mechanism. Such intermediates could actually exist and yet the products form directly from such reactants. Taube *et al.* 1976) have demonstrated such possibilities when they prepared a stable analog of an inner-sphere complex



and demonstrated that electron transfer occurred independent of the connecting chains.

1.4.3. Product Analysis

The transfer of the bridging ligand from one metal ion to another provides an empirical evidence for the operation of the inner-sphere mechanism.

For example, the redox reaction involving $Co(NH_3)_5Cl^{2+}$ and Cr^{2+}, the $CrCl^{2+}$ product identified have been associated with the binuclear intermediate $[(NH_3)_5Co\text{-}Cl\text{-}Cr^{4+}]^{n}$ advancing evidence in favour of the inner-sphere mechanism for the reaction.

This criteria should be used cautiously as:

(i) Atom transfer does not occur in all the inner-sphere reactions e.g.

$$Co(EDTA)^{2-} + Fe(CN)_6^{3-} \rightarrow Co(EDTA)^{-} + Fe(CN)_6^{4-} \quad \text{.....(17)}$$

(Huchital and Wilkins, 1976).

(ii) The products of some reactions involving reductants such as Fe^{2+}, V^{2+}, Cu^{2+}, Cu^{+}, Eu^{2+} hydrolyses rapidly, making detection of MX^{2+} products difficult (x = brigding ligand).

1.4.4 Reactivity Pattern

Below are some of the reactivity patterns that can be used to assign mechanism to redox reactions.

(i) Reactivity pattern with wide range of reactants

The comparison of the rate of reaction when similar complexes e.g. $Co(NH_3)_5X^{2+}$ (X = Cl^-, F^-, Br^- or NO_3^-) are reacted with a particular reductant gives possible insight into the mechanism that is operating. If the rates of the reactions are similar then the outersphere mechanism is operating, since this mechanism does not depend on the identity of the bridging ligands. However, when the rates of the reactions depend on the nature of the bridging group, the inner-sphere mechanism is predicted (Sykes 1967, Shaw and Haim, 1973).

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

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

1.4.5 The effect of added ions

Marked catalysis by added ions have been reported for a variety of reactions known or at least confidently believed, to occur by outersphere mechanism. Effects of added anions on known inner-sphere redox reactions are much smaller. Hence an examination of the dependence of redox rate on added anion such as chloride, has been used as an indication of mechanism. For instance, in the cases of Yb^{2+} (Chriestensen and Espenson, 1970) and U^{3+} (Wang and Espenson, 1971), reduction. However addition of chloride can lead to serious complication in the interpretation of observed rates and kinetics. (Thakuria and Gupta 1975).

1.4.6 Use of ambidentate bridging ligand

Distinction between the inner-sphere and the outersphere mechanism can be made on the basis of difference in rate of electron transfer observed with symmetrical and unsymmetrical bridging ligands e.g. azide, thiocyanate and isothiocyanate complex.

If the ratio of the rate constant for the reduction of azide complex to that for reduction of the thiocyanate complex, ($k_{N_3^-}/k_{NCS^-}$) or for isothiocyanate and thiocyanate complex (k_{SCN^-}-k_{NCS^-}) shows no difference or are similar then the outer-sphere mechanism

should be operating, while the converse is true for reactions of the inner-sphere mechanism (Sutin, 1968, Wang and Espenson, 1971, Espenson, 1965, Candlin, Halpern and Trimm, 1964, Fay, 1970).

1.4.7 Marcus Theory

In the outer-sphere mechanism, the weak interaction between the reactants has permitted its theoretical treatments and the correlation between kinetics and thermodynamic parameters (Sutin, 1966, Diebler and Sutin, 1964). Probably, the most widely used of these treatments is the Marcus theory (Marcus, 1956).

Marcus' theory which was initially used for the calculation of absolute rate constants for homonuclear exchange reactions was later extended to cross-reactions. Marcus assumed in his theory small electronic interaction between the reacting species which are treated as rigid spheres of radii a_1 and a_2, inside which no change of interatomic distance occurs during the reaction. He further said that when the work term is small, little re-organization is involved prior to electron transfer; Marcus therefore predicted that for the cross reaction equation,

$$OX_1 + Red_2 \xrightleftharpoons{K_{12}} Red_1 + OX_2 \qquad (18)$$

and relative isotopic exchange reaction equation

$$OX_1 + {}^*Red_1 \xrightarrow{k_{11}} Red_1 + {}^*OX_1 \qquad (19)$$

$$OX_2 + {}^*Red_2 \xrightarrow{k_{22}} Red_2 + {}^*OX_2 \qquad (20)$$

$$k_{12} = (k_{11}\ k_{22}\ K_{12}\ f)^{1/2}$$

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

k_{12} = rate constant for cross reaction

f = transmission Coefficient usually assumed to be 1

Z = frequency of collision, $\approx 10^{11} M^{-1}s^{-1}$ for homogeneous reactions.

K_{12} = equilibrium constant for cross reaction.

k_{11} and k_{22} = the rate constants, for the exchange reactions

Thus from Marcus equation, theoretical rate constants for electron transfer reactions can be calculated from equation below:

$$k = Ze^{-}\Delta G^{*}/RT \quad \ldots\ldots(21)$$

ΔG^{*} = free energy of the cross reaction. A reasonable agreement between k_{calcd} and k_{obsd} is taken as evidence that the reaction is of the outer-sphere type. Marcus theory is now applied in various forms. An example is the linear free energy relationship, given by the equation,

$$\Delta G_{12}^{*} = 0.5\Delta G_{11}^{*} + 0.5\Delta G_{22}^{*} + 0.5\Delta G_{12}^{o} \quad \ldots\ldots(22)$$

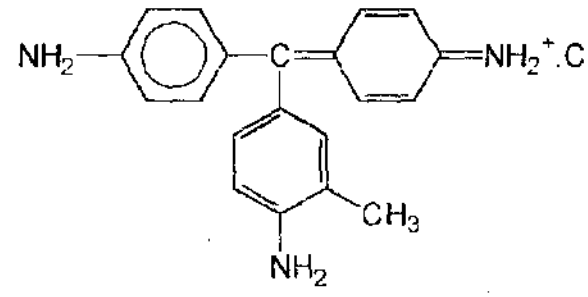
so that for a series of related reactions a plot of ΔG^{*}_{12} versus ΔG^{o}_{12} is a straight line with a slope of 0.50 if reaction is of the outer-sphere mechanism.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Rosaniline monochloride

Rosaniline monochloride is a bright red triphenyl methane dye, used as cotton tannin mordant. It is also suitable for dyeing, printing and biological stains. It has the structure shown below:



The use of rosaniline monochloride as dye and biological stain is enormous. A dye is an organic compound which contains chromophoric and auxochromic groups attached to benzene rings, the colour being attributable to the chromophores and the dyeing property to the salt forming auxochromes.

Biological stains on the other hand are dyes which are adapted for very special purposes, for example, in making microscopic objects more visible than they would be if unstained.

Stains are very useful in the field of zoology as seen in animal macrotechnic, in botany as seen in plant histology and cytology; and in microbiology where biological stains are employed in the study of bacteria and related micro-organisms such as fungi and protozoa.

In spite of the enormous use of rosaniline (a basic fuchsin) as a biological stain and in the textile industry there have been no kinetic studies on the dye. Therefore data on the rate of its reaction, which should throw light on the conditions best suitable for its reactions and the mechanism for such reactions are not available.

2.2.0 Reactions of Chlorite Ions

In the study of the oxidation of *tris*-(1, 10-phenanthroline) iron (II) ion by chlorate, chlorite ions and chlorine dioxide (Shakhashiri and Gordon, 1969), the rate of the reaction is controlled by the first dissociation step of $Fe(Phen)_3^{2+}$ and Fe(III) product is a dimeric specie. Chlorine dioxide reacts via an outer-sphere path, since the Fe(III) product is the monomeric specie $Fe(phen)_3^{3+}$. Chlorate ion is unreactive with $Fe(Phen)_3^{2+}$.

Ramanauskas and Sapragoniene (1970), indirectly determined chlorite ions by its reaction with triphenyl methane dyes. In the study the ClO_2^-/triphenyl methane dye mole ratios for the reactions with brilliant green, malachite green and crystal violet were 1:2.

In the chlorite oxidation of formaldehyde (Kudesia, 1972) an order of one was obtained with respect to oxidant and reductant concentrations respectively.

The rate equation obtained is:

$$-\frac{d[ClO_2^-]}{dt} = k_2[HCHO][ClO_2^-]$$

and the probable mechanism was a two step mechanism. Similar redox reaction of the reductant (ClO_2^-) with nitrite ion gave a stoichiometry of 1:2 and a rate equation

$$-\frac{d[NO_2^-]}{dt} = k_2[H^+]^2[ClO_2^-][NO_2^-],$$ (Nagaishi *et. al.*, 1977)

while in the kinetics of oxidation of ethanol by chlorite ion (Kudesia, 1979), the reaction was first order each in the concentration of the oxidant and reductant and H^+ and Cl^- accelerated the reaction.

Chlorite ion have been used in the pre-oxidation and dissinfection of water (Dernat and Pouillot, 1994); and in the desorption of protein deposits from the surface of hydrophilic contact lens (Powell, Karageozian and Currie, 1994); and also in antimicrobial printing ink vehicles for packaging films (Endo, 1995). In treating and disinfecting shredded infectious wastes, a mixture of organic acid and chlorite ions have given good result with detection time equal or less than 5 minutes (Mason, 1995).

2.3.0 Reactions of Nitrite Ions

Kolesnikov, (1960) studied the oxidation reaction of riboflavine and $NaNO_2$. In the study H_2O_2 was the product of the reaction, while ammonia was the product in the reduction of nitrite by ascorbic acid and enzymes from cucurbita-Pepo (Gurevich and Trubachev, 1964; Cress-well *et al.*, 1965). With ascorbic acid as oxidant only 12% of NH_3 was obtained while yields of 90 - 100% was obtained with the enzyme from cucurbita-pepo.

The kinetics of reaction of Pt [CO-phenylene-*bis*-dimethylarsine $Br_2]^{2+}$(I) and NaSCN (II), $NaNO_2$ (III); and NaI (IV) in anhydrous MeOH were investigated. The reaction involves reduction by the corresponding anions (Y) of II, III and IV with the formation of Pt[*O*- phenylene-*bis*-dimethylarsine]$^{2+}$ (VI). The reaction proceeds by a redox inner-sphere mechanism that involves 2-steps wherein the anions first transfer two electrons to the substrate to form (VI) and subsequently VI and y form a co-ordination complex that further reacts to give the reaction products (Dolcetti and Peloso, 1967).

Fraser, Lee, and Hayden (1967) established that the final product in the europium (II) ion reduction of nitrite and Nitropentammine cobalt (III) ions contain nitrogen - N_2O. NO and possibly nitroxylic acid are intermediates in the reduction of HNO_2. Co-ordinated nitrite is reduced more slowly than pentammine Cobalt (III) and much more slowly than HNO_2.

The kinetics and mechanism of nitrite oxidation with permanganate was studied in the presence of a large excess of $NaNO_2$ so that the rate depended solely on the concentration of $KMnO_4$. The reaction was generally terminated within 0.03 - 0.1 s and proceeded through two stages. Only the second (faster) stage was quantitatively studied. The first (slower) stage is supposed to be the complex formation between MnO_4^- and HNO_2 and is viewed as an induction period for the gross reaction while the second reaction is characterized by the acceleration of the complex decomposition (Yatsimirkii and Budarina, 1968).

The order of reactivity in the reductions of NO_2^- by monovalent zinc, cadmium and Nickel cations is $Zn^{2+} \geq Cd^+ \geq Ni^+$; the order is correlated with the electronic structure of the monovalent cations (Meyerstein and Mulac, 1968).

The oxidation of NO_2^- and some other inorganic oxyanions by $H_2PO_5^-$ was studied by using various oxidizing agents, oxidizable ions and water labelled with oxygen. The data do not indicate a free radical mechanism. One atom of oxygen from the oxidizing agents enters into the oxidation product while oxygen from water does not. The kinetics of the oxidation of NO_2^- by $H_2PO_5^-$ is first order relative to NO_2^- concentration and to $H_2PO_5^-$ concentration and the rate constant of the reaction between NO_2^- and undissolved H_3PO_5 is 6 times as great as the rate constant of the oxidation of NO_2^- by $H_2PO_5^-$ (Luenok - Burmakina, Aleeva, Frankchuk, 1968).

Low concentrations of Mn^{2+} (0.01 - 0.001%) has been found to stimulate the oxidation of NO_2^- by Nietrobacter agilis at pH 7.0 and 5.5. High concentrations of Mn^{2+} were more toxic at lower pH's. At pH 8.0 and 9.0 the rate of NO_2^- oxidation was generally unaffected by Mn^{2+} concentration in the range 0.001 to 0.05% (Mishara and Tandon, 1969).

The measurement of the rate of reaction between permanganate and nitrite ion (Dozsa and Beck, 1970) shows that the rate of the reaction is independent of MnO_4^- concentration in the range 5×10^{-5} - 5×10^{-3}M and between pH 1.8 and 2.6. The rate as a function of NO_2^- and H^+ concentrations can be described by the following equation:

$$\text{rate} = k_1 [HNO_2] + k_2 [HNO_2]^2 + k_3 [HNO_2]^3 [H^+]^3$$

In the kinetic and modelling of sodium chloride and nitrite penetration in pork (Yang, Tin, Lin, Kuo, 1994) it was found that the existence of NaCl significantly affected the penetration rate of sodium nitrite only before 11hr of curing time, mass transfer coefficients for sodium nitrite at 400, 800, 1,200 and 2,800 ppm were established as 5.08, 7.95, 10.28, 21.25 and 22.90 ppm/h respectively.

Nitrite ions have been used in decomposing and removing nitrogen compounds from waste waters (Nakahara, Takabayashi, Sakamoto, 1995) while the synthetic waste water containing various proportions of NO_3^- and NO_2^- were denitrified by a suspended growth batch reactor (Her and Huang, 1995). The kinetic study of the reaction shows a competitive phenomenon between NO_3^- and NO_2^- reductase in an anaerobic environment at 30 °C with CH_3COOH as C source. By a non-linear regression technique, biokinetic constants of the maximum specific NO_3^- and NO_2^- reduction rates (k_1, k_2) were calculated.

2.4.0 Reactions of Dithionite Ions

Sodium dithionite is the most versatile, powerful and widely used reducing agent available to biochemists (Lambert and Palmer, 1973). Representative uses of dithionite are found in the preparation of the reduced state of purified enzymes, electron transfer proteins, and co-factors. It is also used in the depletion of solutions of dissolved oxygen when studying the kinetics of dissociation of oxyheamoglobin and in recording of the optical spectra of reduced oxidation - reduction components in mitochondria or whole cell suspensions. In the study of purified nitrogenase system dithionite is used as a source of reducing equivalents and in maintaining the anaerobiosis necessary for the stability of the nitrogenase system.

The reaction of dioxygen with sodium dithionite was reported by Rinker, *et al.*, (1960) to be first order in dioxygen concentration and half-order in dithionite concentration.

The reaction conforms to the rate law:

$$-\frac{d[S_2O_4^{2-}]}{dt} = k_1[O_2][S_2O_4^{2-}]^{\frac{1}{2}} \text{ with } k_1 = 0.15 M^{-\frac{1}{2}} s^{-1}$$

at 30 °C in 0.10 M NaOH. They invoked the following scheme for the reaction:

$$S_2O_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2SO_2^{-}$$

$$SO_2^{-} + O_2 \xrightarrow[\text{Slow}]{k_3} \text{Products}$$

Wolfen (1961) reported the synthesis of dyes by using sodium dithionite and 5-chloro-4-nitro-aminophenol in proportion of 3:1. Sodium dithionite have been used in bleaching of garan tannin (Azizur and Mofizuddin, 1962). It was found that leathers produced by bleaching with dithionite compared favourably with leather made from

unbleached wattle tannin.

In the gas phase reduction of anthraquinone with dithionite the order of one in dithionite concentration was reported (Peter and Lepenge, 1962).

Rinker, *et al*'s (1960) dioxygen and dithionite reaction was re-investigated by Morello, et. al. (1964) at 37 °C in 0.10M NaOH, and found the reaction to be zero order in dioxygen concentration and first order in dithionite concentration, with the initial rate constant 42.50 s^{-1}. Although the reaction conforms to the scheme proposed by Rinker, *et al*., the $S_2O_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2SO_2^{-}$ step was considered the slow step.

The reduction of *p*-phenylazobenzene sulfonic acid with dithionite ion gave an order of half with respect to the dithionite ion concentration (Wasmuth *et al*., 1965). SO_2 radical ion was found to be a reaction intermediate in the proposed mechanism.

The polarographic investigation of the auto oxidation of sodium dithionite shows that in an unstirred solution the rate of oxidation is detected by the slowest process of diffusion. The stabilities of the dithionite solutions increases if exposure to air is avoided (Peter, 1965). Dithionite ion has also been found to be a reducing agent for Macroreticular polymers (Kenneth, 1965); dyes (Baumgarte and Kenser, 1966); Cytochrome oxidase and its derivatives (Lemberg and Mansley, 1966). In all these redox reactions the kinetics and mechanism of the reactions were studied.

The kinetics of the reduction by dithionite of several biochemically interesting substances has been investigated under anaerobic conditions by stopped flow spectrophotometry at pH 8.0 and 25 °C. Under Pseudo first order conditions the reactions of spinach ferredoxin, horse metmyoglobin, lumiflavin - 3-acetate, horseheart

ferricytochrome-C and spinach plastocyanin conform to first order kinetics for several half-lives. Dependence of the observed pseudo-first order rate constant k_{obs} on the dithionite concentration is described by the equation, $k_{obs} = a\,[S_2O_4^{2-}]^{½}$ where a = 8.6, 100 and 960 $M^{½}s^{-1}$ for ferredoxin, metmyoglobin and lumiflavin 3 - acetate respectively. These results support a mechanism involving SO_2^- as the kinetically important reducing species.

With Cytochrome-C and Plastocyanin, the dependence of k_{obs} on dithionite concentration is described by the equation:

$$k_{obs} = a[S_2O_4^{2-}]^{½} + b\,[S_2O_4^{2-}]$$

where a and b are 1450 $M^{-½}s^{-1}$ and 1.5×10^4 $M^{-1}s^{-1}$, in the case of cytochrome-C and 1100 $M^{-1}s^{-1}$ and 1.35×10^5 $M^{-1}s^{-1}$ in the case of Plastocyanin. These two proteins apparently react with both SO_2^- and $S_2O_4^{2-}$. Analysis of the reaction of cytochrome C with dithionite in the presence of oxygen gave an estimated rate constant of 47 $M^{-1}s^{-1}$ for the oxygen - dithionite reaction.

The rate constant for the reaction of ferricyanide with $S_2O_4^{2-}$ is 1.4×10^5 $M^{-1}s^{-1}$.

Evidence is presented that ferricyanide also react rapidly with SO_2^-.

When dithionite reacts with excess ferricytochrome C, lumiflavin 3 - acetate, or oxygen, the reaction rate is virtually independent of the oxidant concentration and a limiting first order rate constant of 1.70 s^{-1} is approached in each case. The rate constant has been assigned to the monomerization rate of $S_2O_4^{2-}$, and its temperature dependence gives an activation energy of 24.10 cal per mole for the dissociation of $S_2O_4^{2-}$. Determination of the equilibrium constant (K) for the reaction,

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^-$$

by electron paramagnetic resonance spectroscopy has given a value of $1.4 \pm 0.4 \times 10^{-9}$ M (Lambeth and Palmer, 1973).

Creutz and Sutin (1974) studied the kinetics of reaction of dioxygen and Hydrogen peroxide with dithionite ion and showed that, for the $S_2O_4^{2-}$ - O_2 reactions, the disappearance of $S_2O_4^{2-}$ was exponential, giving excellent first order fits for at least 2 half-lives when oxygen is in excess and the dissociation of the dithionite is essentially rate determining. The value of 1.80 s^{-1} obtained for the dithionite dissociation constant (k_2) when dithionite was in excess was in excellent agreement with the value of 1.70 s^{-1} measured by Lambeth and Palmer; while the $S_2O_4^{2-}$ - H_2O_2 reaction conforms to the rate law:

$$-\frac{d[S_2O_4^{2-}]}{dt} = k_{H_2O_2}[H_2O_2][S_2O_4^{2-}]^{\frac{1}{2}}, \text{ with } k_{H_2O_2} = 0.096\ M^{-1/2}s^{-1}$$

Dithionite ion has been used as a component for cysteamine permanent wave composition (Nandagiri, Abbott, Nardone, Borish, 1992). The composition has been found to give mild permanent waving or reshaping of human hair that provides a strong, long lasting curl and protects the hair from damage.

In the manufacturing of high quality, color changeable hair, dithionite ions acts a reducing agent (Li, Xin, Chen; 1995) and also as material for treatment of wastes (Nomura and Kamikita, 1995).

2.5.0 Reactions of Metabisulphite Ions

Presence of metabisulfite ion has been observed to slow the combustibility of tobacco (Borbolla and Munoz, 1950).

The study of the Raman spectra of solid $K_2S_2O_5$ and $Na_2S_2O_5$ and of a solution of

$Na_2S_2O_5$ in MeOH have been compared with those of the aqueous solution in order to assign frequencies in the latter. The important equilibrium present are:

$S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^-$, and $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ (Simon and Waldmann, 1955).

In the study of stoichiometry with inorganic sulfur compounds (Woolfolk and Whiteley, 1962), extracts of V. alcalescens are capable of utilizing H_2 for the reduction of metabisulfite to thiosulfate via dithionite as an intermediate. The first step of metabisulfite reduction is reversible and when dithionite is added as a substrate, there is evolution of H_2 accompanied by the formation of equilibrium concentrations of metabisulfite.

The chronometric determination of furfural in its aqueous solution by its effect on the induction period on the reaction between IO_3^- and $S_2O_5^{2-}$ in acid medium shows the rate of the reaction to be linearly dependent on the furfural and the oxidant concentration (Tikhonova, 1964).

The kinetic study of oxygen exchange between the sulfite ion and water (Betts and Voss, 1970) in which ^{18}O was used as a stable tracer to measure the rate of exchange between the sulfite ion and water as a function of pH and total sulfite concentration; the value of the rate constants for the pyrosulfite equilibrium.

$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ were obtained to be $k_2 = 7.00 \pm 0.21 \times 10^2$ Mol^{-1} s^{-1}, $k_{-2} = 10^4$ s^{-1} at 24.7 °C at an ionic strength of 0.9 M.

Metabisulphite ions have been shown to be more intensive electron acceptor in bioreactor microbiocenosis than SO_4^{2-} (Radchenko and Sobchuk, 1994) while the independent studies by Hara (1994) and Ikebe *et al.*, (1995), have shown that metabisulphite

ions forms part of the composition for skin-lightening preparations containing licorice extract and that containing ascorbic acid derivatives and other substances.

2.6.0 Objectives of the Project

One of the mostly used biological stain for bacteria staining in the laboratory diagonosis of disease is rosaniline (a basic fuchsin). In numerous diseases, for example, tuberculosis and diphtheria, staining procedures play a prominent role in diagnosis (Conn, 1961).

Various combinations of stains including basic fuchsin have been employed for highly specialized purposes, such as staining fungi in tissues, or for demonstrating pollen tubes in the styles. Being a dye, rosaniline is also used as constituents of culture media, indicators and bacteriostatic effects.

Most bacteria stain well when subjected to basic dyes e.g. basic fuchsin, due to the affinity of the nucleic acids contained in the bacteria for the dye.

There are different types of stains e.g. the gram stain (a very important differential stain) capsule stains, flagella stains, granule stains, spore stains, acids-fast stains and these are used for specific purposes.

On application of some of the stains on the organism (gram and acid-fast stains) it was discovered that the stained part of the organism became resistant to decolourization/destaining. Explanation for the observed behaviour was based on the chemical composition at or near the surface of the bacteria (Conn, 1961).

Destaining stained smears means destroying the colour-imparting group of the dye; reduction of the dye however, destroys its colour-giving group (chromophore) and this is of

special significance as dyes can often be used as indicators of reduction.

Kinetic and mechanistic studies on the redox reaction of the dye will therefore generate kinetic data and give insight into the mechanism of the reaction. Availability of these data and knowledge of the mechanistic pathway for the reaction will be a useful tool in improving on the uses of rosaniline monochloride as a biological stain and indicator; also as a dye, the study will enable its use in the textile industry to be improved upon, particularly its fading and fastness property.

CHAPTER THREE

3.0 EXPERIMENTAL

3.1.1 Materials and Reagents

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

3.1.2 Rosaniline monochloride

The Rosaniline monochloride (dye) was obtained from Aldrich Chemical Company (analar grade). Stock solution of the dye was prepared by weighing a known amount and dissolving in a known volume of distilled water. The electronic spectrum of the solution was run and the wavelength of maximum absorption (λ_{max}) was obtained to be 545 nm (Figure 1.2). This value is however close to literature value of about 550 nm (Conn, 1961).

3.1.3 Preparation of Sodium Chlorite ($NaClO_2$) Solution

A standard solution of sodium chlorite (B.D.H) was prepared by dissolving 6.20 of the salt in 100 cm^3 of distilled water. This was again standardized gravimetrically as follows: 2.00 cm^3 of the stock solution was taken and evaporated to dryness in a pre-weighed bottle dried at about 100 - 110 ^0C and cooled in the dessicator until constant weight was obtained. By difference the amount of salt in 2.00 cm^3 was determined, after which the mass concentration of the salt and hence its molar concentration was calculated.

3.1.4 Preparation of Standard Solution of Sodium Nitrite ($NaNO_2$), Sodium metabisulphite ($Na_2S_2O_5$, Sodium Dithionite Solution ($Na_2S_2O_4$).

Standard solution (0.7 M) of $NaNO_2$ (M & B), 0.92 M $Na_2S_2O_5$ (B.D.H), 0.56M $Na_2S_2O_4$ were prepared by dissolving known amount in a given volume of distilled water. The concentrations were determined gravimetrically as described in 3.1.3.

3.1.5 Salt Solutions

The solutions of $NaNO_3$ (M & B), $Na_2C_2O_4$, HCOONa, $LiNO_3$, KNO_3, $Mg(NO_3)_2$, LiCl, $CaCl_2$, $BaCl_2$ were all prepared by dissolving known weights of the respective salts in known volume of distilled water. All salts were analar grade.

3.1.6 Preparation of Standard Nitric Acid Solution

A stock solution of Nitric acid (Analar grade) 0.87 M was made by diluting 69 - 70.5% Nitric acid (specific gravity is 1.42).

The nitric acid was standardized volumetrically using sodium carbonate as primary standard and methyl orange as indicator.

3.1.7 Preparation of Standard Hydrochloric Acid Solution

A stock solution of hydrochloric acid (analar grade) was made by diluting 36% hydrochloric acid of specific gravity 1.8. The hydrochloric acid solution was standardized volumetrically using sodium carbonate as primary standard and methyl orange as indicator.

3.1.8 Stoichiometric Studies

The Stoichiometry of the reaction for the rosaniline-$S_2O_5^{2-}$ system was determined by spectrophotometric titration using the mole ratio method. The concentration of the oxidant was kept constant while that of the reductant was varied. [ROS] = 4.0×10^{-6} M, and $[S_2O_5^{2-}]$ = 4.0×10^{-5} - 4.0×10^{-7} M at $[H^+] = 3.0 \times 10^{-4}$ M, and I = 0.25 M (LiCl). The reaction was allowed to go to completion at 30 °C and the absorbance of the solutions were measured at 545 nm. The stoichiometry was determined from the plot of absorbance versus the volume of $S_2O_5^{2-}$.

3.1.9 Kinetic Measurements

The rate of the reactions was monitored on a Corning Spectronic 20 colorimeter. The rates of the reactions of the oxidant with the reductants (sodium chlorite, sodium nitrite, sodium metabisulphite, sodium dithionite) were studied by monitoring the decrease in absorbance of the oxidant at a wavelength λ_{max} = 545 nm, characteristic of rosaniline.

All kinetic measurements were carried out under pseudo first order conditions with respective reductant concentrations at least 100 fold in excess of the oxidant concentration at 30 °C and ionic strength of 0.5 M ($NaNO_3$) and $[H^+] = 1 \times 10^{-3}$ M (HNO_3) for chlorite ions, and 0.25 M (LiCl) and $[H^+] = 3 \times 10^{-4}$ M (HCl) for nitrite, metabisulphite and dithionite ions. The pseudo-first order plots of log A_t - A_∞ versus time were made. From the slope of the plots, the pseudo-first order rate constants k_1 were determined. The second order rate constants (k_2) were obtained from k_1 as $k_1/[R]$ (R = $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^-) and the three-half rate constants were obtained from k_1 as $k_1/[ClO_2^-]^{3/2}$.

3.2.0 Hydrogen ion dependence

The influence of acid on the rate of the reaction was investigated in the acid range 1 x 10^{-5} - 1 x 10^{-3} M, (outside this acid range the rosaniline was no longer stable) while the concentration of rosaniline and the reductants were kept constant.

The reaction was carried out at 30 °C and I = 0.5 M ($NaNO_3$) for chlorite and 0.25 M (LiCl) for nitrite, metabisulphite and dithionite ions.

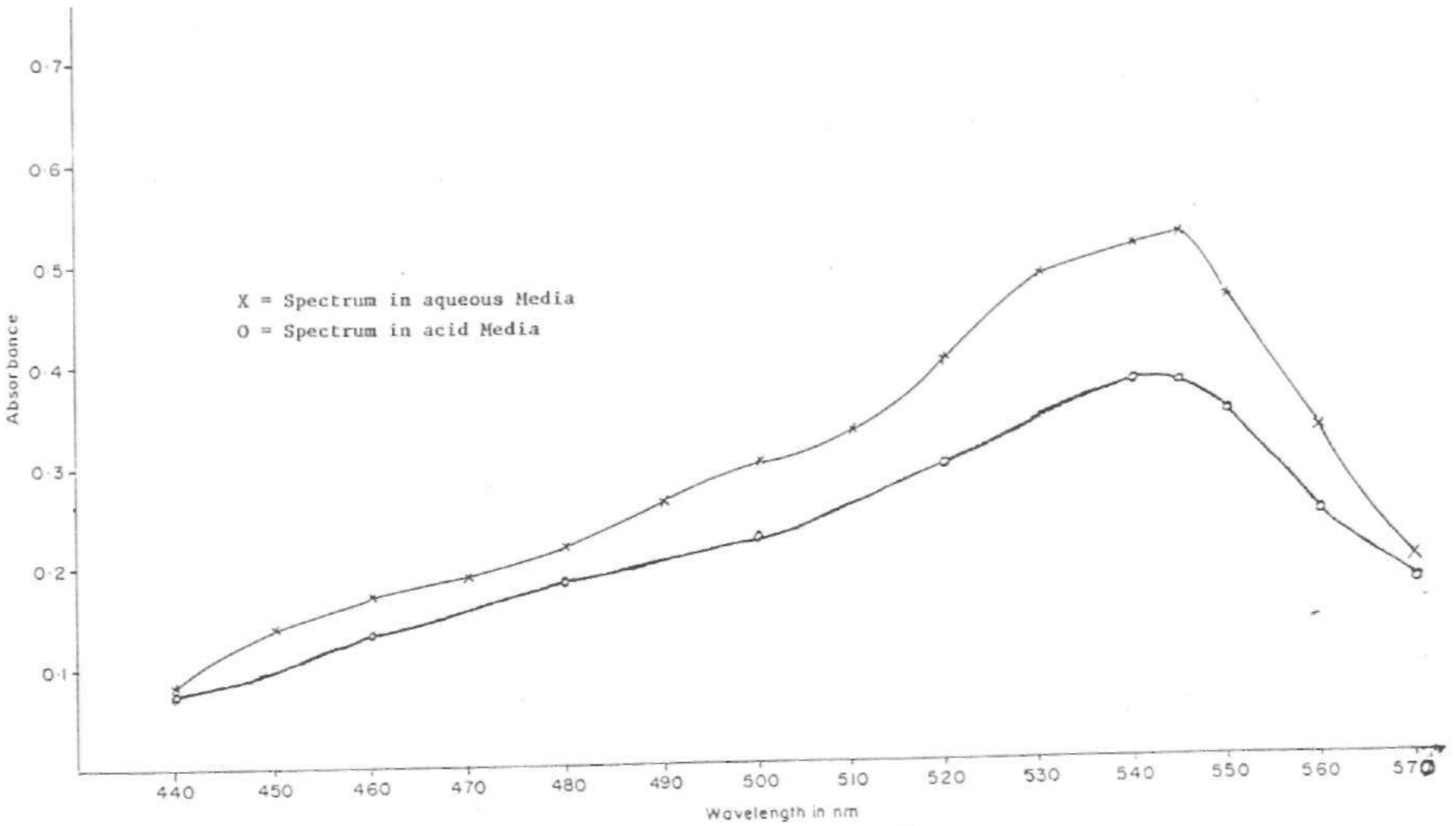


Fig 1·2 Spectra for rosaniline

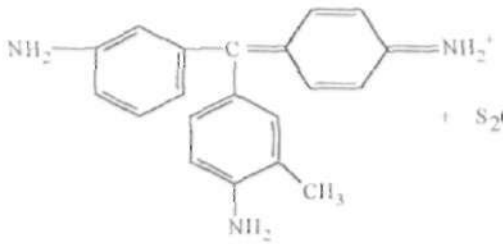
CHAPTER FOUR

4.0 RESULTS

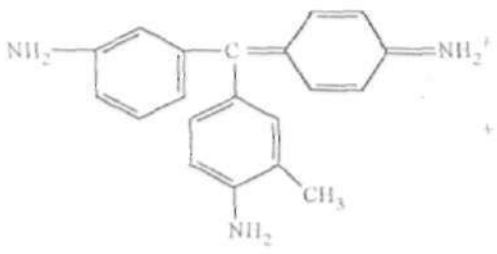
4.1 Stoichiometry

The stoichiometry determined for the reaction of rosaniline-$S_2O_5^{2-}$ showed that one mole of the rosaniline is consumed by one mole of $S_2O_5^{2-}$. The titration curve from which the stoichiometry was determined is presented in figure 4.1. Based on stoichiometry already obtained for the reaction of the oxidant and other reactants (Unpublished work) and the one obtained for the rosaniline-$S_2O_5^{2-}$ system, the stoichiometry of 1:1 is assumed for the rosaniline-$S_2O_4^{2-}$, rosaniline-NO_2^- and rosaniline-ClO_2^- reactions.

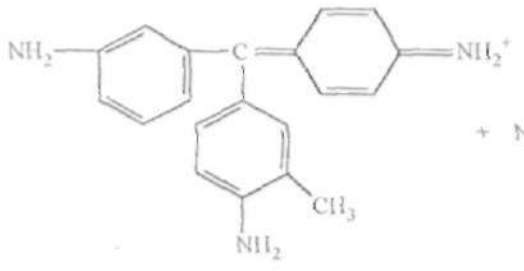
On the basis of the stoichiometry determined and the ones assumed, the overall equations for the reactions can be represented by the following:



+ $S_2O_5^{2-}$ ⟶ Products .....(23)



+ $S_2O_4^{2-}$ ⟶ Products .....(24)



+ NO_2^- ⟶ Products .....(25)

$$-\frac{d[ROS]}{dt} = k_2[ROS][R] \quad \text{.....(27)}$$

where R = $S_2O_5^{2-}$ or $S_2O_4^{2-}$ or NO_2^-

ROS = Rosaniline

k_1 = Pseudo-first order rate constant

k_2 = Second-order rate constant.

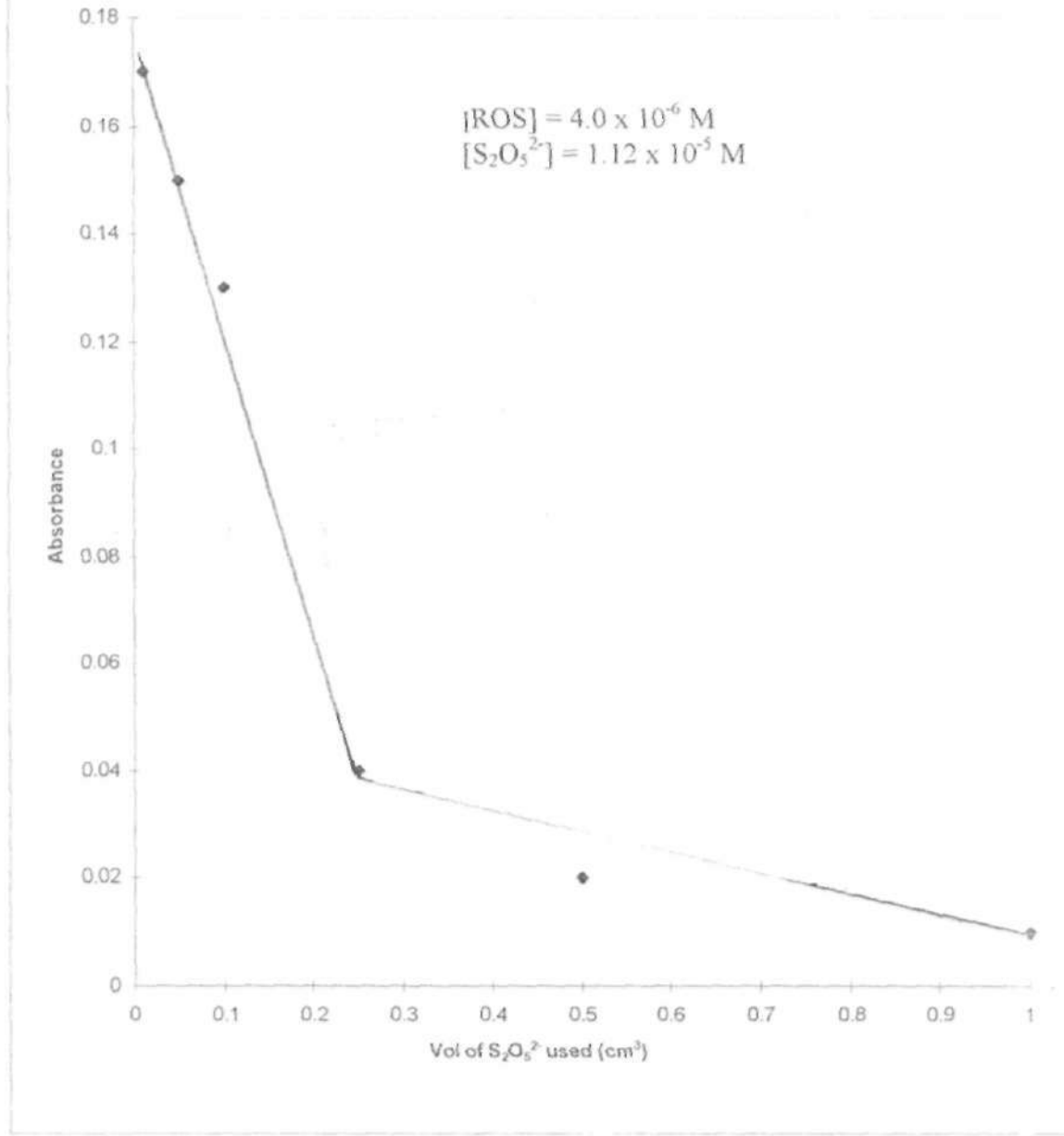


Fig. 4.1 Stoichiometry of the redox reaction between rosaniline and $S_2O_5^{2-}$

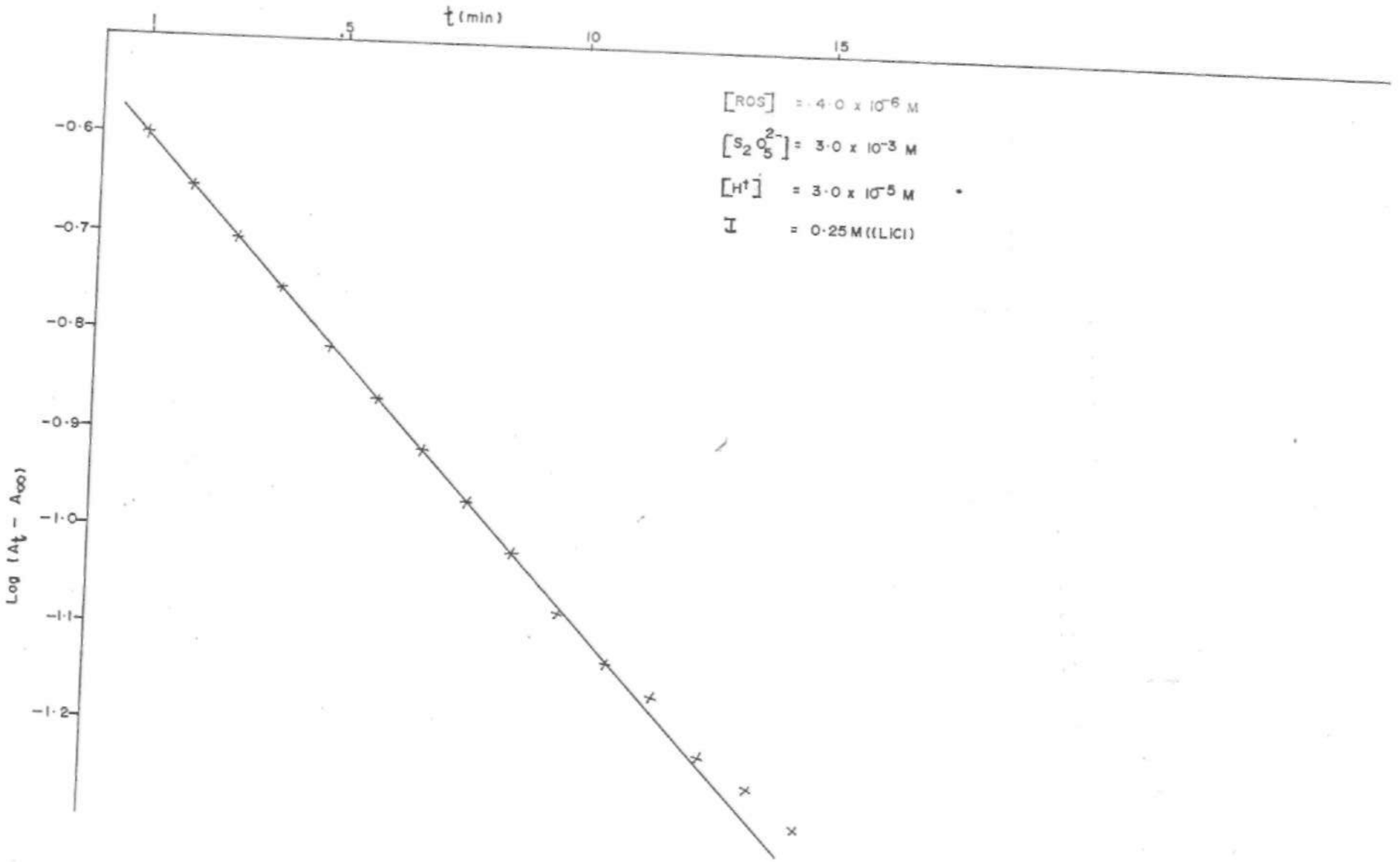


Fig. 4. 2·0 Pseudo-first order plot for the redox reaction between Rosaniline and $S_2O_5^{2-}$

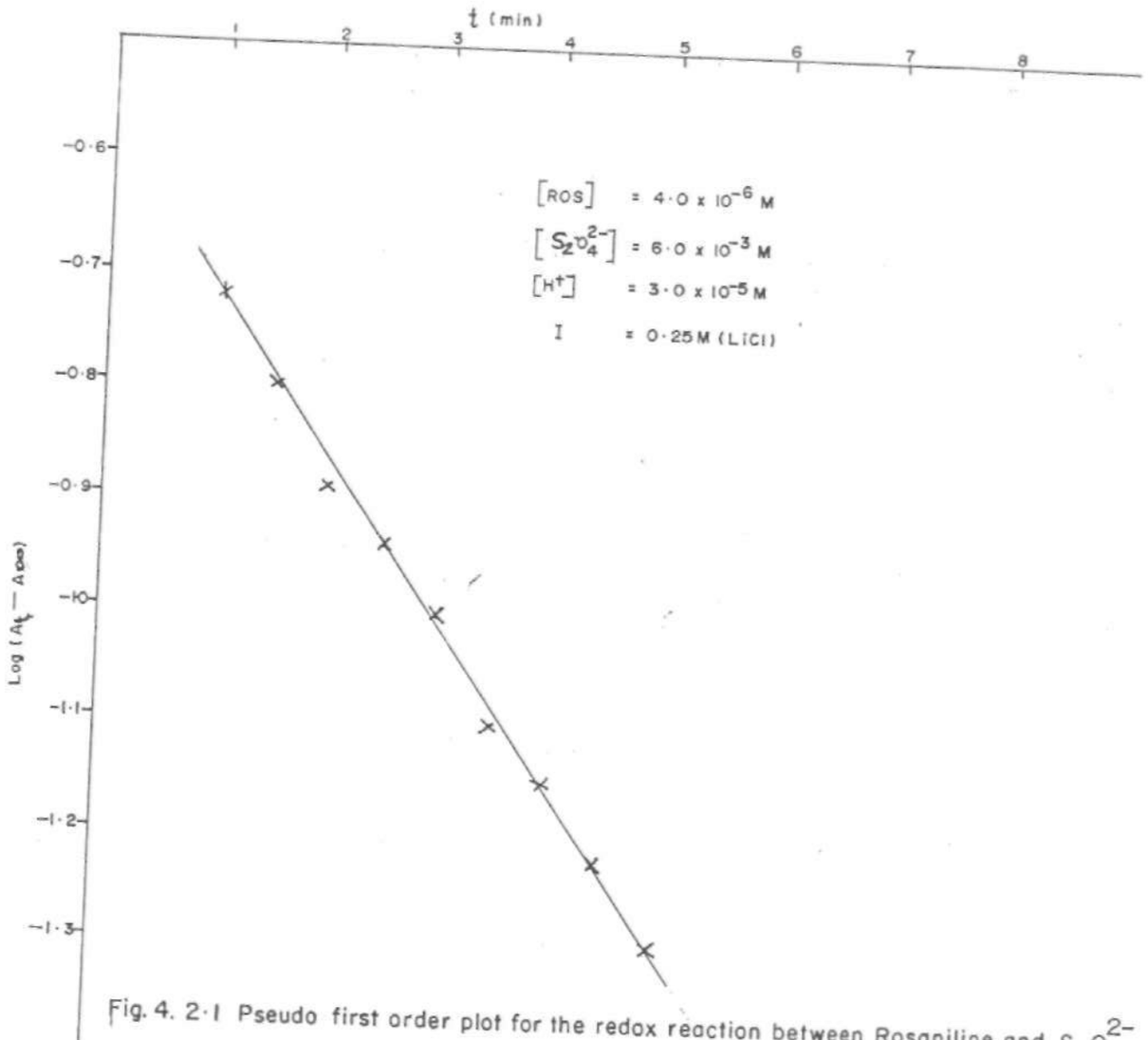


Fig. 4. 2·1 Pseudo first order plot for the redox reaction between Rosaniline and $S_2O_4^{2-}$

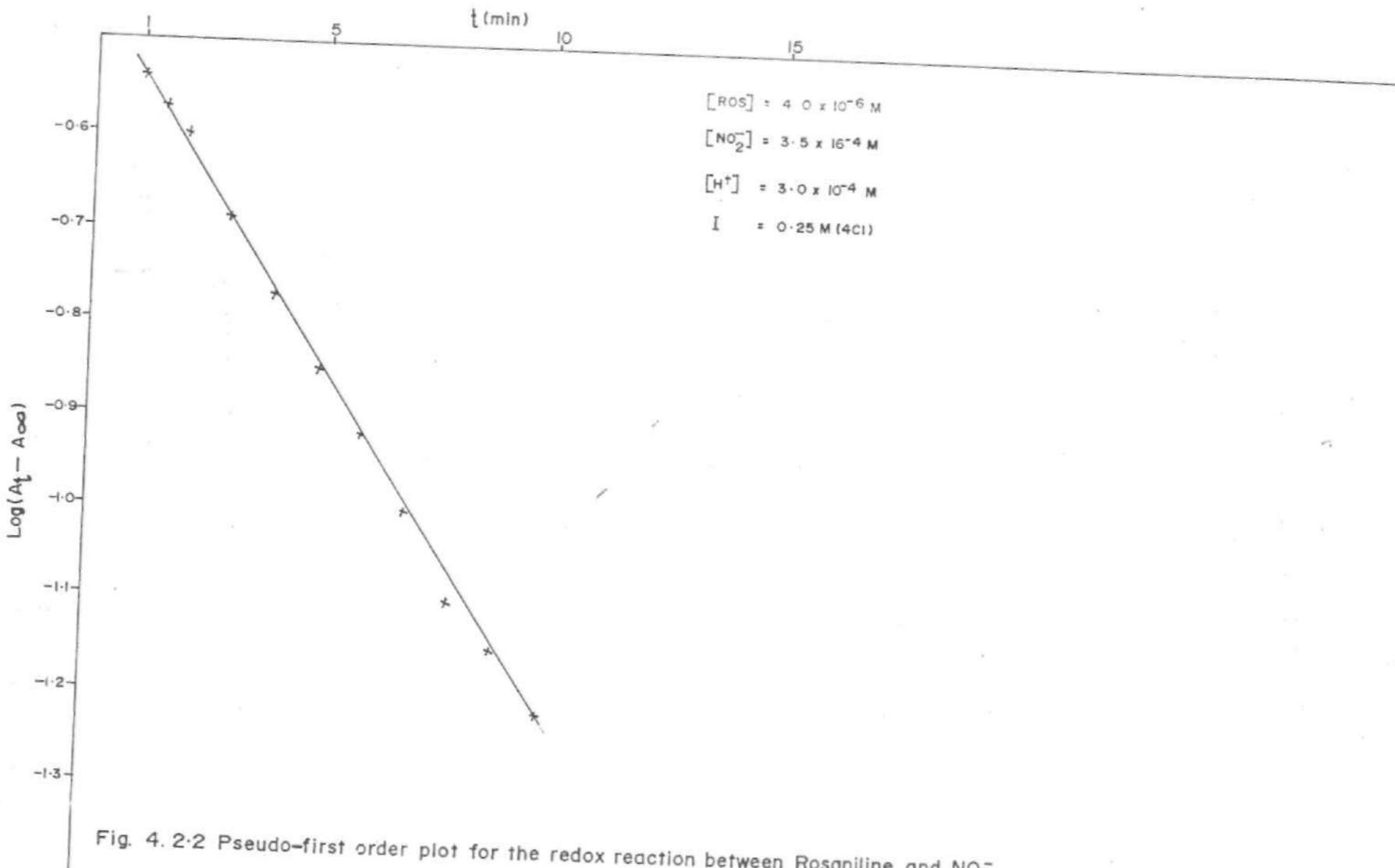


Fig. 4.2·2 Pseudo-first order plot for the redox reaction between Rosaniline and NO_2^-

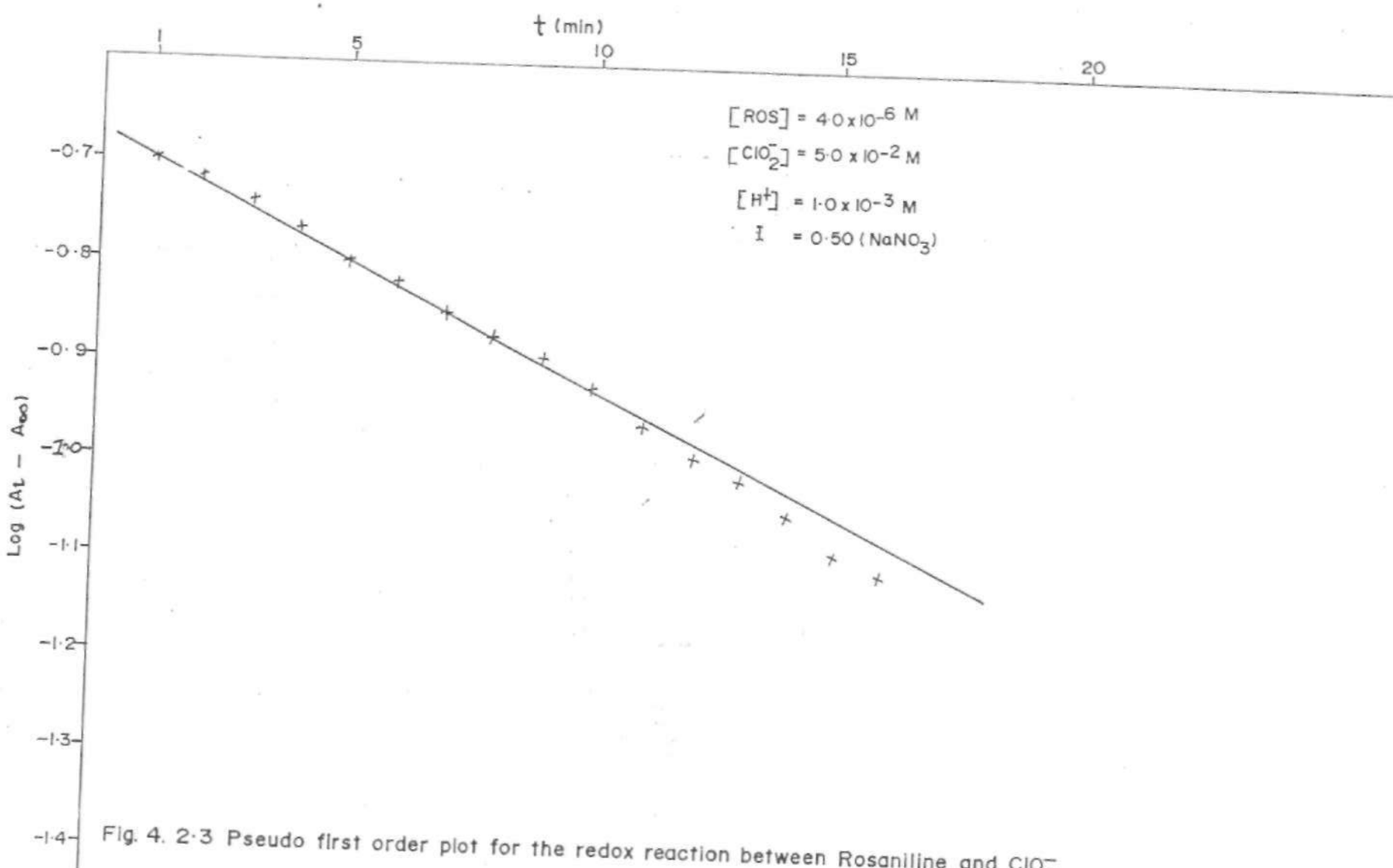


Fig. 4. 2·3 Pseudo first order plot for the redox reaction between Rosaniline and ClO_2^-

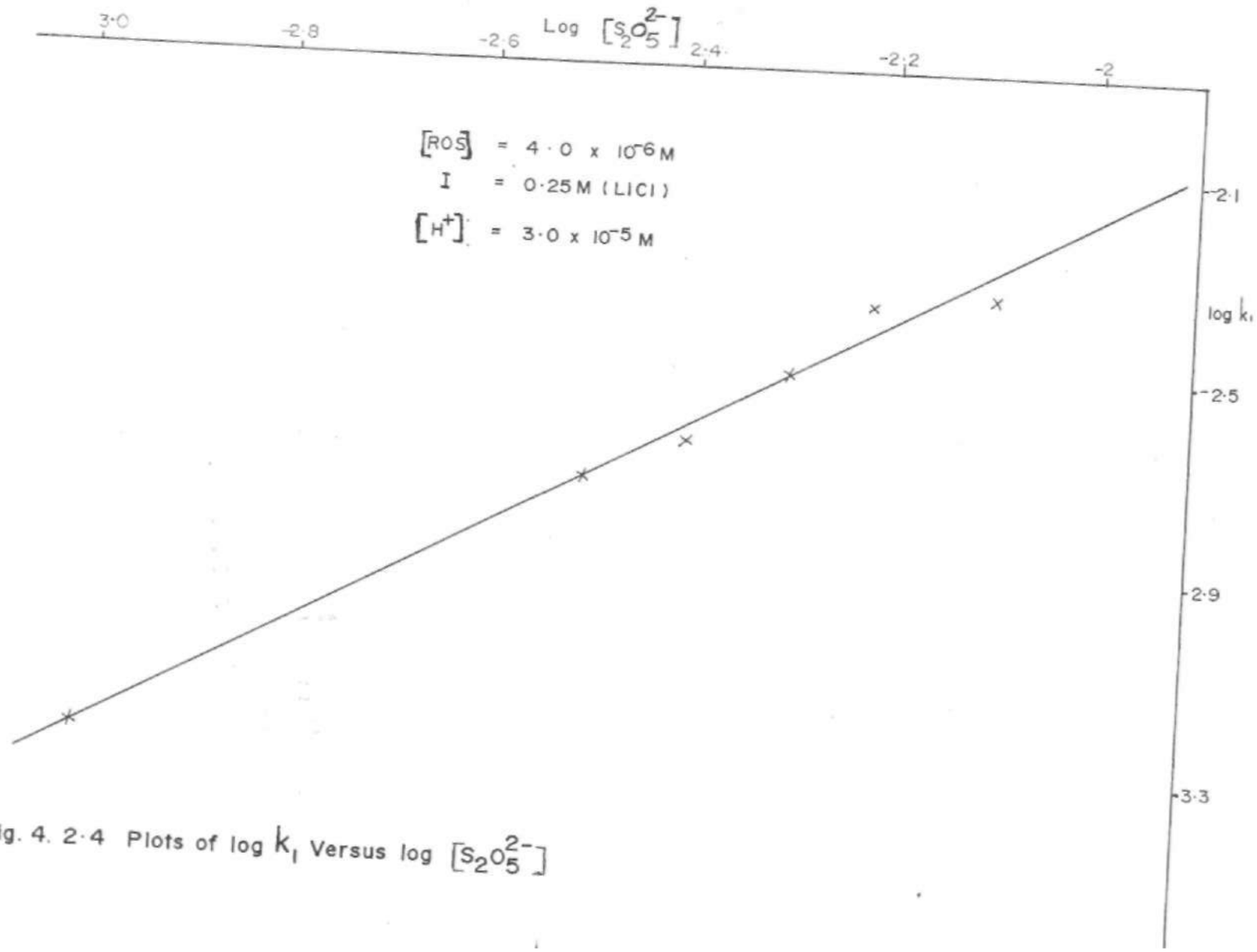


Fig. 4. 2·4 Plots of log k_1 Versus log $[S_2O_5^{2-}]$

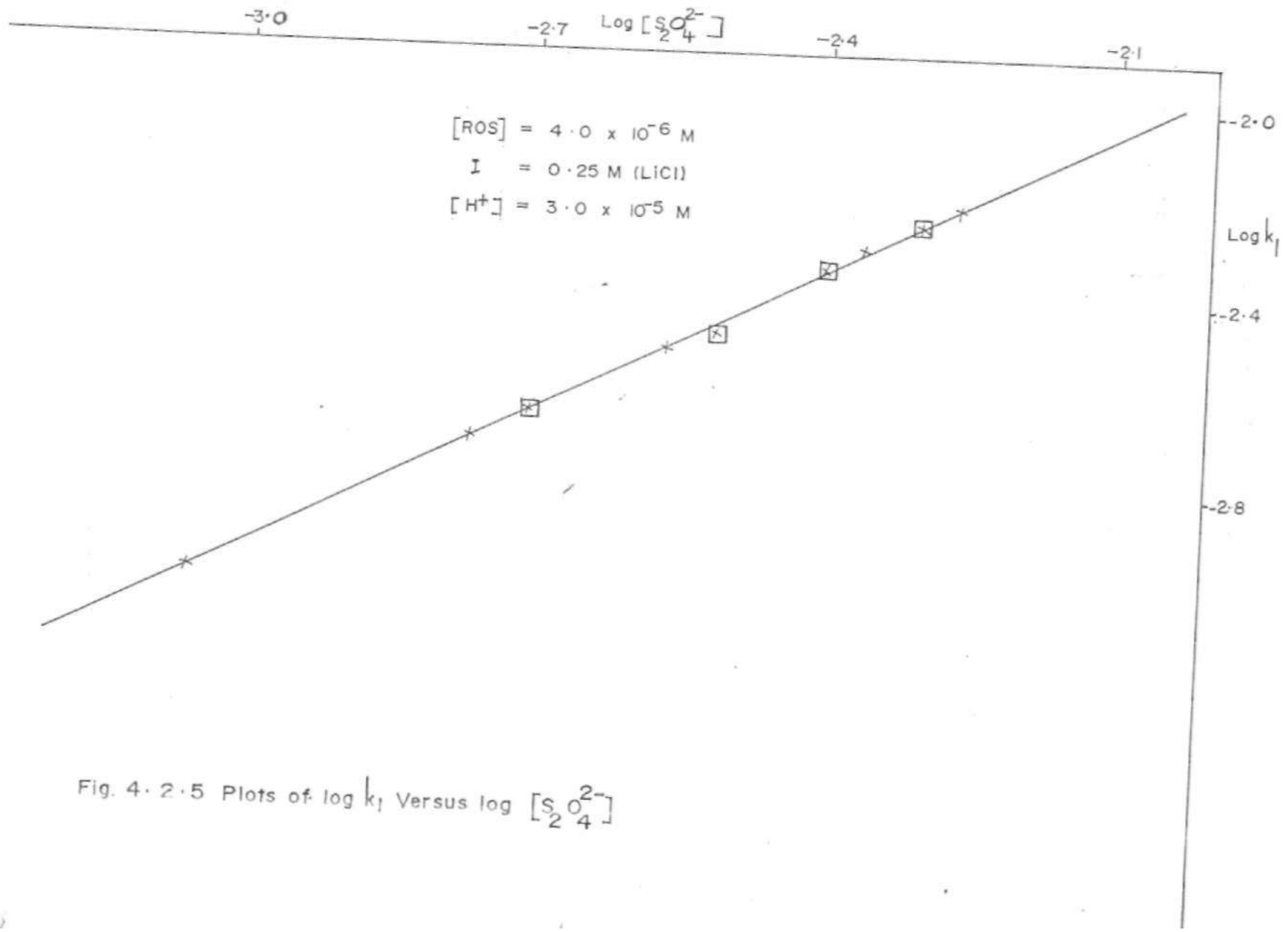


Fig. 4·2·5 Plots of log k_1 Versus log $[S_2O_4^{2-}]$

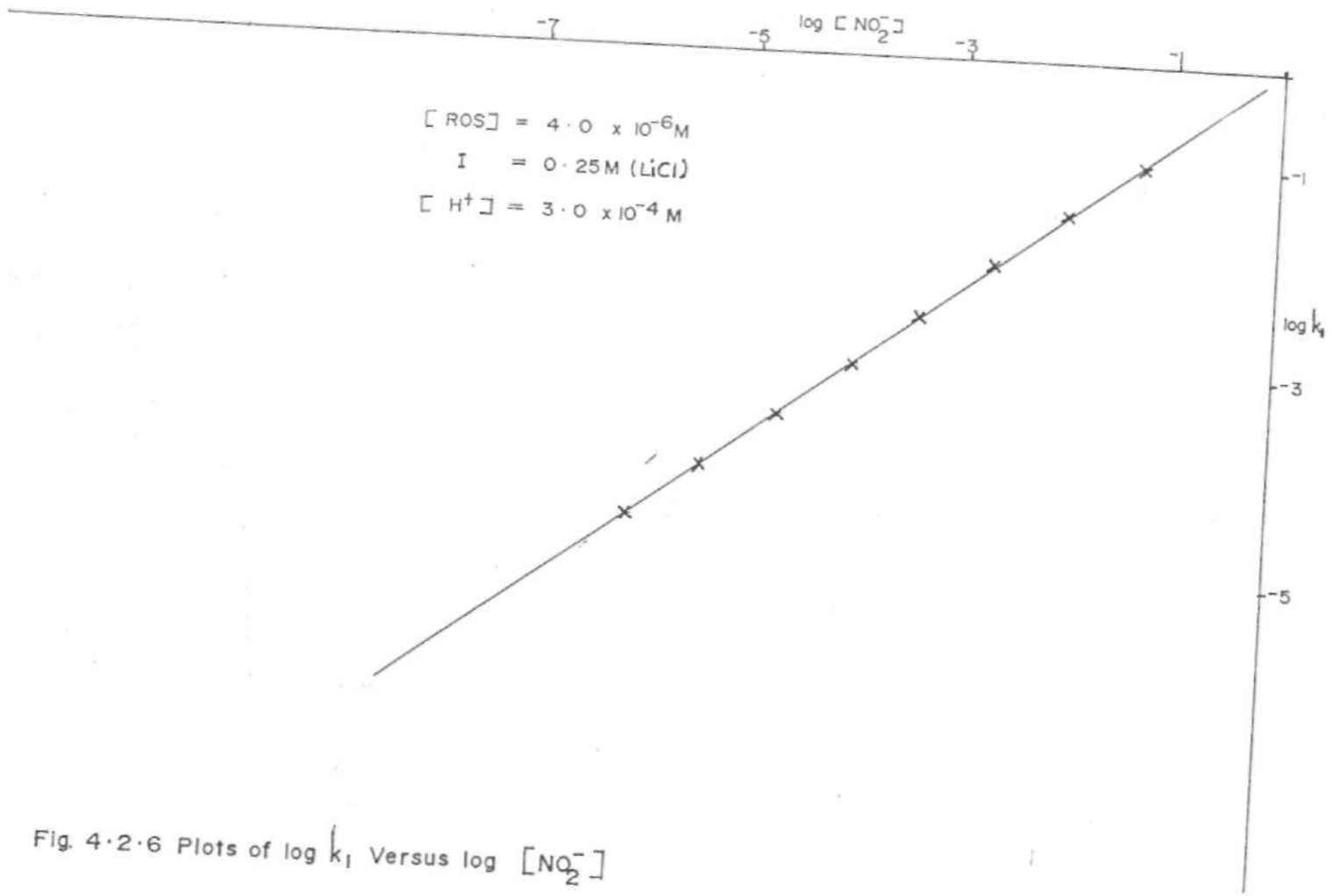


Fig. 4·2·6 Plots of log k_1 Versus log $[NO_2^-]$

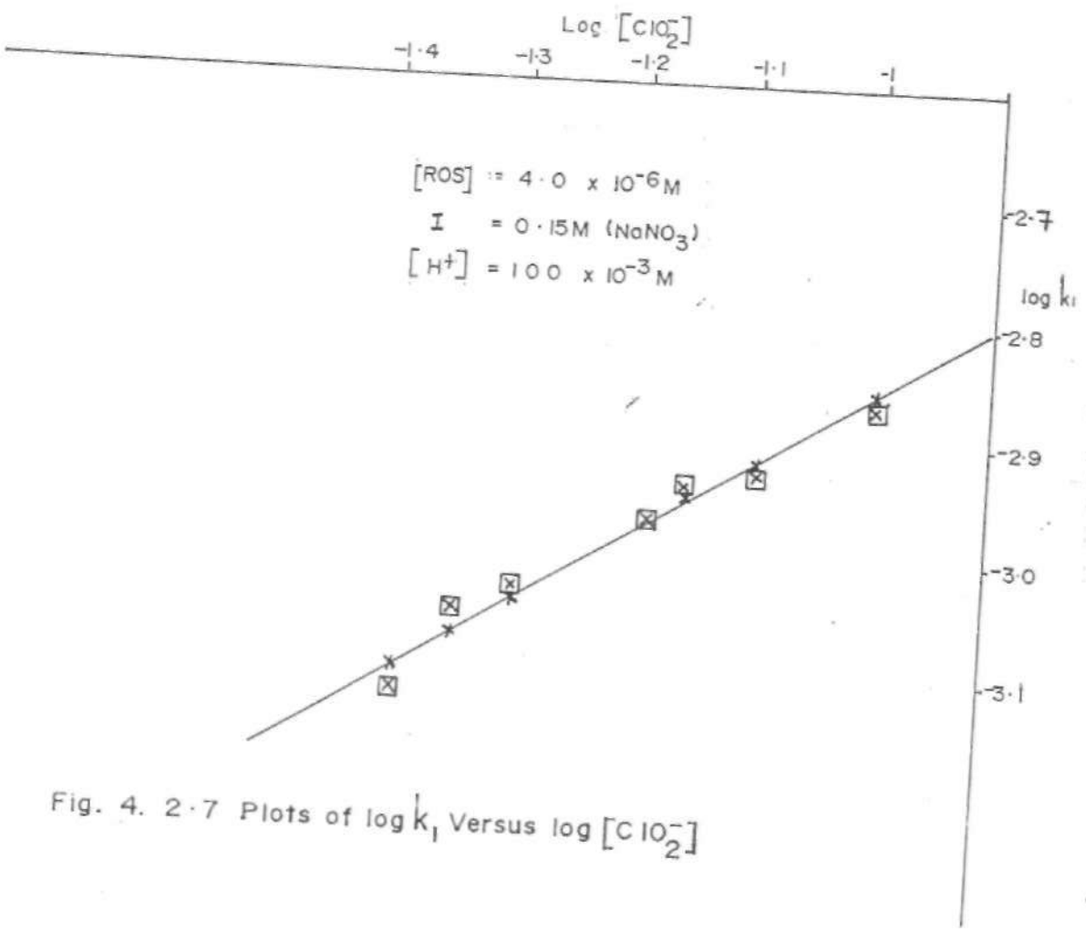


Fig. 4. 2·7 Plots of log k_1 Versus log $[ClO_2^-]$

and for chlorite ion at I = 0.5 M ($NaNO_3$),$[H^+]$=3x 10^{-4}M(HNO_3) the rate of the reaction conforms to equation (28) below:

$$-\frac{d[ROS]}{dt} = k_{\frac{3}{2}}[ROS][ClO_2^-]^{\frac{1}{2}} \quad \text{..... (28)}$$

$k_{3/2}$ = Three-half rate constant

The second order rate constant and three-half order rate constants, calculated from $k_1/[ClO_2^-]^{1/2}$ were fairly constant, further supporting that the reaction is first order with respect to $[S_2O_5^{2-}]$, $[S_2O_4^{2-}]$, $[NO_2^-]$ and half order with respect to $[ClO_2^-]$. The plot of log k_1 versus log [R] are given in figure 4.2.4 - 4.2.7.

Rosaniline - $S_2O_5^{2-}$ System

$k_2 = (6.24 \pm 0.53) \times 10^{-1}\ M^{-1}s^{-1}$ at $[H^+] = .3 \times 10^{-4}$ M I = 0.25 M(LiCl)

Rosaniline - $S_2O_4^{2-}$ System

$k_2 = (10.42 \pm 1.10) \times 10^{-1}\ M^{-1}s^{-1}$ at $[H^+] = 3 \times 10^{-4}$ M I = 0.25 M(LiCl)

Rosaniline - NO_2^- System

$k_2 = 7.81 \pm 1.58\ M^{-1}s^{-1}$ at $[H^+] = 3 \times 10^{-4}$M I = 0.25 M(LiCl)

Rosaniline - ClO_2^- system

$k_{3/2} = (4.16 \pm 0.26) \times 10^{-2}\ M^{-1/2}\ s^{-1}$ at $[H^+] = 1 \times 10^{-3}$ M I = 0.5 M($NaNO_3$)

TABLE 4.0

Pseudo-first order and second order rate constants for the reaction of rosaniline and $S_2O_5^{2-}$.

[ROS] = 4×10^{-6} M, I = 0.25 M (LiCl), T = 30 °C λ_{max} = 545 nm.

$10^3[S_2O_5^{2-}]$M	$10^5[H^+]$M	I.(LiCl)M	$10^4k_1s^{-1}$	$10^1k_2M^{-1}s^{-1}$
1.0	30.0	0.25	6.31	6.31
2.4	30.0	0.25	13.99	5.83
3.0	30.0	0.25	19.63	6.56
4.0	30.0	0.25	23.03	5.76
5.0	30.0	0.25	31.28	6.26
6.0	30.0	0.25	44.07	7.35
8.0	30.0	0.25	46.06	5.76
3.0	1.0	0.25	42.22	14.10
3.0	5.0	0.25	34.73	11.56
3.0	9.0	0.25	31.74	10.56
3.0	30.0	0.25	19.58	6.53
3.0	100.0	0.25	12.98	4.33
3.0	30.0	0.05	40.40	13.47
3.0	30.0	0.07	36.71	12.24
3.0	30.0	0.12	31.19	10.40
3.0	30.0	0.25	19.68	6.56
3.0	30.0	0.30	17.21	5.74
3.0	30.0	0.35	15.45	5.15

TABLE *4.1*

Pseudo-first order and second order rate constants for the reaction of rosaniline and $S_2O_4^{2-}$

[ROS] = 4×10^{-6} M, I = 0.25 M (LiCl) T = 30 °C

λ_{max} = 545 nm.

$10^3[S_2O_4^{2-}]$M	$10^5[H^+]$M	I.(LiCl)M	$10^4 k_1 s^{-1}$	$10^1 k_2 M^{-1} s^{-1}$
1.0	30·0	0.25	8.90	8.90
2.4	30·0	0.25	22.14	11.07
3.0	30·0	0.25	33.48	11.16
4.0	30·0	0.25	46.06	11.51
5.0	30·0	0.25	55.98	11.20
6.0	30·0	0.25	55.07	9.18
8.0	30·0	0.25	79.17	9.90
3.0	9·0	0.25	94.21	31.40
3.0	20·0	0.25	44.38	14.79
3.0	30·0	0.25	32.90	10.97
3.0	40·0	0.25	29.85	9.95
3.0	50·0	0.25	26.26	8.75
3.0	60·0	0.25	20.32	6.77
3.0	100·0	0.25	18.10	6.03
3.0	30·0	0.14	48.33	16.11
3.0	30·0	0.17	41.41	13.80
3.0	30·0	0.21	36.36	12.12
3.0	30·0	0.25	32.24	10.75
3.0	30·0	0.30	22.16	7.39

Table 4.2 Pseudo-first order and second order rate constants for the reaction of rosaniline and NO_2^- I = 0.25 M (LiCl), T = 30 °C λ_{max} = 545 nm.

[ROS] = 4 x 10^{-6}M.

$10^4[NO_2^-]$M	$10^4[H^+]$M	I(LiCl)M	$10^3 k_1 s^{-1}$	$k_2 M^{-1} s^{-1}$
2.5	3.0	0.25	2.31	9.24
3.5	3.0	0.25	2.88	8.23
4.0	3.0	0.25	2.96	7.40
5.0	3.0	0.25	3.36	6.72
6.0	3.0	0.25	3.84	6.40
8.0	3.0	0.25	4.80	6.00
2.5	1.0	0.25	0.27	1.08
2.5	3.0	0.25	2.35	9.40
2.5	7.0	0.25	5.85	23.40
2.5	10.0	0.25	11.20	44.80
2.5	30	0.25	0.93	3.72
2.5	30	0.05	1.27	5.08
2.5	30	0.10	1.87	7.48
2.5	30	0.17	2.27	9.08
2.5	30	0.25	2.43	9.72
2.5	30	0.35	2.88	11.52
2.5	30	0.40	3.31	13.24

Table 4.3 Pseudo-first order and three-half order rate constants for the reaction of rosaniline and ClO_2^-

[ROS] = 4 x 10^{-6} M, I = 0.5 ($NaNO_3$), T = 30 °C λ_{max} = 545 nm.

$10^2[ClO_2^-]$M	$10^3[H^+]$M	I($NaNO_3$)M	$10^4 k_1 s^{-1}$	$10^3 k_{3/2} M^{-1/2} s^{-1}$
4.0	1.00	0.50	7.68	3.84
4.5	1.00	0.50	8.87	4.18
5.0	1.00	0.50	9.29	4.15
6.5	1.00	0.50	10.62	4.17
7.0	1.00	0.50	11.44	4.32
8.0	1.00	0.50	11.83	4.18
10.0	1.00	0.50	13.56	4.29
10.0	0.03	0.50	27.72	8.77
10.0	0.05	0.50	22.26	7.04
10.0	0.07	0.50	21.32	6.74
10.0	0.10	0.50	17.59	5.56
10.0	0.70	0.50	16.21	5.12
10.0	0.90	0.50	14.73	4.66
10.0	1.00	0.50	13.52	4.28
10.0	1.00	0.15	32.90	10.40
10.0	1.00	0.25	30.71	9.71
10.0	1.00	0.35	21.59	6.83
10.0	1.00	0.45	18.25	5.77
10.0	1.00	0.50	13.65	4.32
10.0	1.00	0.65	11.67	3.69
10.0	1.00	0.85	9.95	3.15
10.0	1.00	1.00	8.60	2.72

4.3.0 Effect of hydrogen ion on the rates of reaction of rosaniline and reductants.

From the results in Table 4.0-4.3, the rate constants were found to be dependent on hydrogen ion concentration in the range investigated.

Least square plots of k_H vs $1/[H^+]$ pass through the origin for the reaction involving dithionite ion and similar plot had an intercept for metabisulphite and chlorite ions reactions respectively (The plots are shown in Fig. 4.2.8 - 4.3.0).

The Plot of k_H vs $[H^+]$ for nitrite ion reaction was linear with no intercept (Fig. 4.3.1).

The acid dependent rate constant can be represented by equation (29) below for dithionite reaction and equation (30) for metabisulphite and chlorite reactions.

$$k_H = a[H^+]^{-1} \quad \ldots\ldots (29)$$

$$k_H = b + a[H^+]^{-1} \quad \ldots\ldots (30)$$

while for nitrite ion reaction:

$$k_H = a[H^+] \quad \ldots\ldots (31)$$

The overall rate equations in the acid range investigated for dithionite ion equation 32, metabisulphite and chlorite reactions (equation 33) are:

$$-\frac{d[ROS]}{dt} = a[H^+]^{-1}[ROS][R] \quad \ldots\ldots (32)$$

$$-\frac{d[ROS]}{dt} = (b + a[H^+])^{-1}[ROS][R] \quad \ldots\ldots (33)$$

R = metabisulphite, chlorite and dithionite ions while the overall rate equation for the nitrite ion reaction is as shown in equation 34.

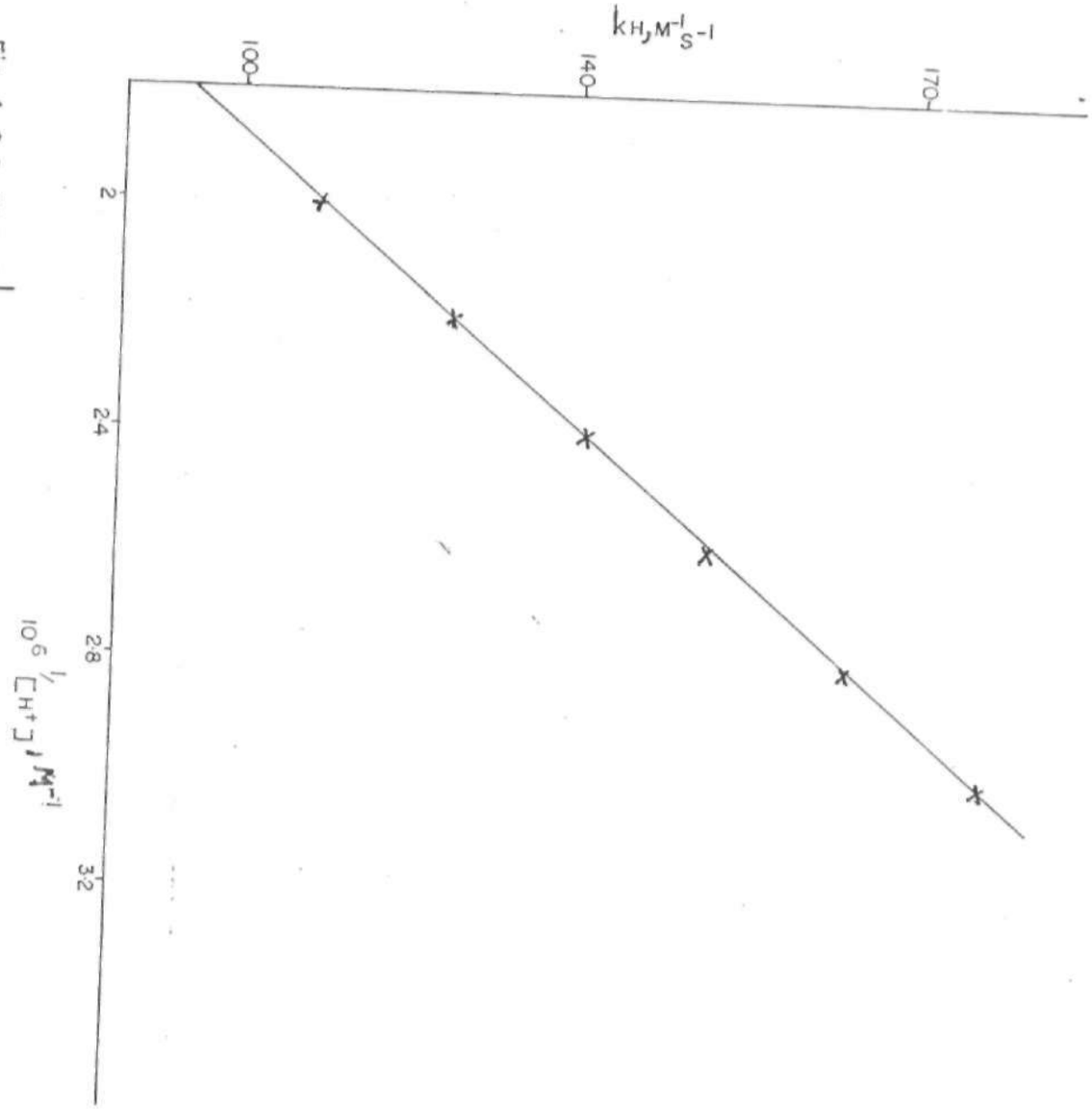


Fig. 4. 2·8 Plot of k_H Versus $[H^+]^{-1}$ for the redox reaction between Rosaniline and $S_2O_5^{2-}$

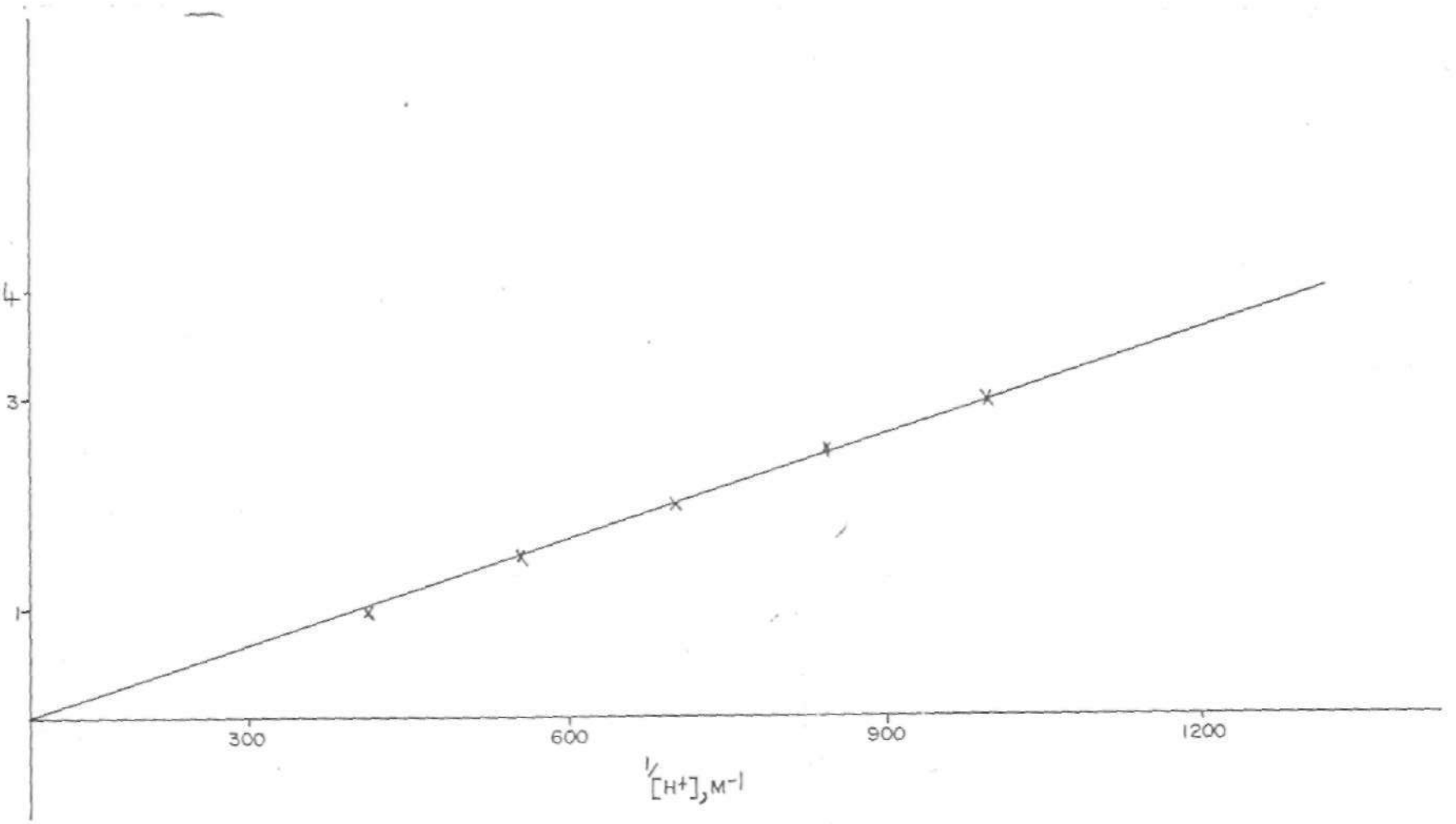


Fig. 4.2·9 Plot of k_H Versus $[H^+]^{-1}$ for the redox reaction between Rosaniline and $S_2O_4^{2-}$

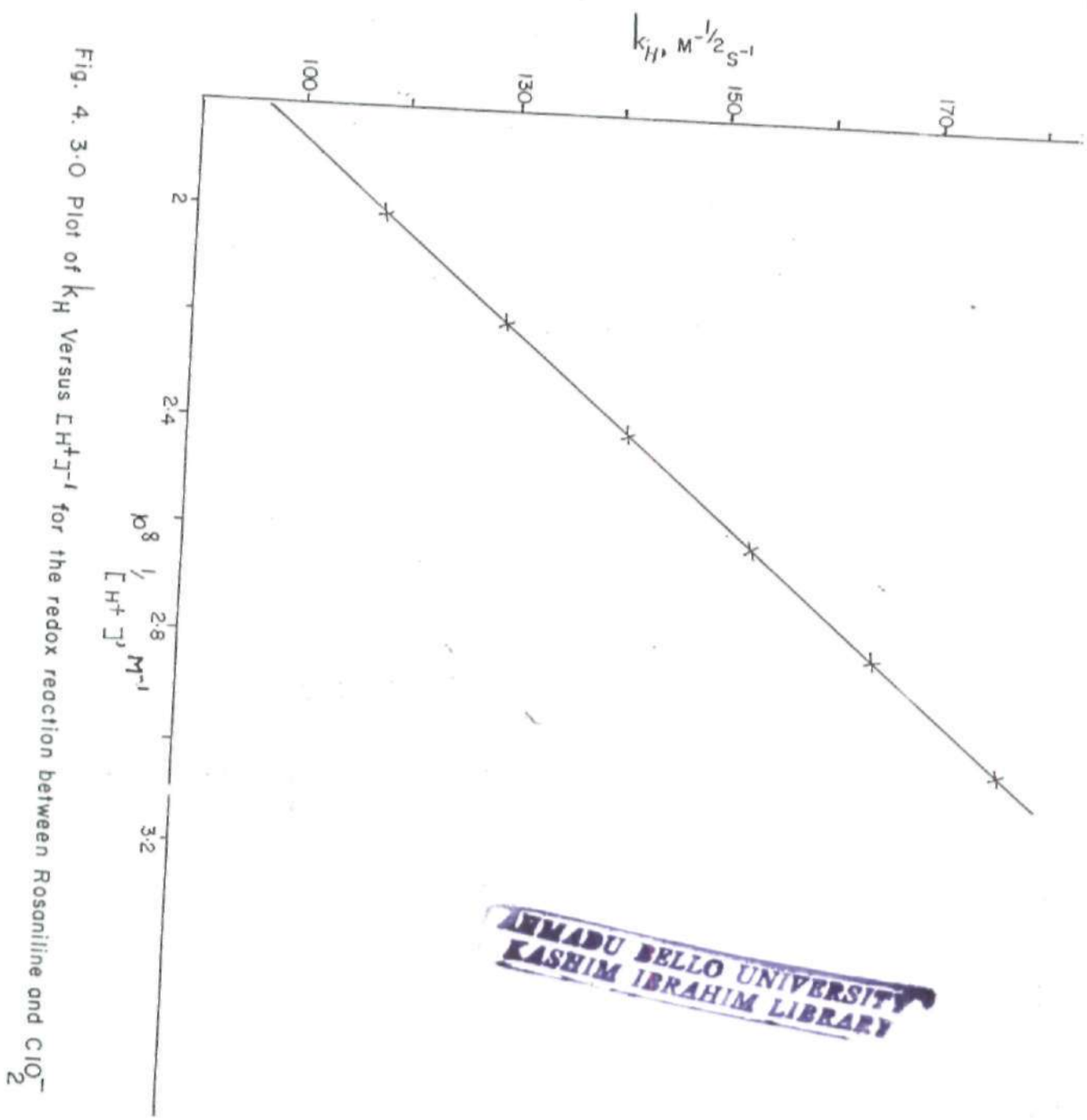


Fig. 4. 3·0 Plot of k_H Versus $[H^+]^{-1}$ for the redox reaction between Rosaniline and ClO_2^-

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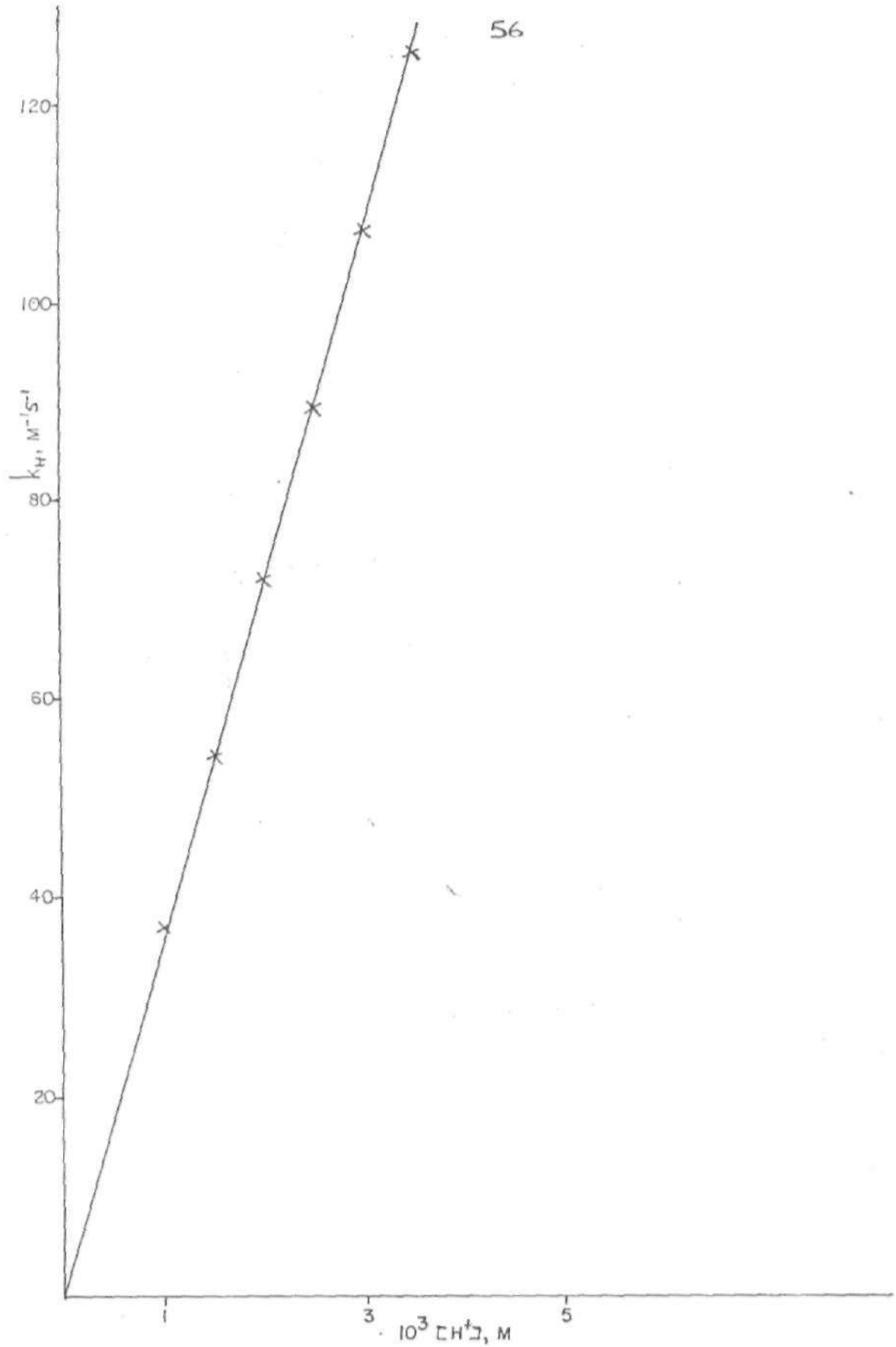


Fig. 4.3·1 Plot of k_H Versus $[H^+]$ for the redox reaction between Rosaniline and NO_2^-

$$-\frac{d[ROS]}{dt} = a[H^+][ROS][NO_2^-] \quad \text{.....(34)}$$

ROS = Rosaniline.

'a' is the slope of k_H versus $[H^+]$ or $[H^+]^{-1}$ and 'b 'is the intercept.

The values of 'a' and 'b' for the reactions were determined and are presented in table 4.4.

Table 4.4: Values of the slope (a) and the intercept (b) for the acid dependence studies.

System	'a'	'b'	I (M)	10^4 $[H^+]$ M range
ROS - $S_2O_3^{2-}$	1.53×10^{-4} s^{-1}	55.0 M^{-1} s^{-1}	0.25 (LiCl)	0.1 - 3.0
ROS - $S_2O_4^{2-}$	3.33×10^{-4} s^{-1}	-	0.25 (LiCl)	0.9 - 10.0
ROS - NO_2^-	0.903 M^{-2} s^{-1}	-	0.25 (LiCl)	1.0 - 3.0
ROS - ClO_2^-	$6.93 \times 10^{-7} M^{-3/2}$ s^{-1}	60.0 $M^{-1/2}$ s^{-1}	0.5M ($NaNO_3$)	0.1 - 10

4.4. The effect of added anions

The concentrations of all other reactants were kept constant at I = 0.25 M (LiCl) for metabisulphite, dithionite and nitrite ions and I = 0.5 M ($NaNO_3$) for chlorite ions. The effect of added anions on the rates of the reactions were investigated for $[X^{n-}] = (1 \times 10^{-5} - 1 \times 10^{-1}$ M) and x = $C_2O_4^{2-}$, $HCOO^-$, CH_3COO^-, NO_3^-. It was ascertained that the anions did not react with the oxidant or reductant.

For the rosaniline - $S_2O_5^{2-}$ system, addition of CH_3COO^- and NO_3^- were observed to increase the rate constants of the reaction, while the addition of the $HCOO^-$ and CH_3COO^- increased the rate constant for the rosaniline - $S_2O_4^{2-}$ reaction. Similar effects on the rate constant were observed when $HCOO^-$, was added to the rosaniline - ClO_2^- reaction while the addition of the anions $HCOO^-$, $C_2O_4^{2-}$, CH_3COO^- to the rosaniline - NO_2^- system were observed to decrease the rate constant of the reaction.

Results are presented in Tables 4.5 - 4.8. The anion-dependent rate constants k(x) are represented by equation 35.

$$k(x) = p + q[x] \quad \text{..... (35)}$$

k(x) = $k_2(x)$ for rosaniline $S_2O_5^{2-}$, rosaniline-$S_2O_4^{2-}$, and rosaniline - NO_2^- systems.

k(x) = $k_{3/2}(x)$ for rosaniline - ClO_2^- system.

The plots of k(x) versus [x] were linear figures (4.3.2 - 4.3.9).

<u>For rosaniline - $S_2O_5^{2-}$ system</u>

$P(NO_3^-) = 0.75\ M^{-1}s^{-1}$ $\quad$ $P(NO_3^-) = 91.84\ M^{-2}s^{-1}$

I = 0.25 M(LiCl)

For rosaniline - $S_2O_4^{2-}$ system

$P(HCOO^-) = 100\ M^{-1}s^{-1}$ $q(HCOO^-) = 8.800\ M^{-2}s^{-1}$

$P(CH_3COO^-) = 1.4\ M^{-1}s^{-1}$ $q(CH_3COO^-) = 2222.22\ M^{-2}s^{-1}$

I = 0.25 M(LiCl)

For rosaniline - NO_2^- system

$p(HCOO^-) = 8.40 \times 10^{-3}\ M^{-1}s^{-1}$ $q(HCOO^-) = 5.13 \times 10^{-2}\ M^{-2}s^{-1}$

$p(CH_3COO^-) = 8 \times 10^{-3}\ M^{-1}s^{-1}$ $q(CH_3COO^-) = 0.091 M^{-2}s^{-1}$

$p(C_2O_4^{2-}) = 9.4 \times 10^{-3}\ M^{-1}s^{-1}$ $q(C_2O_4^{2-}) = 0.11\ M^{-2}s^{-1}$

I = 0.25 M (LiCl)

For rosaniline - ClO_2^- System

$p(HCOO^-) = 6.0 \times 10^{-4}\ M^{-1/2}s^{-1}$ $q(HCOO^-) = 0.183\ M^{-3/2}s^{-1}$

I = 0.5 M ($NaNO_3$)

4.5. Effect of added Cations.

The concentration of all other reactants were kept constant and at ionic strength of 0.25M (LiCl) and 0.5M ($NaNO_3$) for $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^- and ClO_2^- respectively. The effect of the cations on the rate of the reaction was investigated for $[Z^{n+}] = 1 \times 10^{-5} - 1 \times 10^{-1}$M ($Z^{n+} = Li^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}$)

For the rosaniline - NO_2^- systems, addition of cation (Ca^{2+}, Ba^{2+}) were observed to decrease the rate constant of the reaction while for the rosaniline - ClO_2^- system, addition of Li^{2+} and Mg^{2+} were observed to decrease the rate constant for the reaction.

Results are presented in Tables 4.5 - 4.8.

The plot of the cation - dependent rate constant versus $[Z^{n+}]$ are shown in figures 4.4.0 - 4.4.3.

The rate constant fit the equation of the form

$$k(Z^{n+}) = n + m\,[Z^{n+}] \qquad \ldots\ldots (36)$$

where n = intercept, m = slope

The values of n and m are given

rosaniline - NO_2^- system

$n(Ba^{2+}) = 3.75 \times 10^{-3}\,M^{-1/2}s^{-1}$ $M(Ba^{2+}) = 5.62 \times 10^{-5}\,M^{-3/2}s^{-1}$

$n(Ca^{2+}) = 3.70 \times 10^{-3}\,M^{-1/2}s^{-1}$ $M(Ca^{2+}) = 1.28 \times 10^{-4}M^{-3/2}s^{-1}$

rosaniline - ClO_2^- System

$n(Li^+) = 5 \times 10^{-4}\,M^{-1/2}s^{-1}$ $M(Li^+) = 0.05\,M^{-3/2}s^{-1}$

$n(Mg^{2+}) = 6 \times 10^{-4}\,M^{-1/2}s^{-1}$ $M(Mg^{2+}) = 0.5\,M^{-3/2}s^{-1}$

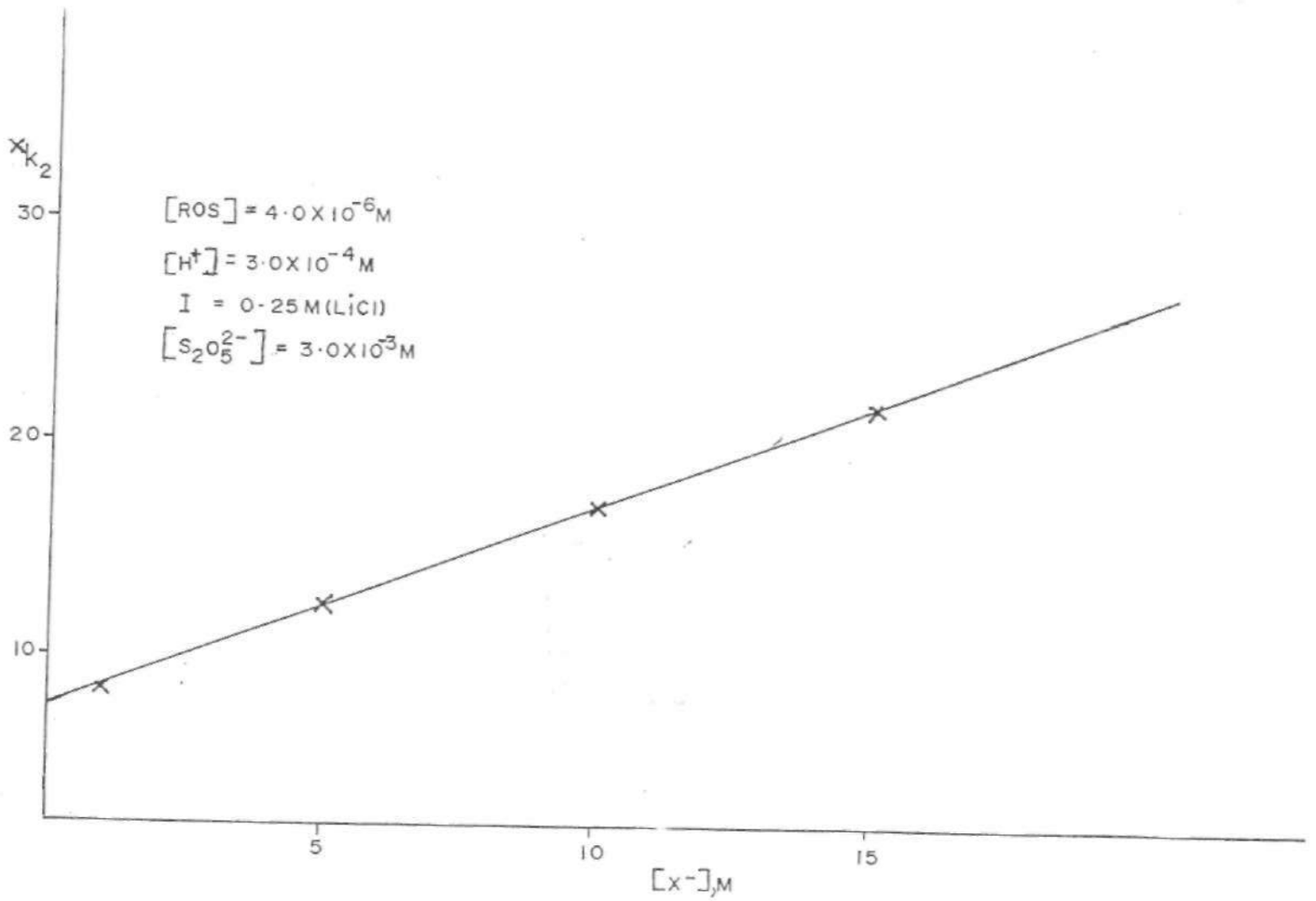


Fig. 4·3·2 Plot of $^{X}k_2$ versus $[CH_3COO^-]$ for the redox reaction between Rosaniline and $S_2O_5^{2-}$

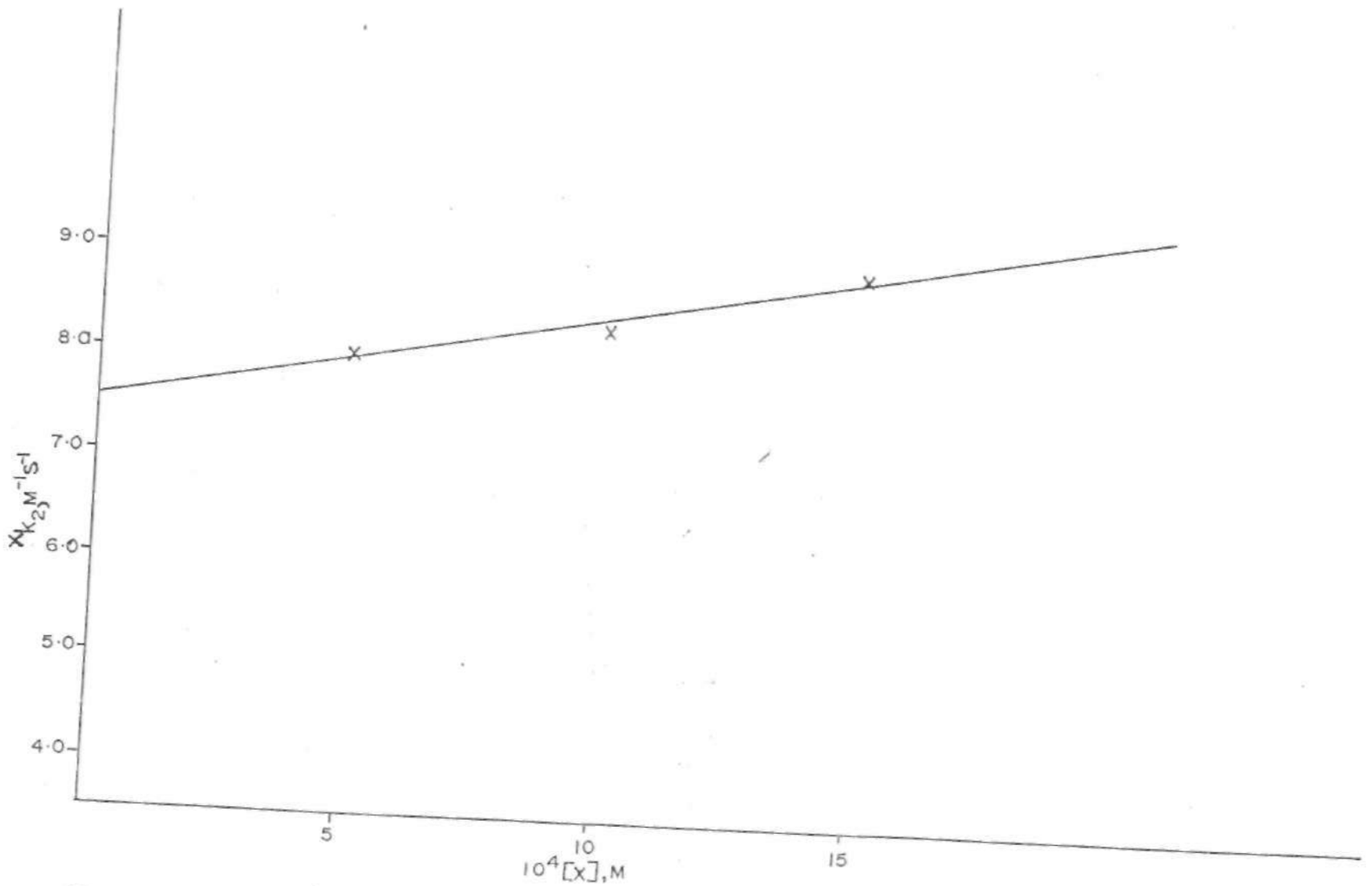


Fig. 4·3.3 Plot of $^{X}k_{2}$ Versus $[NO_3^-]$ for the redox reaction between Rosaniline and $S_2O_5^{2-}$

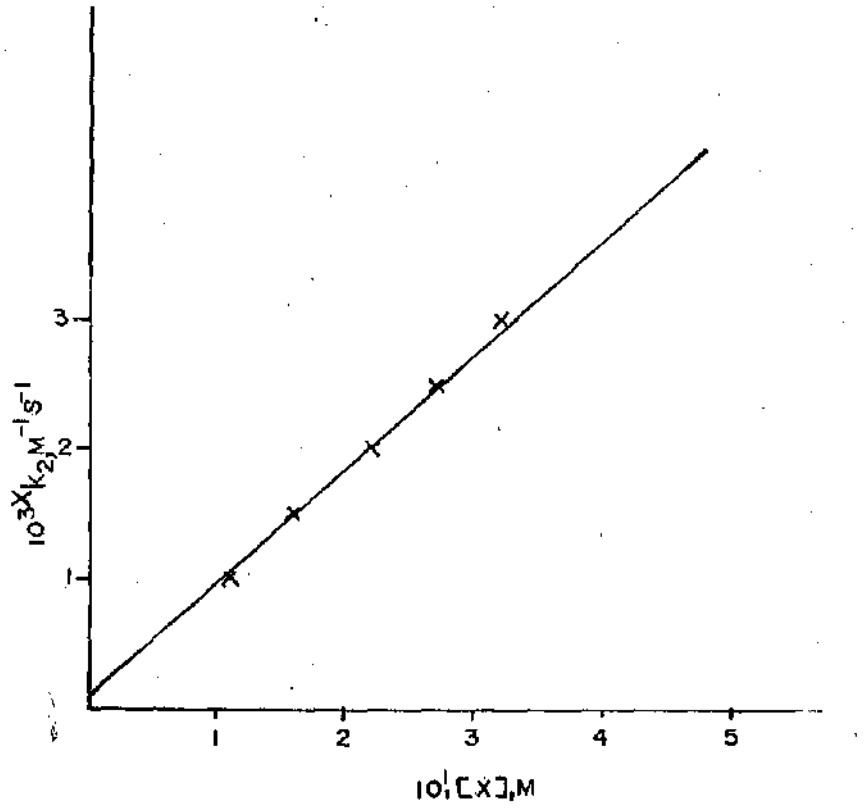


Fig. 4·3·4 Plot of ${}^{X}k_2$ versus $[HCOO^-]$ for the redox reaction between Rosaniline and $S_2O_4^{2-}$

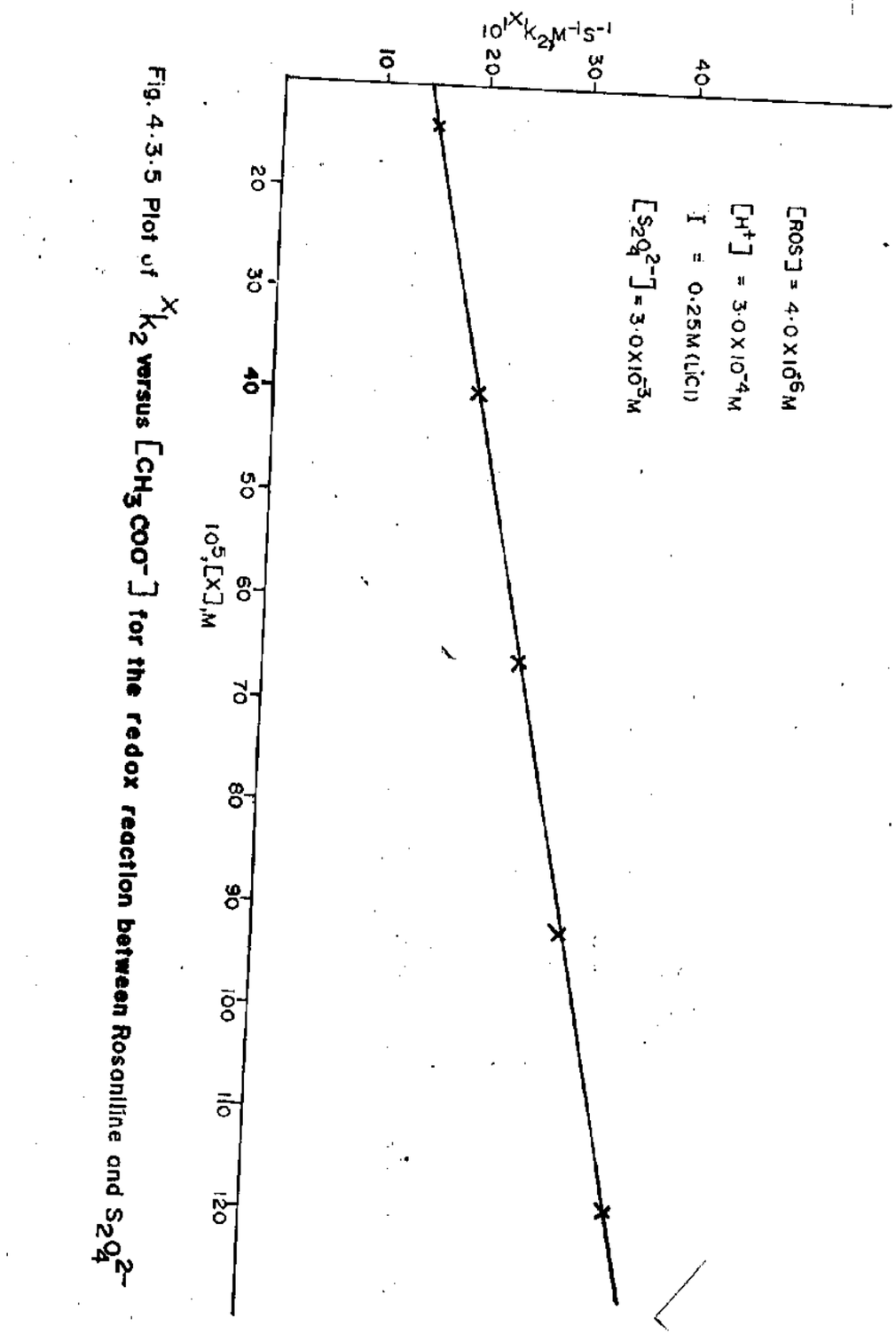


Fig. 4.3.5 Plot of $^{x}k_2$ versus $[CH_3COO^-]$ for the redox reaction between Rosaniline and $S_2O_4^{2-}$

$[ROS^-] = 4.0 \times 10^{-6}$ M

$[H^+] = 3.0 \times 10^{-4}$ M

$I = 0.25$ M (L.C.I.)

$[NO_2^-] = 2.50 \times 10^{-4}$ M

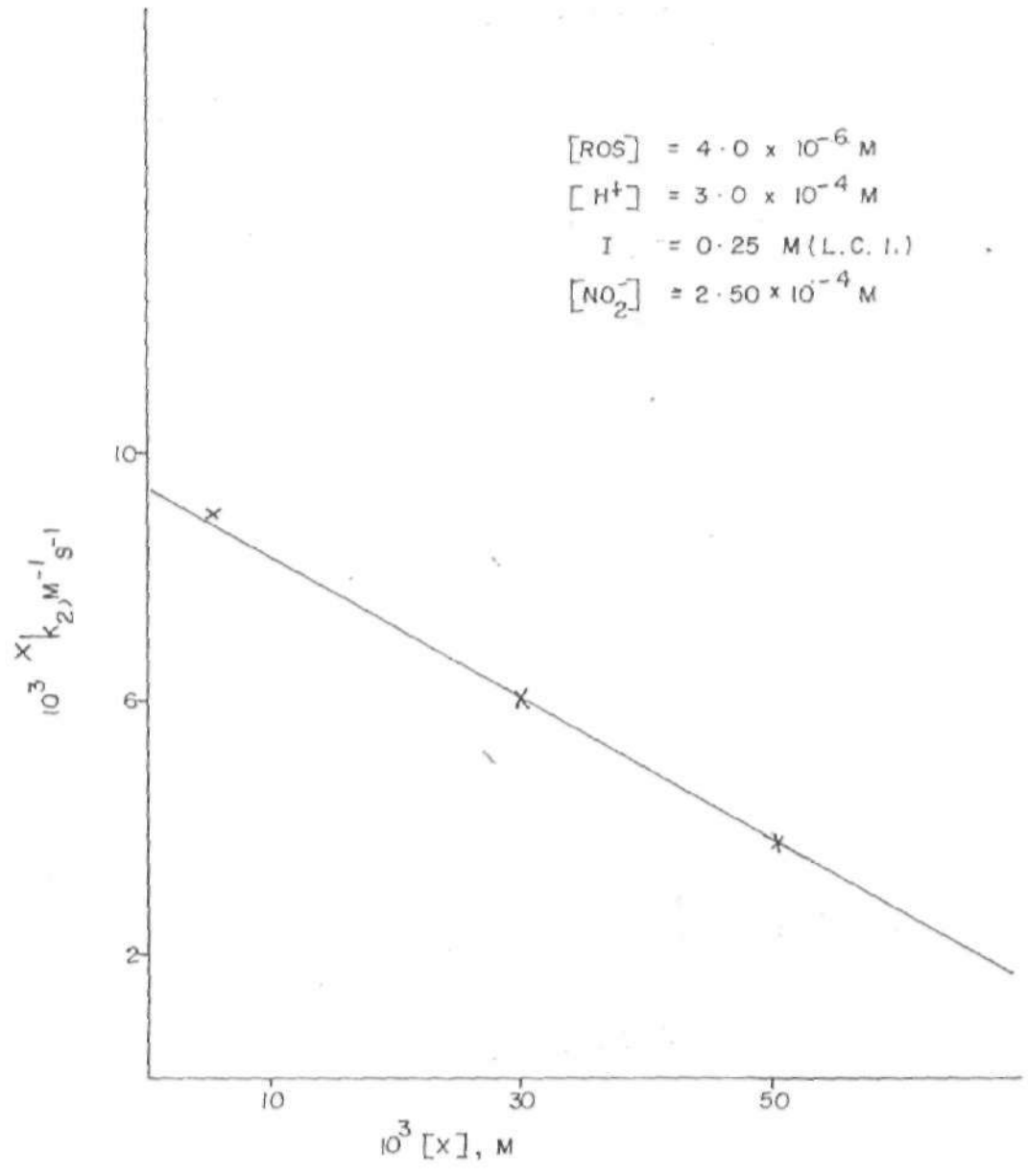


Fig. 4. 3·6 Plot of ${}^{X}k_2$ Versus $[C_2O_4^{2-}]$ for the redox reaction between Rosaniline and NO_2^-

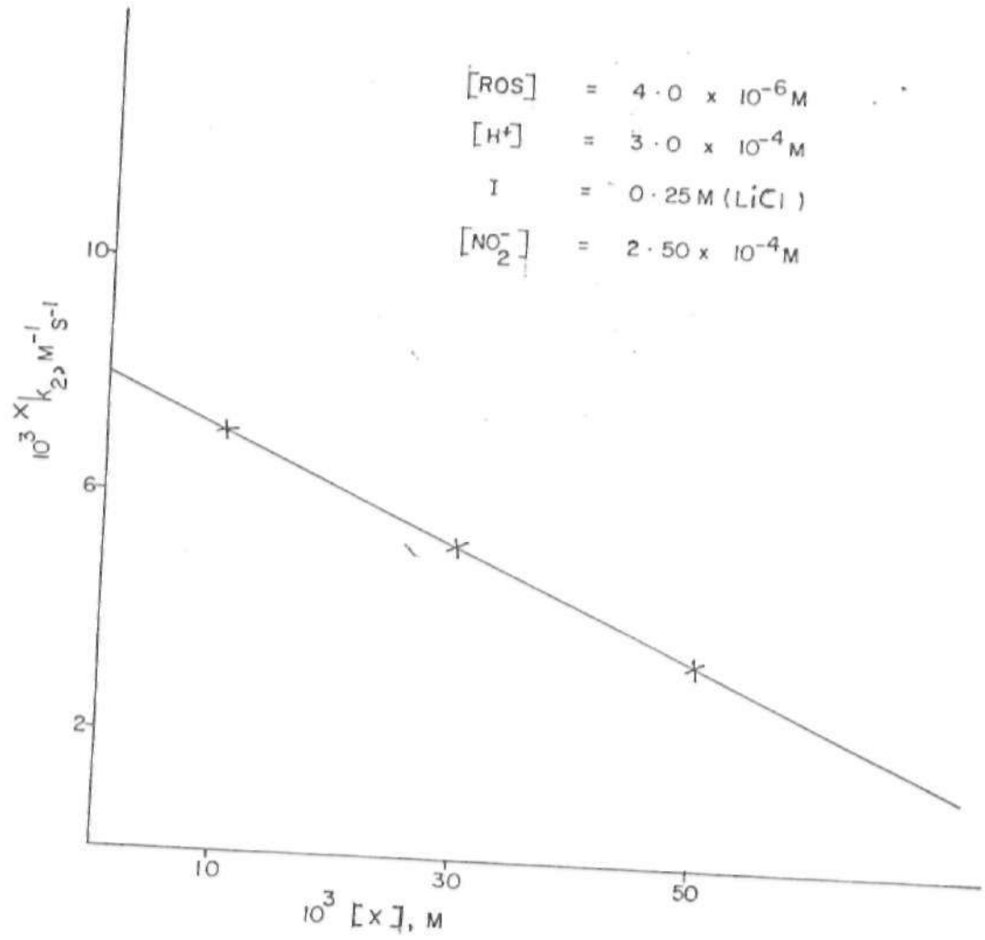


Fig. 4. 3·7 Plot of $^{x}k_2$ Versus $[CH_3COO^-]$ for the redox reaction between Rosaniline and NO_2^-

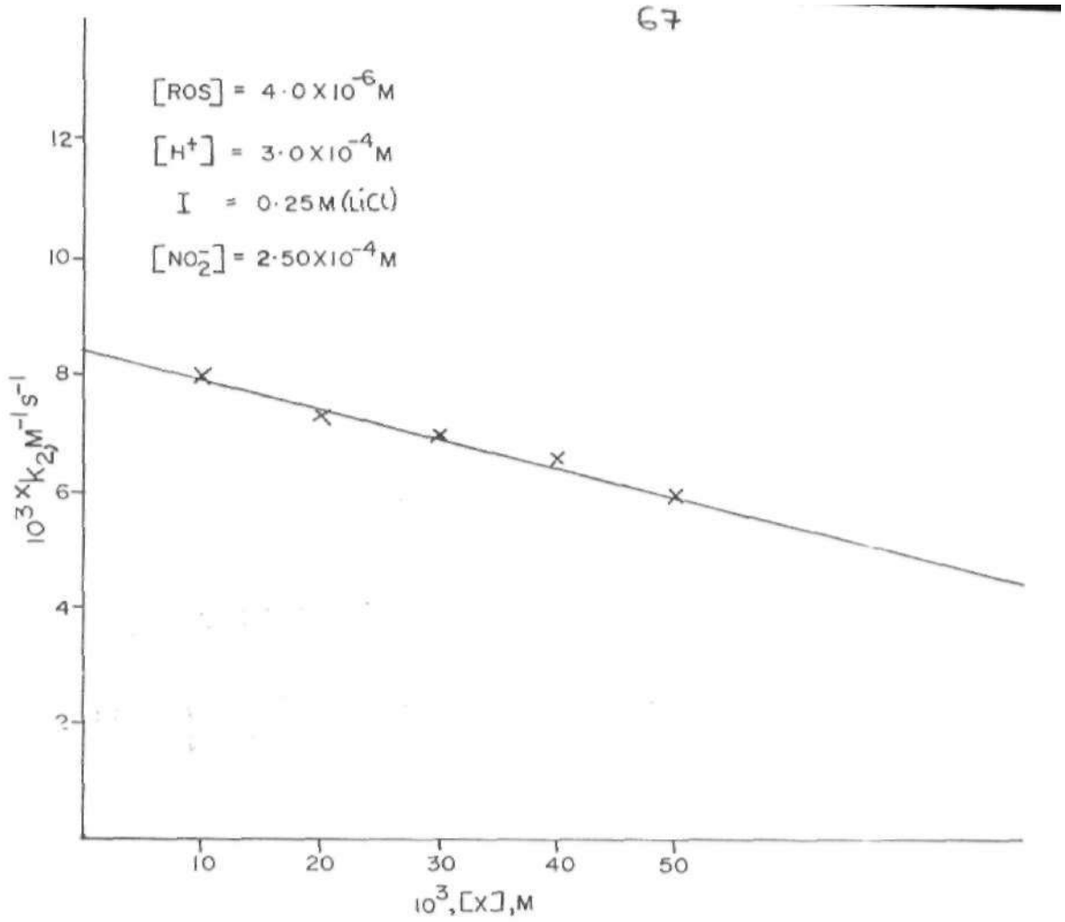


Fig. 4·3·8 Plot of $^{x}k_2$ versus [HCOO⁻] for the redox reaction between Rosaniline and NO_2^-

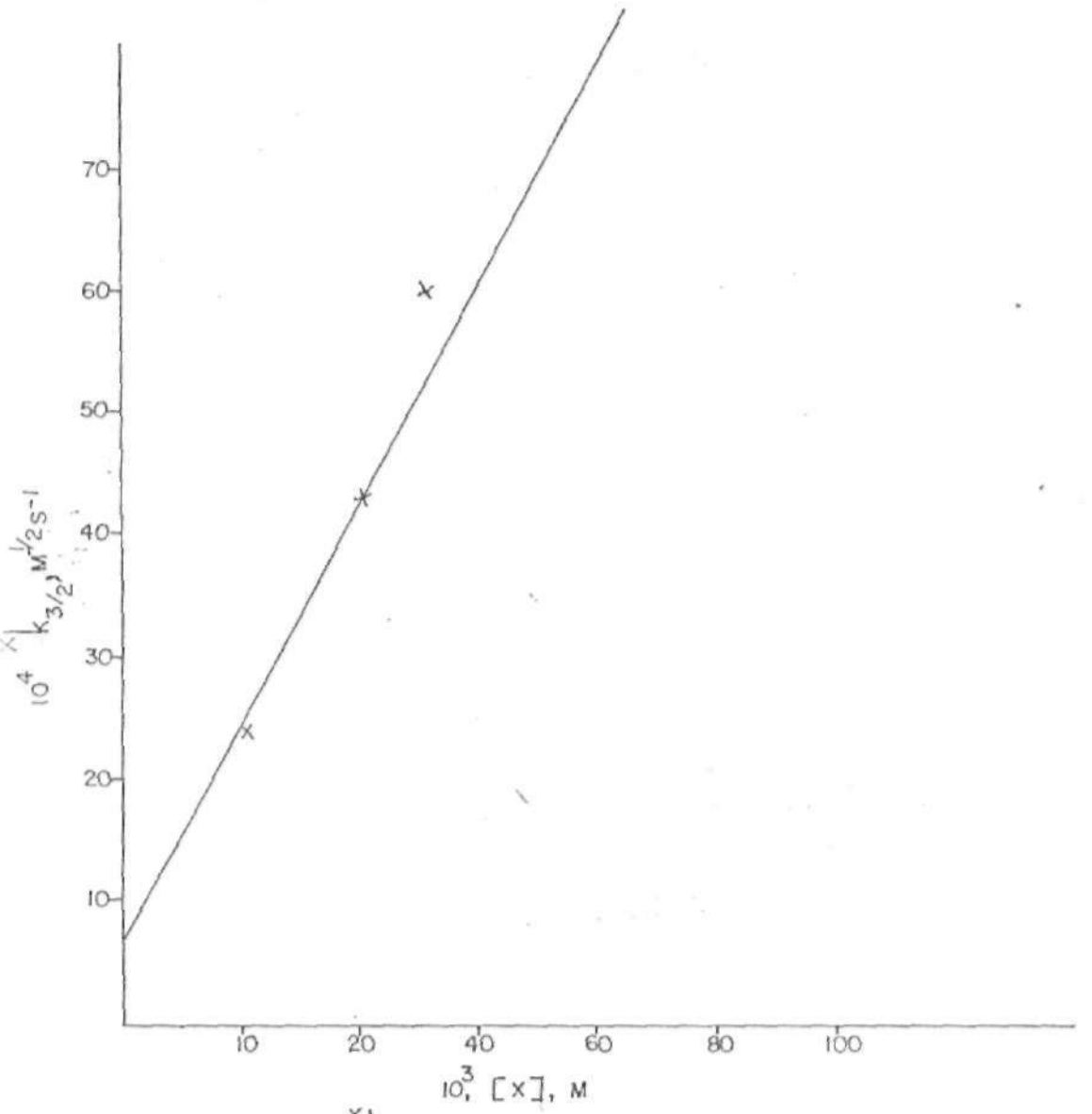
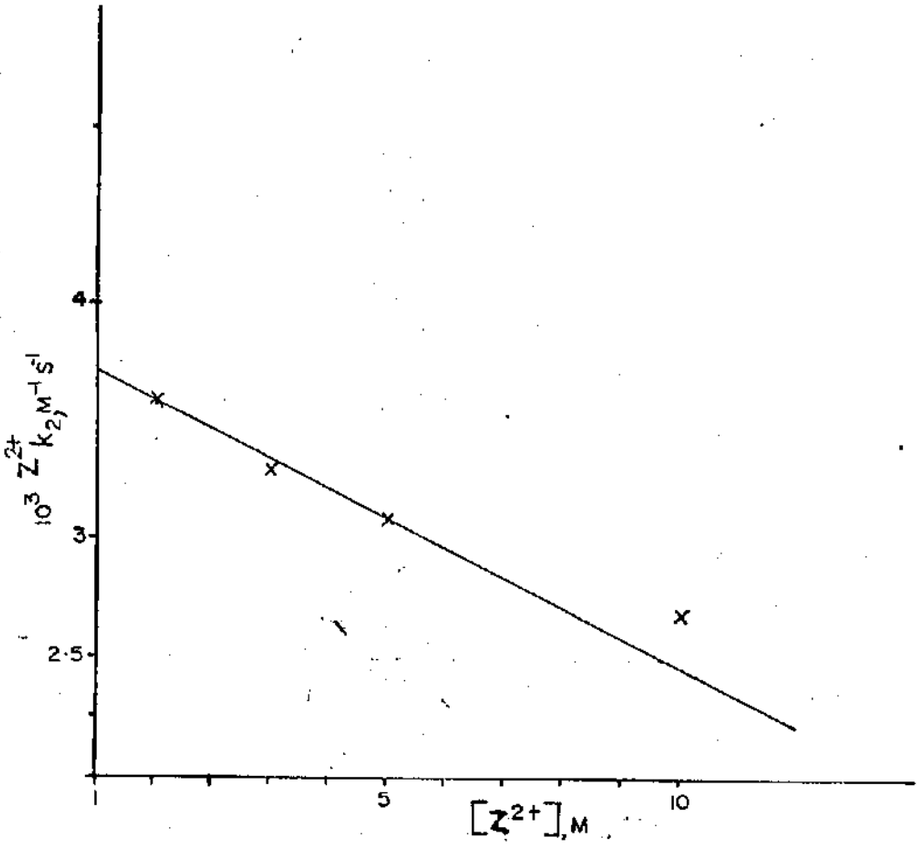


Fig. 4. 3·9 Plot of $^{X}k_{3/2}$ Versus $[HCOO^-]$ for the redox reaction between Rosaniline and ClO_2^-



Fig· 4·4·0 Plot of $^{Z^{2+}}k_2$ Versus $[Ca^{2+}]$ for the redox reaction between Rosaniline and NO_2^-

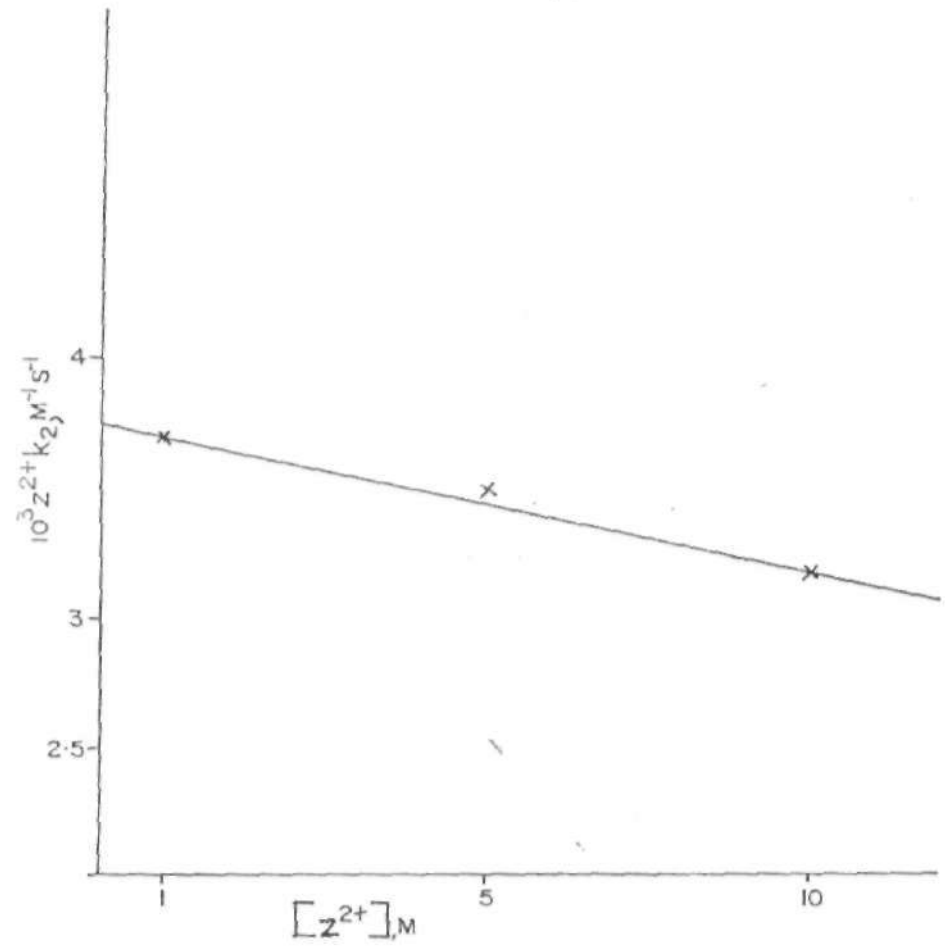


Fig. 4.4.1 Plot of $Z^{n+}k_2$ Versus $[Ba^{2+}]$ for the redox reaction between Rosaniline and NO_2^-

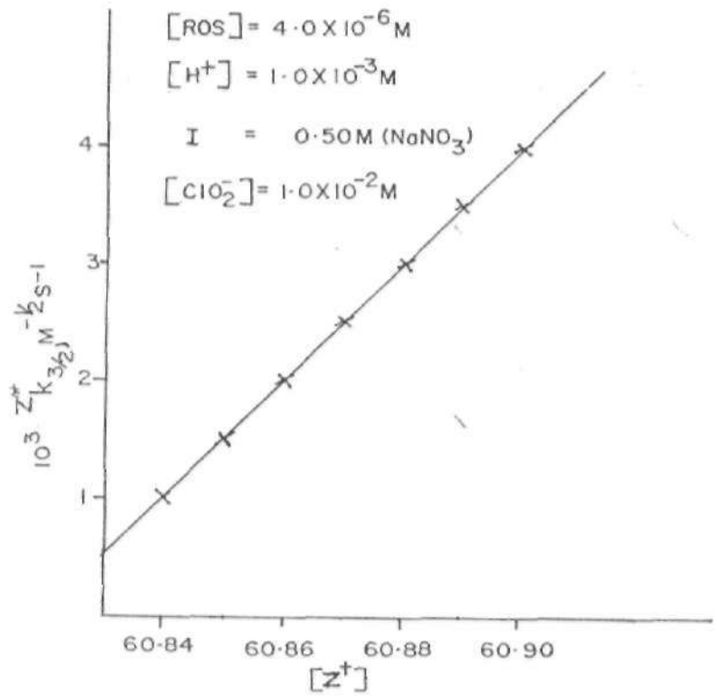


Fig. 4·4·2 Plot of $Z^{n} k_{3/2}$ Versus $[Li^{+}]$ for the redox reaction between Rosaniline and ClO_2^-

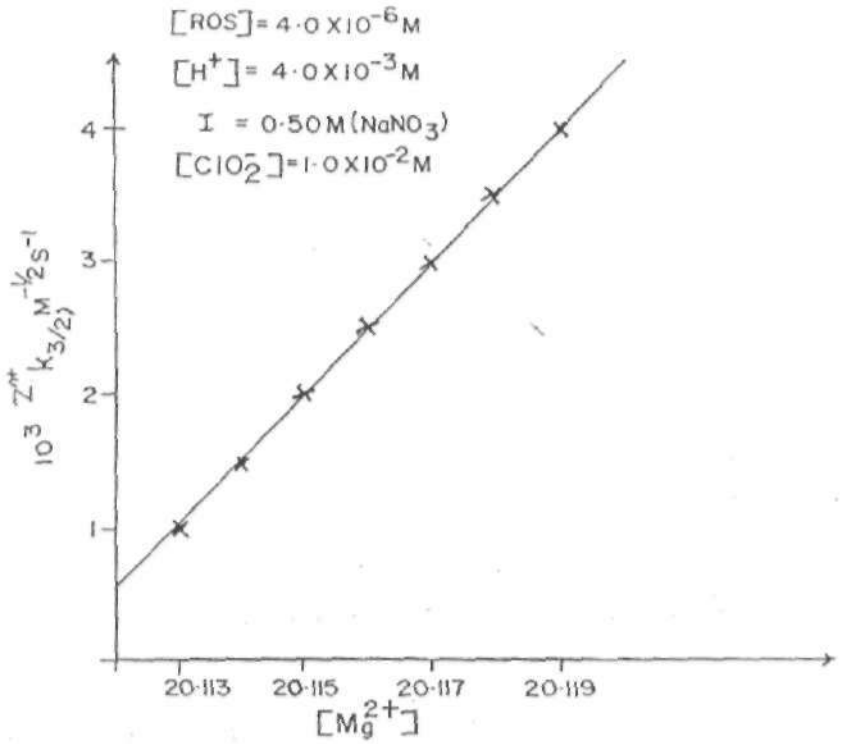


Fig. 4·4·3 Plot of $^{Z''}k_{3/2}$ Versus $[Mg^{2+}]$ for the redox reaction between Rosaniline and ClO_2^-

Table 4.5

Rate data for the effect of anion and cation on the second order rate constants for the ROS - $S_2O_5^{2-}$ reaction.

[ROS] = 4×10^{-6}M, [H^+] = 3×10^{-4}M I = 0.25 M (LiCl)

[$S_2O_5^{2-}$] = 3×10^{-3} M, λ_{max} = 545 nm, T = 30 °C

X	10^4 [x] M	$10^3 k_1 s^{-1}$	$10^1 k_2 M^{-1} s^{-1}$
CH_3COO^-	5	3.75	12.50
	10	5.12	17.06
	15	6.60	22.00
NO_3^-	5	2.40	8.01
	10	2.49	8.32
	15	2.68	8.92
Ca^{2+}	4	1.66	5.54
	8	1.79	5.96
	12	1.54	5.12
	16	1.66	5.54

Table 4.6

Rate data for the effect of anion on the second-order rate constants for the ROS - $S_2O_4^{2-}$ reaction.

$[ROS] = 4 \times 10^{-6}$ M, $[H^+] = 3 \times 10^{-4}$ M I = 0.25 M(LiCl)

$[S_2O_4^{2-}] = 3 \times 10^{-3}$ M, λ_{max} = 545 nm, T = 30 °C

X	10^5 [x] M	$10^3 k_1 s^{-1}$	$k_2 M^{-1} s^{-1}$
$HCOO^-$	10	5.85	19.50
	50	11.35	37.83
	100	23.80	79.33
CH_3COO^-	5	4.24	14.13
	50	8.50	28.33
	100	19.83	66.10

Table 4.7: Rate data for the effect of anion and cation on the second order rate constants for the ROS - NO_2^- reaction.

$[ROS] = 4 \times 10^{-6}M$, $[H^+] = 3 \times 10^{-4}M$ $I = 0.25$ M(LiCl)

$[NO_2^-] = 2.5 \times 10^{-4}M$, $\lambda_{max} = 545$ nm, $T = 30\ ^{\circ}C$.

X	10^3 [x] M	$10^6 k_1 s^{-1}$	$10^3 k_2 M^{-1} s^{-1}$
$HCOO^-$	20	1.83	7.34
	30	1.77	7.08
	40	1.64	6.58
	50	1.52	6.07
CH_3COO^-	10	1.77	7.07
	30	1.33	5.31
	50	0.85	3.39
$C_2O_4^{2-}$	10	1.83	7.32
	30	1.52	6.08
	50	0.95	3.80
Ca^{2+}	1	2.81	11.24
	3	2.59	10.36
	5	2.48	9.92
	10	2.17	8.68
Ba^{2+}	1	2.92	11.68
	5	2.75	11.00
	10	2.56	10.24

Table 4.8

Rate data for the effect of anion and cation on the second order rate constants for the ROS - ClO_2^- reaction.

$[ROS] = 4 \times 10^{-6}$ M, $[H^+] = 1 \times 10^{-3}$ M $I = 0.5$ M($NaNO_3$)

$[ClO_2^-] = 10 \times 10^{-1}$ M, $\lambda_{max} = 545$ nm, $T = 30$ °C.

X	10^3 [x] M	$10^3 k_1$ s^{-1}	$10^3 k_{3/2}$ $M^{-1/2} s^{-1}$
$HCOO^-$	1	1.82	4.06
	10	2.23	4.99
	100	2.53	5.66
$C_2O_4^{2-}$	1	1.61	3.59
	10	1.56	3.49
	50	1.43	3.19
Li^+	1	1.80	4.02
	100	1.56	3.48
	300	1.43	3.20
Mg^{2+}	0.1	1.31	4.13
	1	1.26	3.97
	10	0.97	3.06
	100	0.72	2.26

4.6 The effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range of I = 0.05 - 0.40 M (LiCl) for the rosaniline - $S_2O_5^{2-}$, rosaniline - $S_2O_4^{2-}$, rosaniline - NO_2^- reactions and 0.15 - 1.0 M ($NaNO_3$) for rosaniline - ClO_2^- reaction. The concentration of other reactants were kept constant. The rate constant was found to decrease with increase in ionic strength for rosaniline - $S_2O_5^{2-}$, rosaniline - $S_2O_4^{2-}$ and rosaniline ClO_2^- reactions while the rate constant increased with increase in ionic strength for rosaniline - NO_2^- reaction. The results are presented in Table 4.0 - 4.3.

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

$$\log k = \log k_o + 2\alpha Z_A Z_B I^{1/2} \quad \ldots\ldots (37)$$

k = The rate constant of the reaction

ko = hypothetical rate constant in medium of infinite dielectric constant

I = ionic strength

α = 0.50 at 25 °C

The plots of log k vs $I^{1/2}$ should be linear with slope $Z_A Z_B$ (at 25 °C) and values of log k_o, as intercept (Bronsted 1922)

The equation predicts a positive salt effect, i.e. an increasing rate constant with increasing salt concentration, when reactants carry charges of the same sign, negative salt effect when charges are of opposite sign and zero salt effect if either or both reactants are uncharged (Bronsted, 1922). Linear plots were obtained for the log k_1 vs $I^{1/2}$ plots (Fig. 4.4.4 - 4.4.7).

Increasing ionic strength always reduce the magnitude of the electrostatic effects since the ions become more shielded by their ion atmospheres. Thus repulsion between ions of like sign is reduced allowing them to approach one another more easily, as a result the rate constant increases while attraction between ions of opposite signs is reduced and they approach one another less readily resulting in the decrease in rate constant (Peter, 1979).

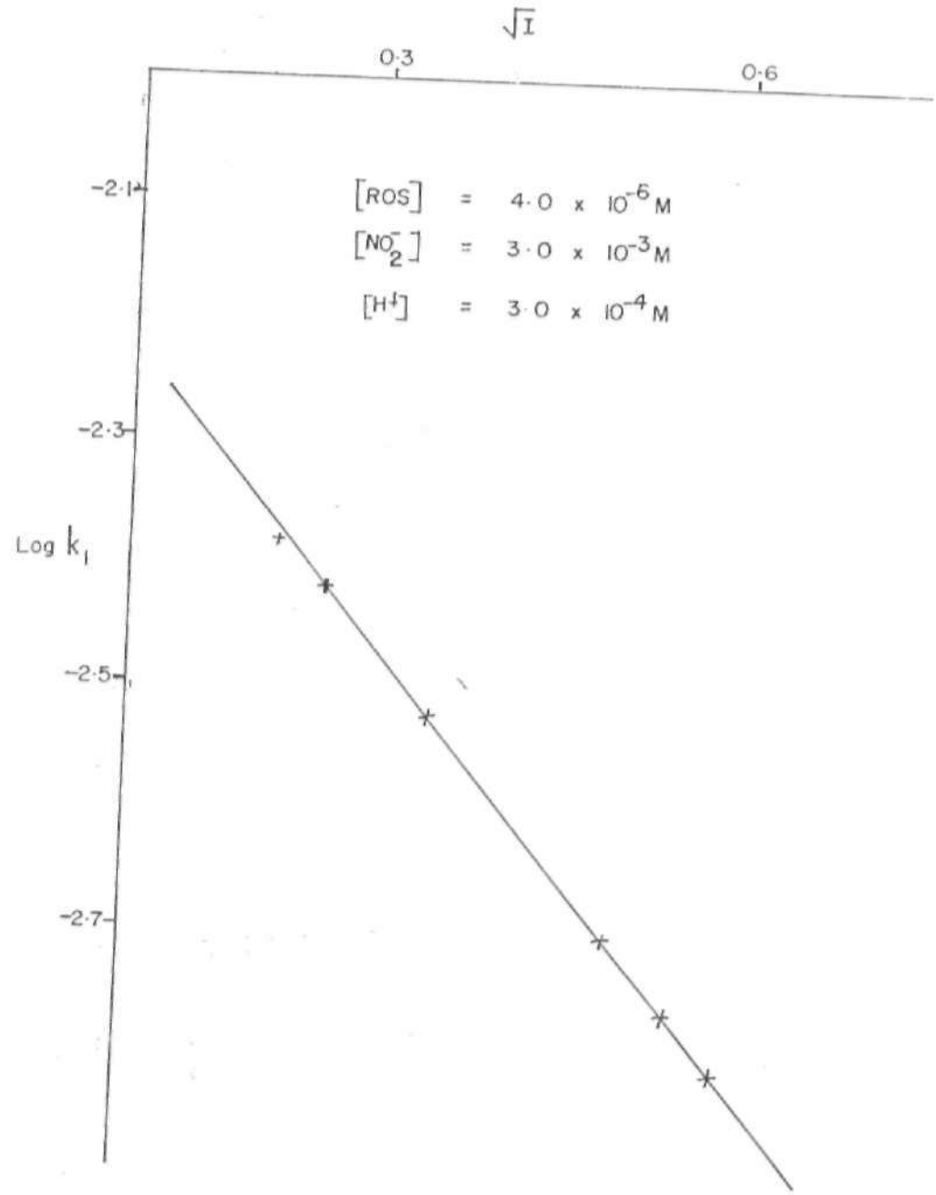


Fig. 4. 4·4 Plot of Log k_1 Versus $\sqrt{I}$ for the redox reaction of Rosaniline and $[S_2O_5^{2-}]$

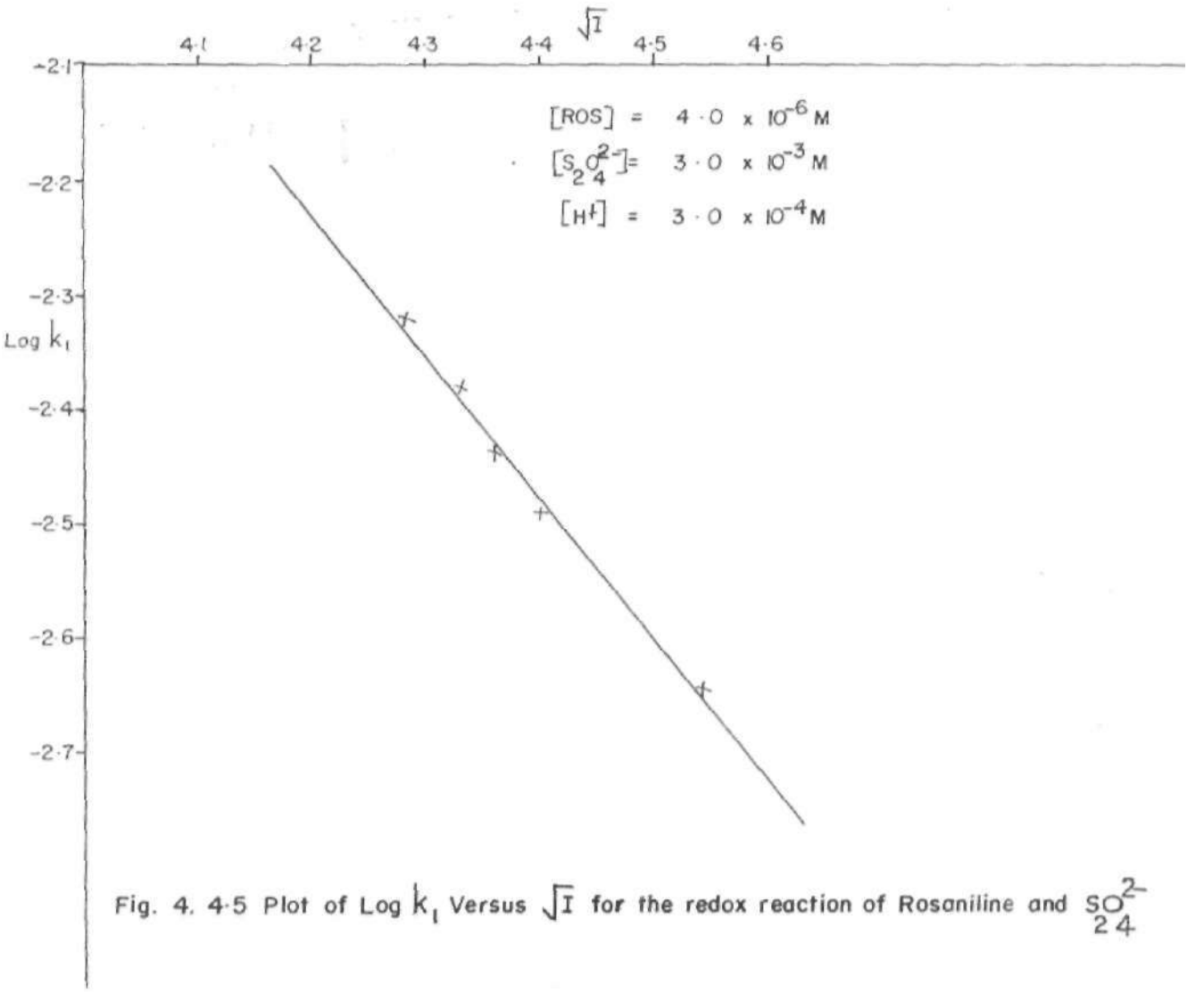


Fig. 4. 4·5 Plot of Log k_1 Versus $\sqrt{I}$ for the redox reaction of Rosaniline and $SO_2^{2-}_4$

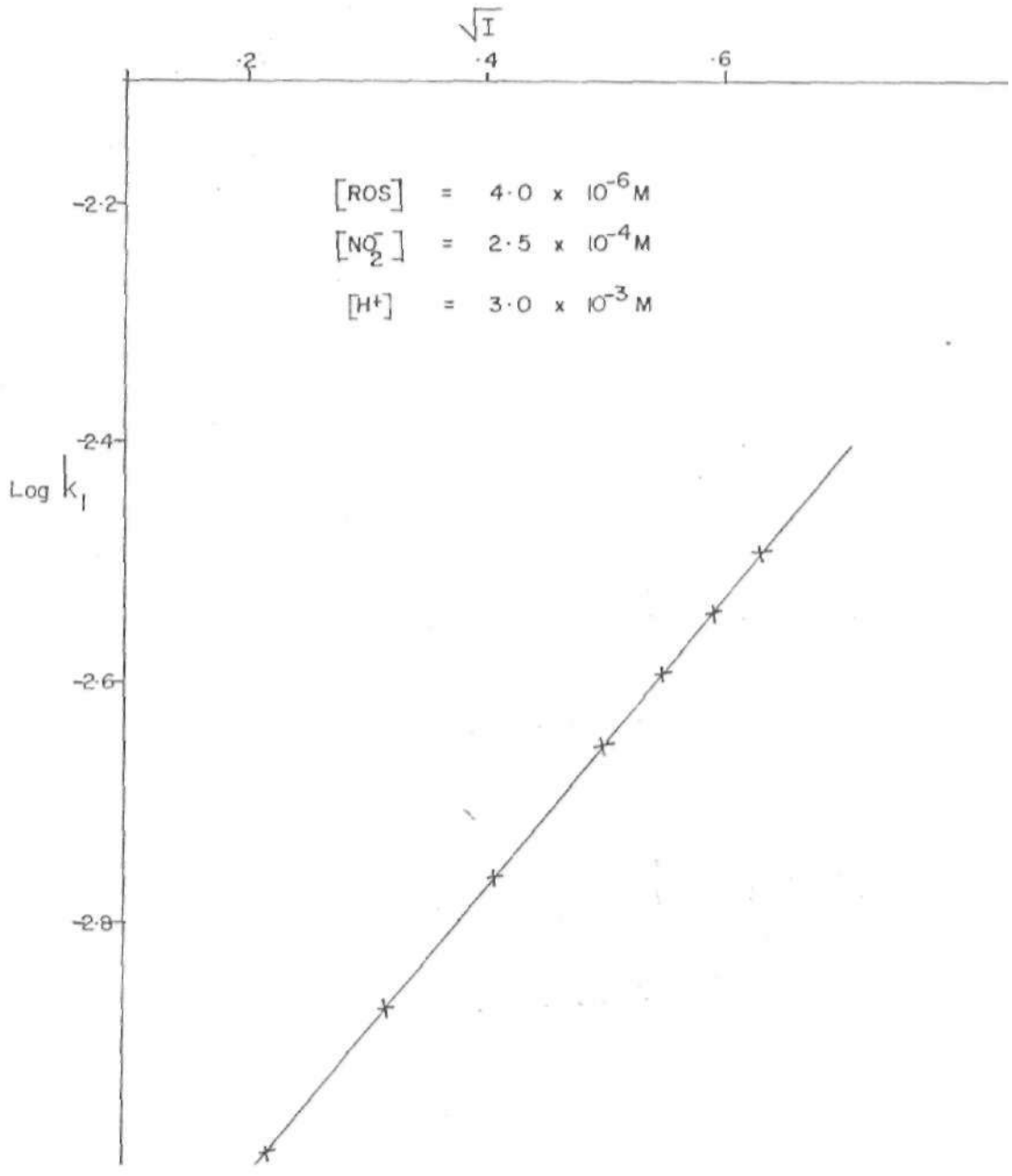


Fig. 4. 4·6 Plot of Log k_1 Versus $\sqrt{I}$ for the redox reaction of Rosaniline and NO_2^-

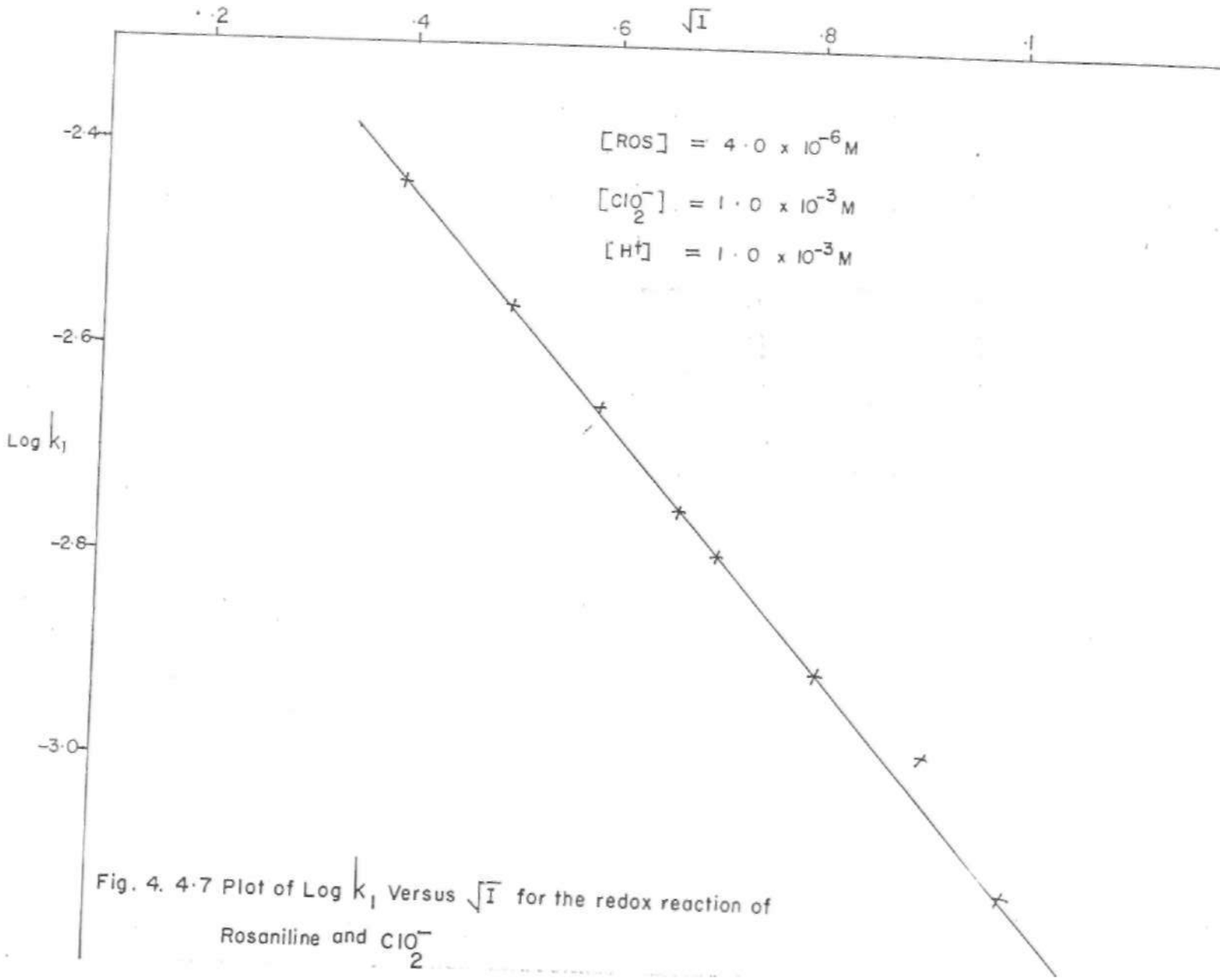


Fig. 4. 4·7 Plot of Log k_1 Versus $\sqrt{I}$ for the redox reaction of Rosaniline and ClO_2^-

4.7 Effect of the medium dielectric constant on the rate of the reaction.

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

$$\ln k = \ln k_o - \frac{e^2}{2DKT}\left[\frac{(Z_A + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \quad \ldots\ldots (38)$$

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

In a reaction between anion Z_A and a non-polar molecule (Z_B = O) equation 38 becomes

$$\ln k = \ln k_o + \frac{Z_A^2 e^2}{2DKT}\left[\frac{1}{r_A} - \frac{1}{r^*}\right] \quad \ldots\ldots (39)$$

The equation predicts a linear plot of log k_2 vs 1/D with a negative slope if the charges of the ions are of the same sign and with a positive slope if the ions are oppositely charged (Wilkins, 1974, Glasstone *et al*, 1941).

The effect of medium dielectric constant on the rate constant was investigated using 2%-18% acetone for rosaniline-ClO_2^- and rosaniline-NO_2^- system. The values for the rate constant are presented in Table 4.90 - 4.10

Typical plots of log k_2 vs 1/D (where D = dielectric constant) are shown in Fig. 4.5.0 - 4.5.1.

There was no noticeable reaction in this medium for rosaniline - $S_2O_5^{2-}$ and rosaniline $S_2O_4^{2-}$ systems.

Table 4.9

Effect of medium dielectric constant on the reaction of rosaniline and NO_2^-.

$[ROS] = 4 \times 10^{-6}$ M, T = 30 °C $\lambda_{max} = 545$ nm,

$[H^+] = 1 \times 10^{-3}$ M, I = 0.25 M (LiCl), $[NO_2^-] = 2.5 \times 10^{-4}$ M

% acetone	D	$10^3 k_1$	$k_{3/2}$
3	76.05	2.70	10.80
6	74.35	3.73	14.92
9	72.46	4.54	18.16
12	70.92	5.76	23.04
15	69.44	7.88	31.52
18	67.57	9.31	37.25

Table 4.10

Effect of medium dielectric constant on the reaction of rosaniline and ClO_2^-

$[ROS] = 4 \times 10^{-6}$ M, T = 30 °C $\lambda_{max} = 545$ nm,

$[H^+] = 1 \times 10^{-3}$ M, I = 0.5 M ($NaNO_3$), $[ClO_2^-] = 0.1$M

% acetone	D	$10_3 k_1$	$k_{3/2}$
3	76.04	1.49	4.71
5	74.91	1.34	4.25
7	73.78	1.16	3.67
13	70.39	1.04	3.29
15	69.26	0.97	3.08

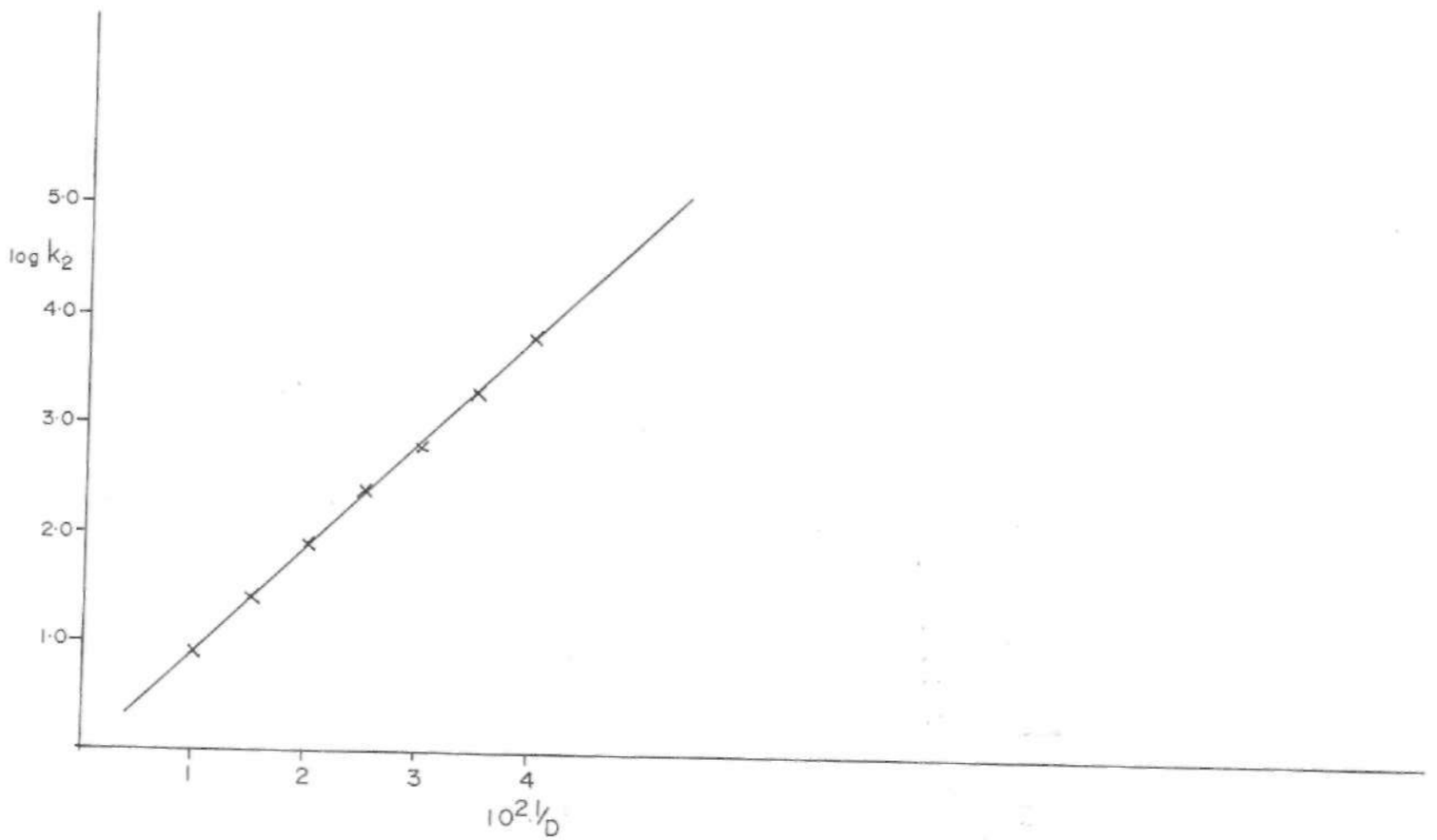


Fig. 4.4.8 Plot of log k_2 versus $1/D$ for the reaction of Rosaniline and NO_2^-

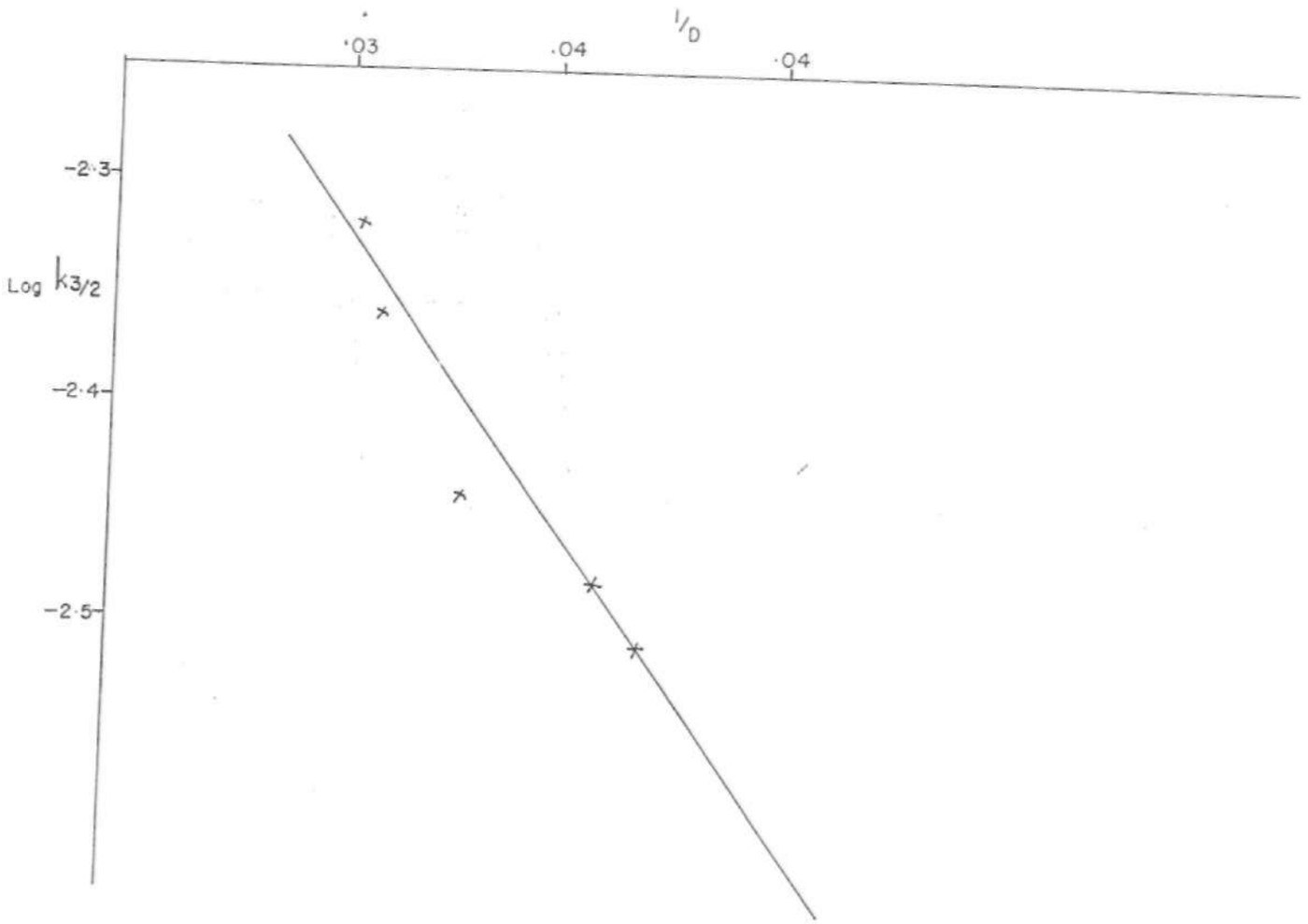


Fig. 4. 4·9 Plot of Log $k_{3/2}$ Versus $1/D$ for the reaction of Rosaniline and ClO_2^-

4.8 Test for intermediate complex

4.8.1 Spectrophotometric Test

Spectrophotometric tests were carried out in order to find out whether any spectroscopically determinable intermediate complex was formed in the redox reaction of rosaniline and the reductants.

The electronic spectra of the reaction mixtures were run after one minute over a range of wavelength 440 - 580nm. A similar run was made for the rosaniline alone. From the spectra(Fig. 4.5.2 - 4.5.5) there was shift in λ_{max} for the rosaniline in the ros - $S_2O_5^{2-}$, ros - $S_2O_4^{2-}$ and ros-ClO_2^- systems but no shift in the ros-NO_2^- system.

The shift in λ_{max} for the three systems may suggest the formation of an intermediate complex.

4.8.2 Michaelis - Menten plot

Plots of $1/k_1$ versus 1/[red] gave straight lines and are presented in figures 4.5.6 - 4.5.9. The line passed through the origin for ros-NO_2^- and ros - ClO_2^- systems but had an intercept for the ros - $S_2O_5^{2-}$ and the ros-$S_2O_4^{2-}$ systems respectively.

4.9.0 Test for free radicals

Acrylamide (0.001 - 0.015 M) was added to partially oxidized reaction mixture in each case. There was no observed gel formation. Formation of gel would have indicated presence of free radicals in the reactions.

4.10 Product Analysis

The isolation and characterization of the products of this reactions could give hints about the possible mechanism of the reaction. The products were analysed for carbonyl group, hydroxyl group, sulphate ion and chlorite ion. The results obtained from these analysis have enabled the identification of the likely products of the reactions.

For the rosaniline - $S_2O_5^{2-}$, $S_2O_4^{2-}$ systems addition of ethanal to the colourless product of the reaction (leuco fuchsin) readily restored a violet-like colour to the solution. Aldehydes are known to restore the colour of Schiff's reagent (Conn, 1961).

The observation suggests that for the rosaniline $S_2O_5^{2-}$, $S_2O_4^{2-}$ reaction the -C= NH_2 group (which is characteristic of Schiff's reagent) of the dye is probably intact at the end of the reaction. Similar treatment to the product of the reaction for the rosaniline - NO_2, ClO_2^- systems did not give positive result for the Schiff's reagent test.

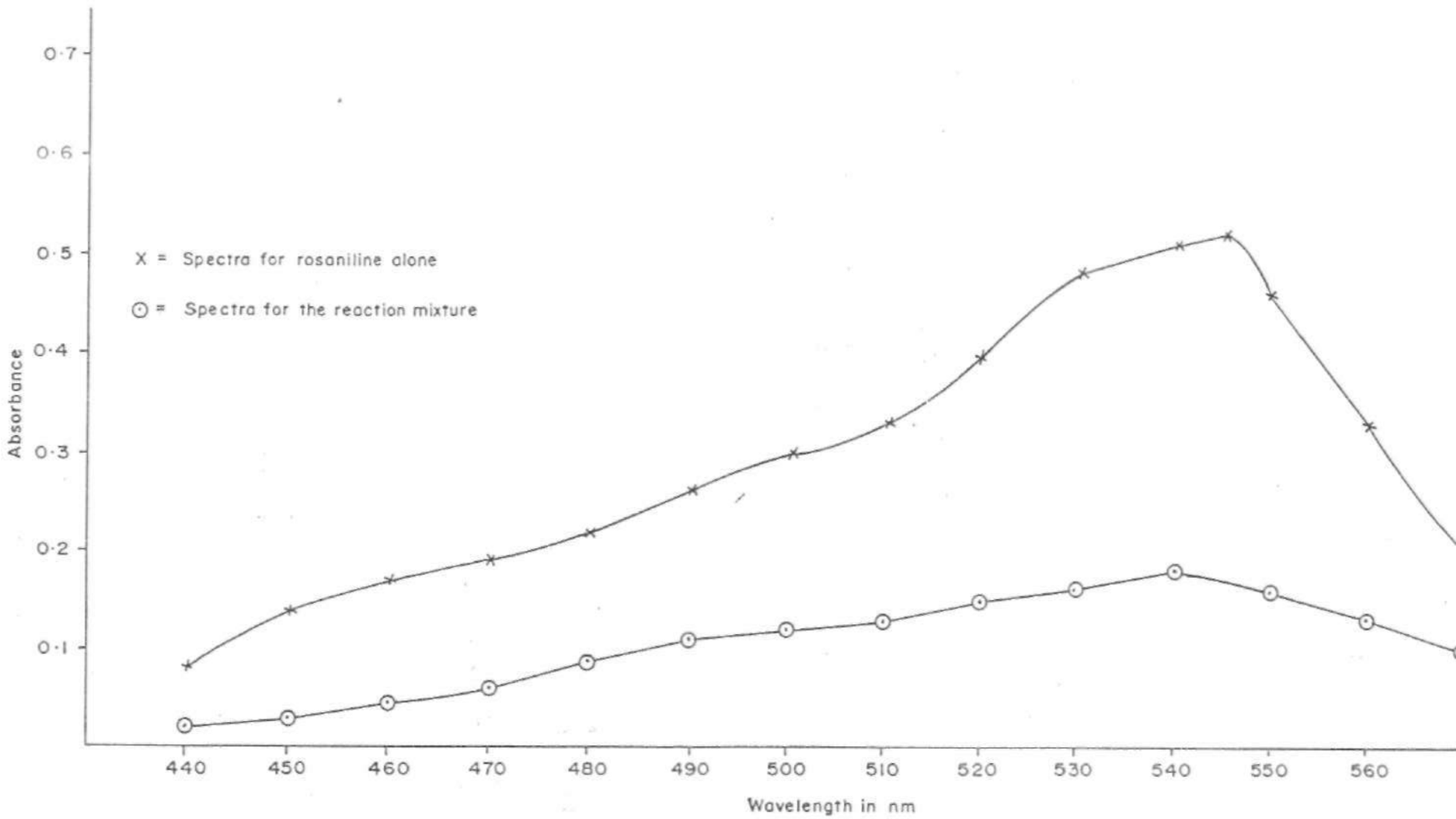


Fig 4·5·0 Spectra of reactants after I minute of mixing for the reaction of rosaniline and $S_2O_5^{2-}$

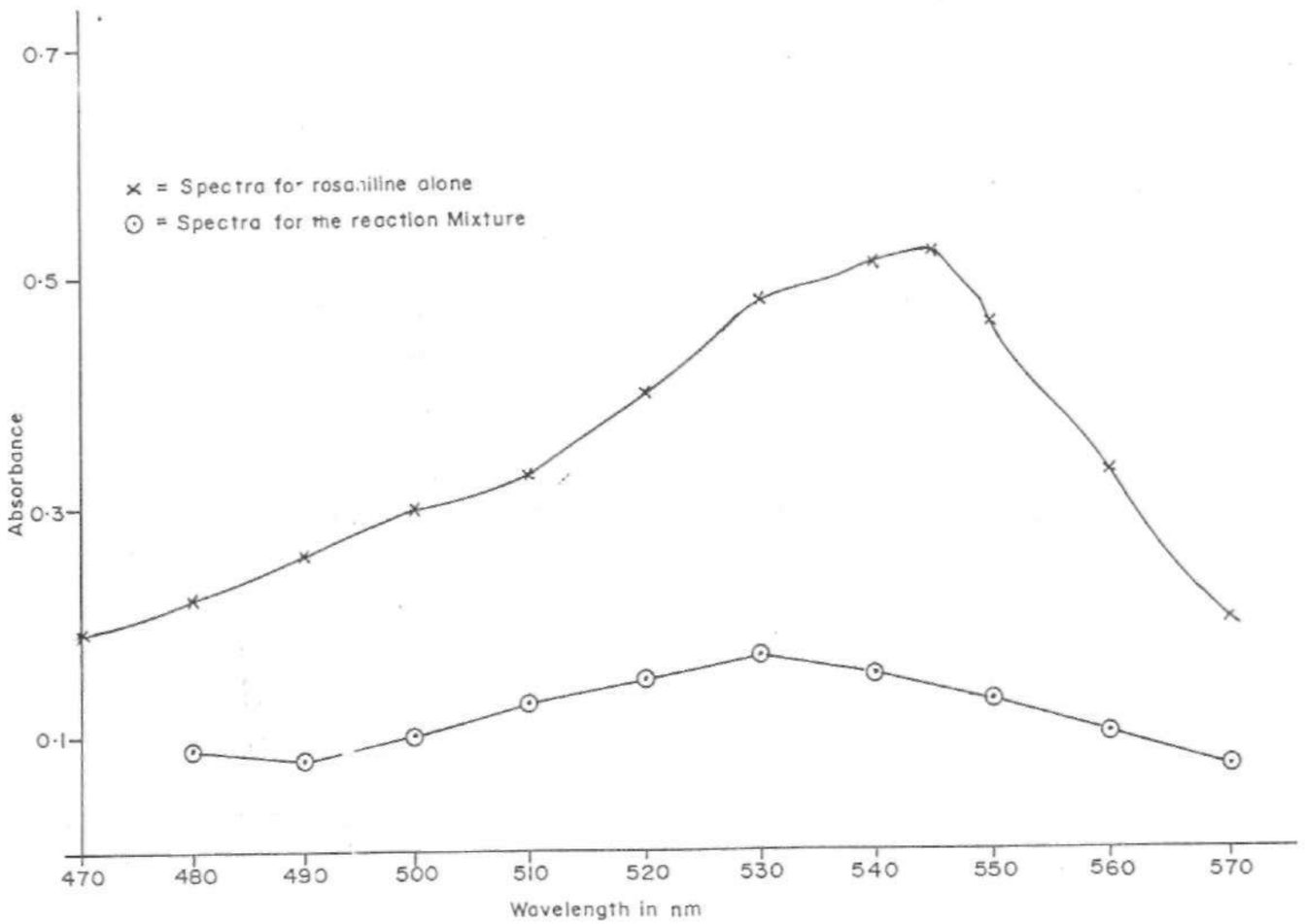


Fig. 4·5·1 Spectra of the reactants after 1 minute of mixing for the reaction of resaniline and $S_2O_4^{2-}$

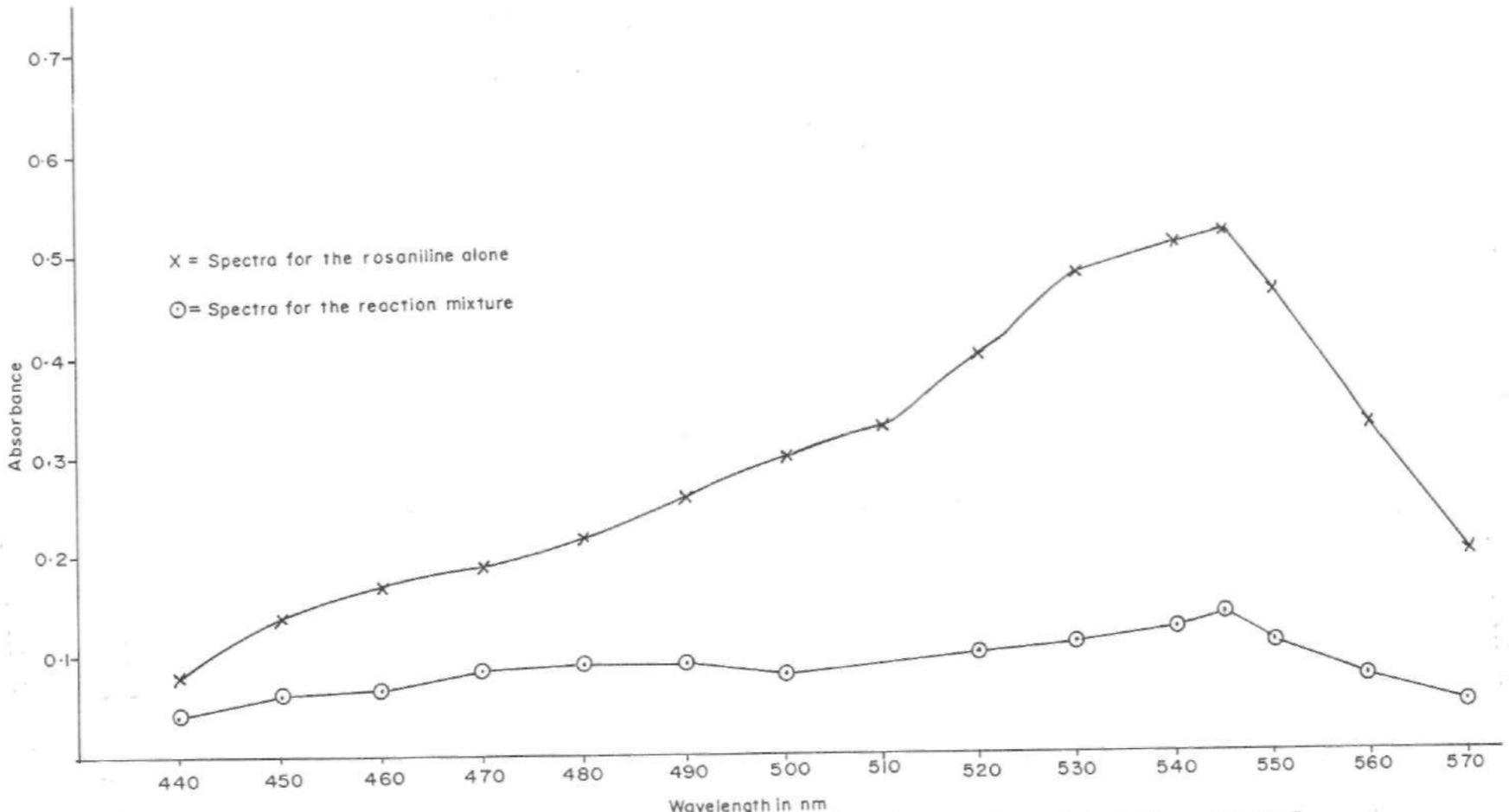


Fig 4·5·2 Spectra of the reactants after 1 minute of mixing for the reaction of rosaniline and NO_2^-

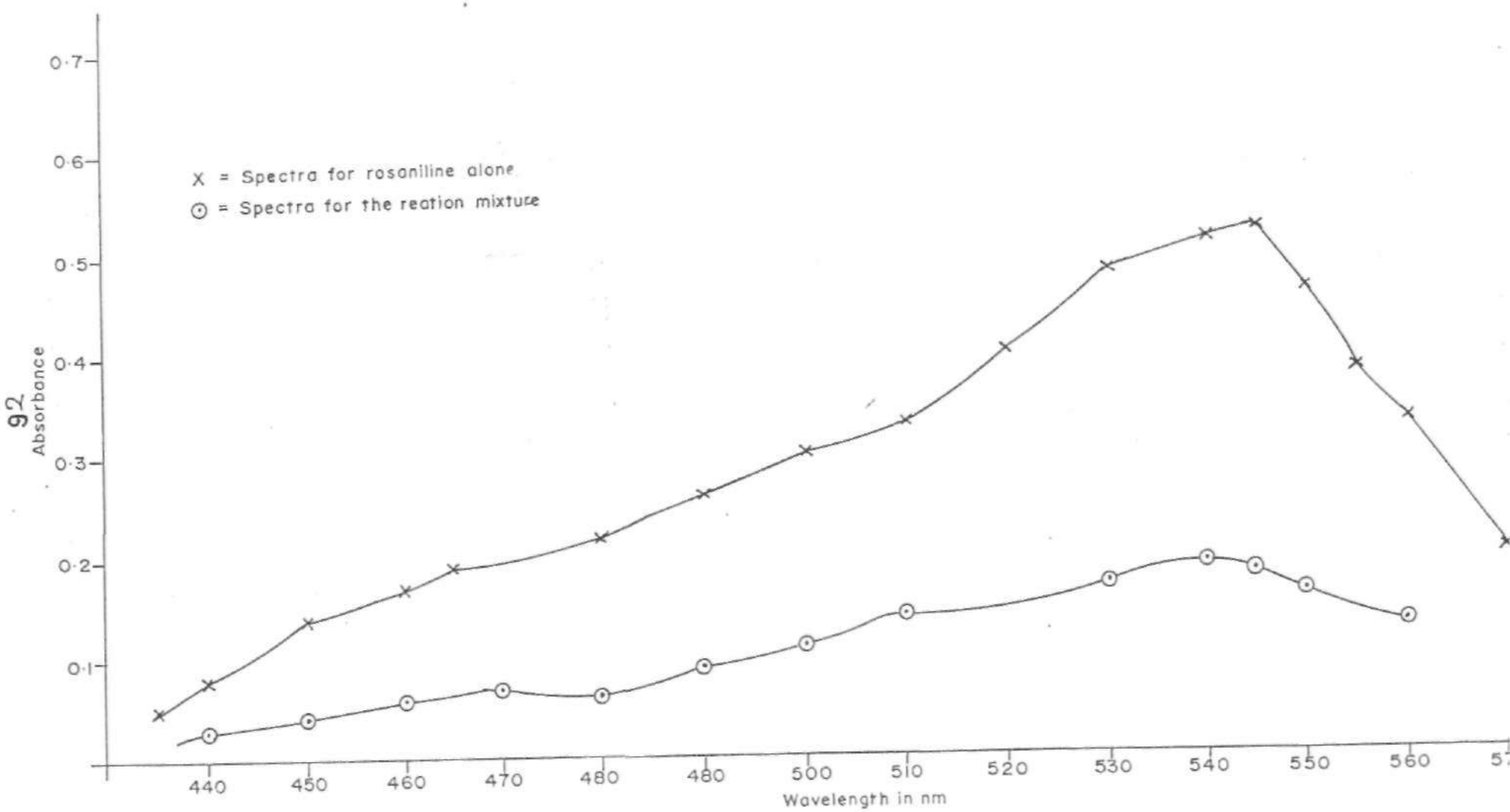


Fig 4·5·3 Spectra for the reactants after I minute of mixing for the reaction of rosaniline and ClO_2^-

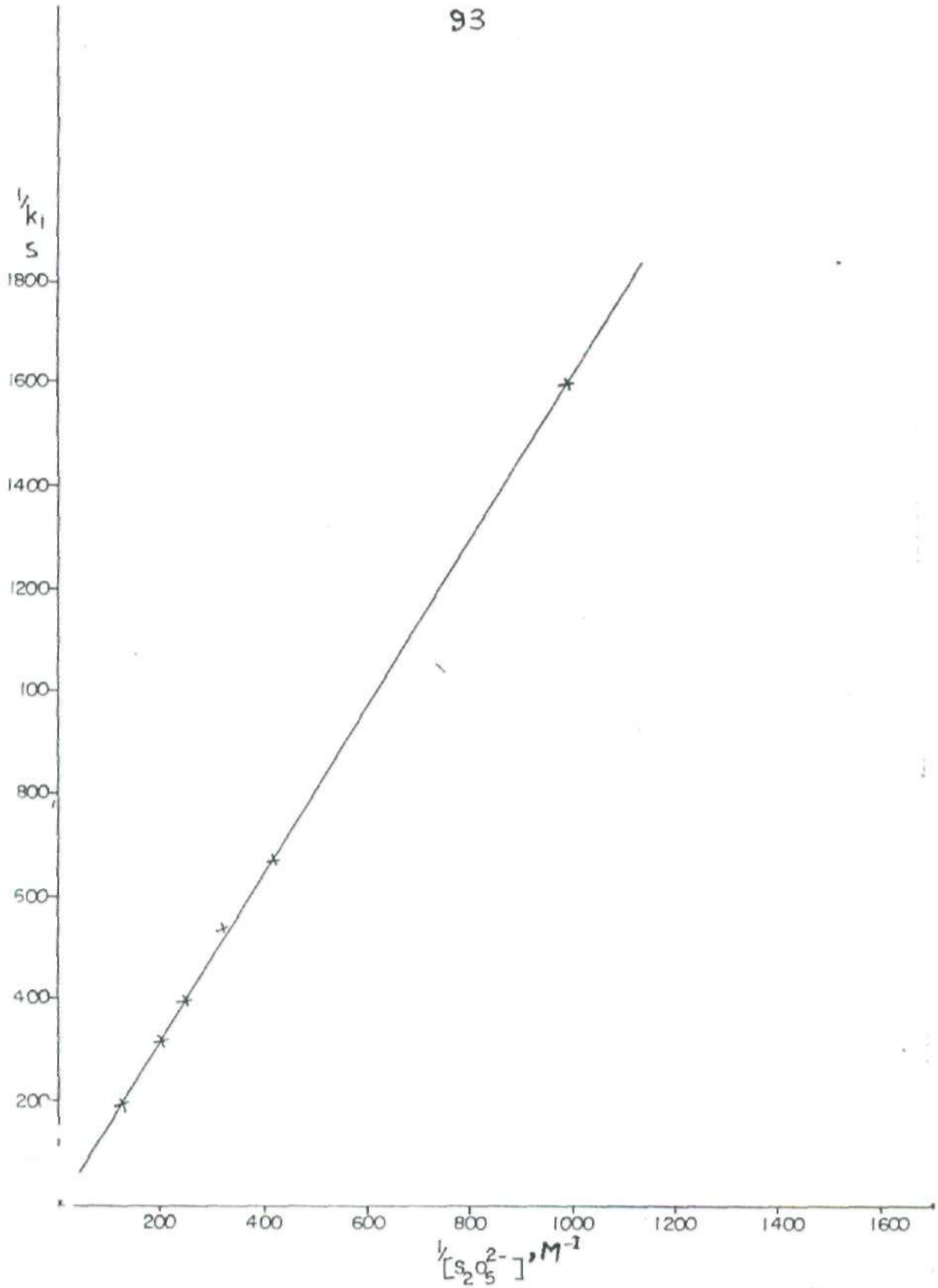


Fig. 4. 5·4 Michealis-Menten plot for the reaction of Rosaniline and $S_2O_5^{2-}$

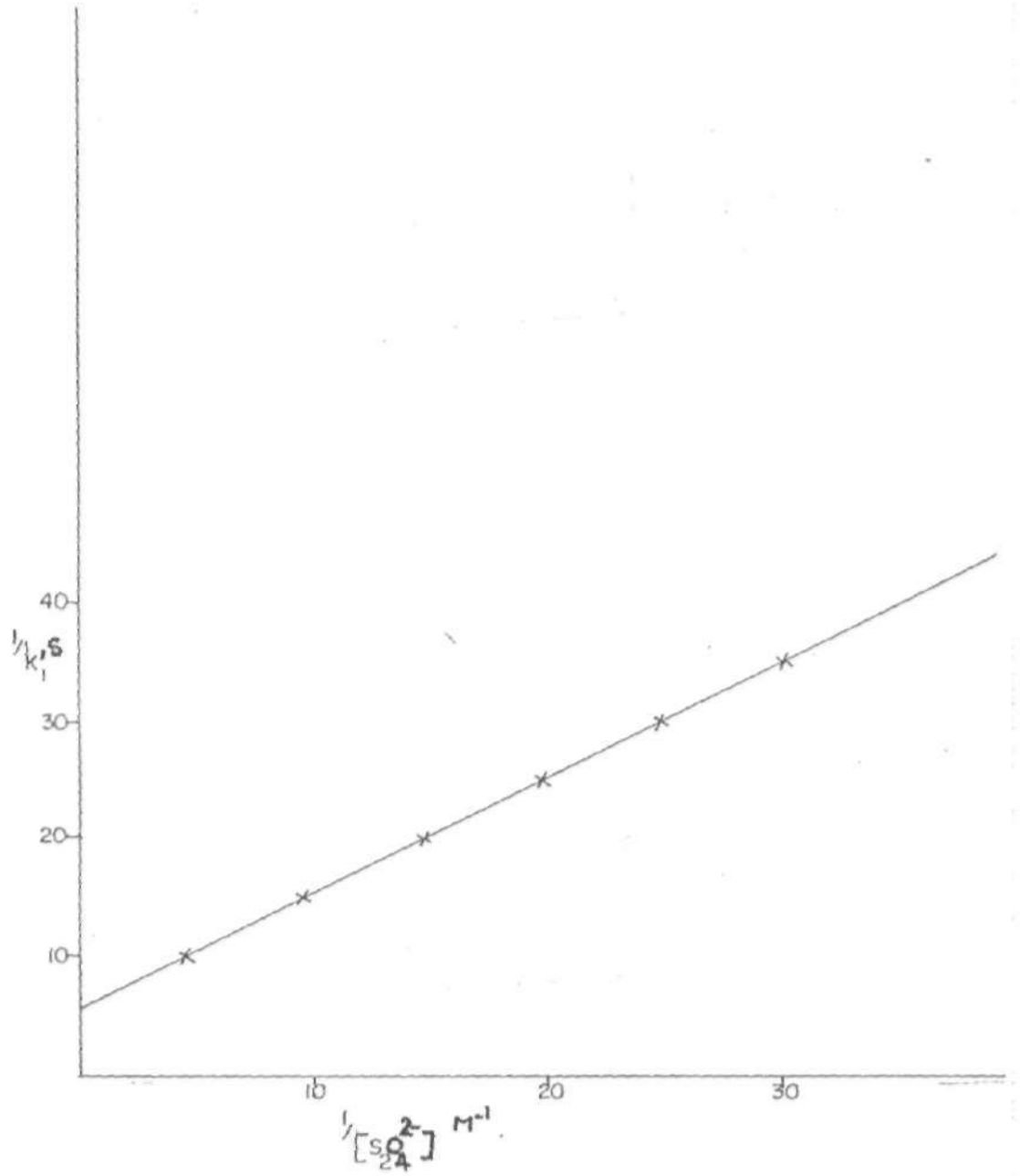


Fig. 4. 5·5 Michealis Menten's Plot for the reaction of Rosaniline and $S_2O_4^{2-}$

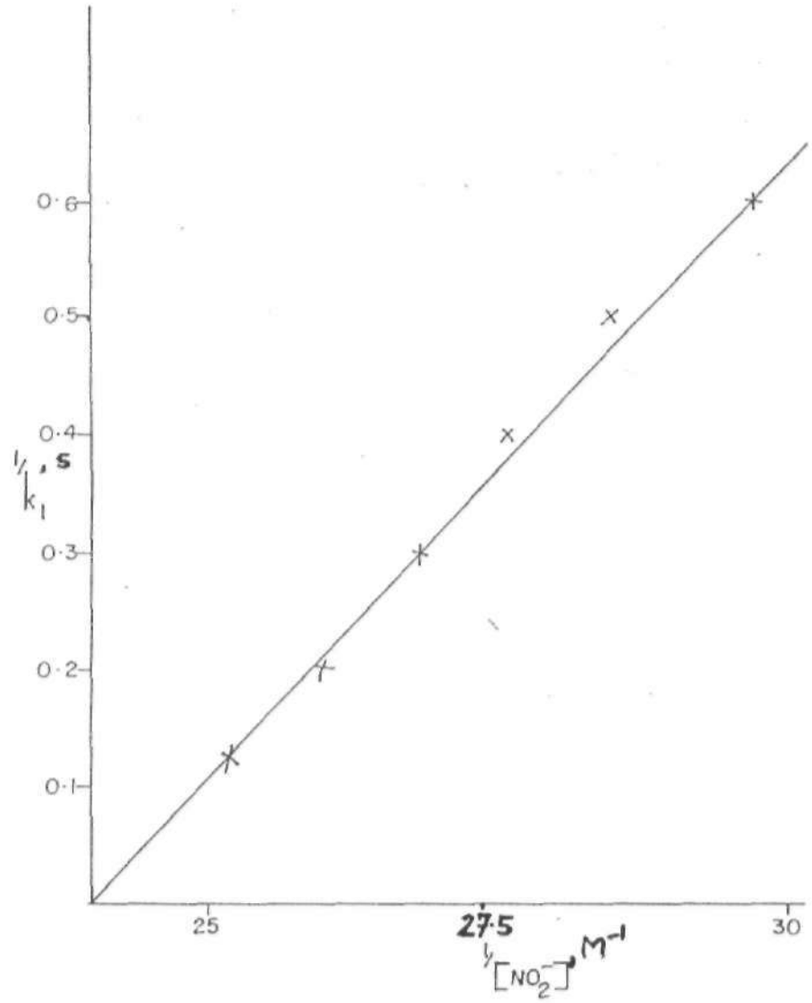


Fig. 4. 5·6 Michealis Menten's Plot for the reaction of Rosaniline and NO_2^-

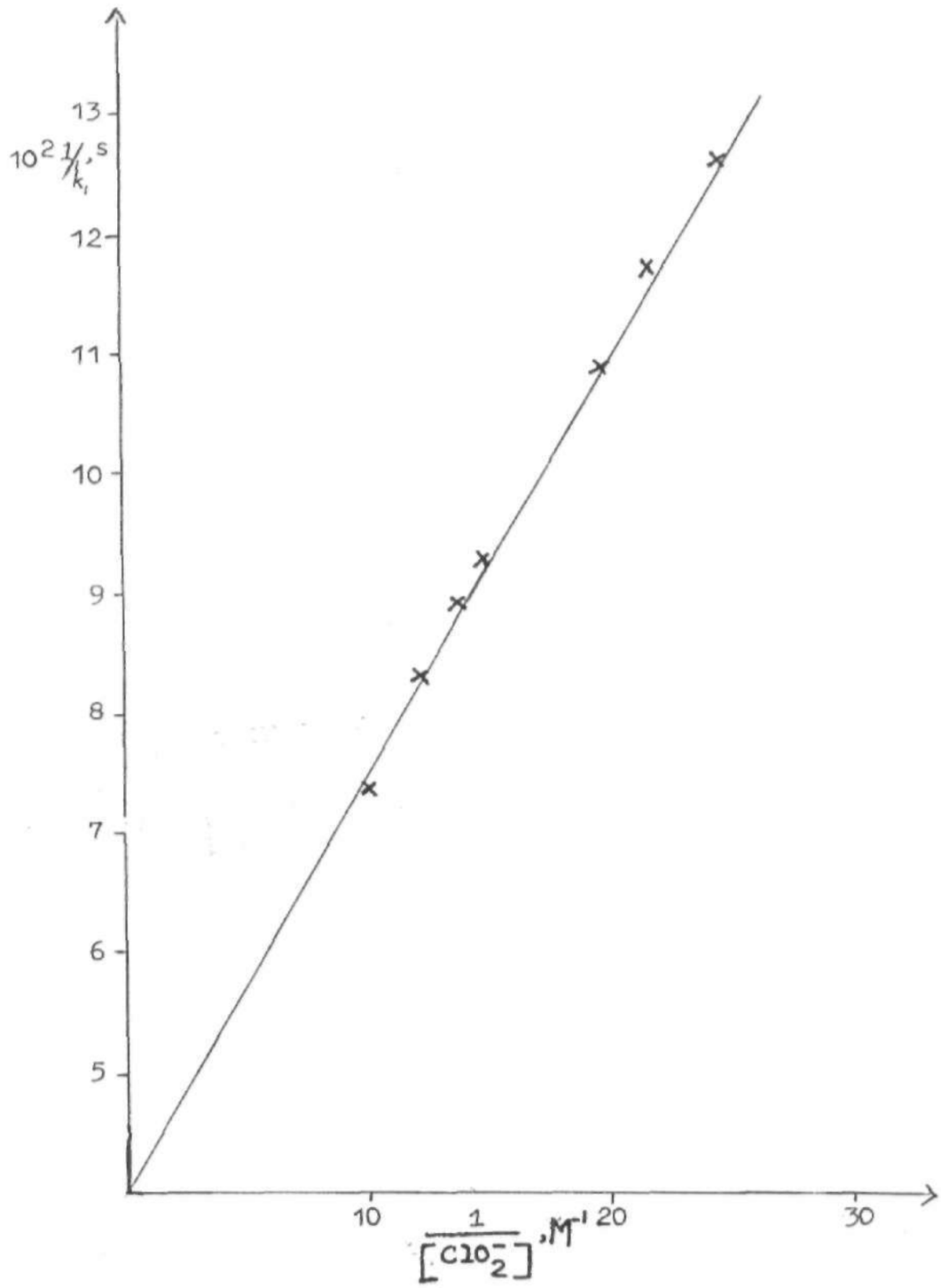


Fig. 4.5.7 Michealis Menten's plot for reaction of rosaniline and $[ClO_2^-]$

CHAPTER FIVE

5.0 Discussion

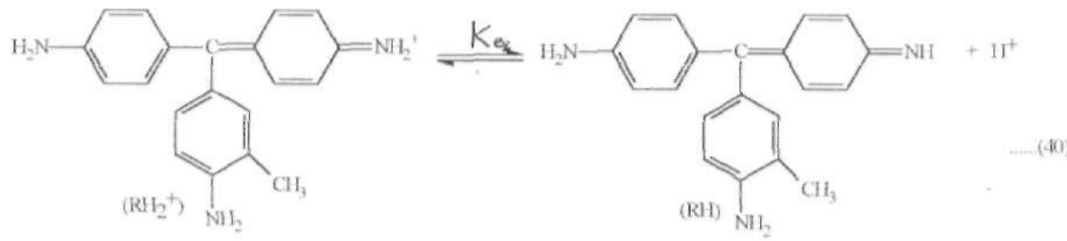
5.1 Rosaniline - $S_2O_5^{2-}$ System

The stoichiometric studies showed that one mole of rosaniline is consumed by one mole of $S_2O_5^{2-}$. This result agrees with the consumption ratio obtained for sulphite in its redox reactions with hexachloroplatinate (IV), dodecatungstantocobaltate (III), hexachloroiridate (IV) and *tris*-(2,2′-bipyridine) osmium (III) (Gupta *et al.*, 1987; Ali and Saha, 1990; Sarala and Stanbury, 1990).

Kinetics studies of the reaction of this system show an order of one with respect to the oxidant and reductant respectively. Similar order was obtained with respect to the reductant concentration by Gupta, *et al.* (1987), but the dependence of the rate on reductant concentration did not follow a simple order in the reaction reported by Banerjee *et al.*, (1990).

The studies on the effect of acid on the rate of the reaction show two pathways, one which is acid dependent and the other which is acid independent. This suggests that both the undeprotonated and deprotonated species are reactive.

Possible mechanism consistent with the observed result is:



.....(40)

$$RH_2^{+} + S_2O_5^{2-} \xrightarrow[H_2O]{k_1} \text{Products} \quad \text{.....(41)}$$

$$RH + S_2O_5^{2-} \xrightarrow[H_2O]{k_2} \text{Products} \quad \text{.....(42)}$$

$$\text{rate} = k_1 [RH_2^{+}] [S_2O_5^{2-}] + k_2 [RH] [S_2O_5^{2-}] \quad \text{.....(43)}$$

From equation (40)

$$[RH] = \frac{K_{eq}[RH_2^{+}]}{[H^{+}]} \quad \text{.....(44)}$$

Putting (40) in (43)

$$\text{Rate} = k_1[RH_2^{+}][S_2O_5^{2-}] + \frac{k_2 K_{eq}[RH_2^{+}][S_2O_5^{2-}]}{[H^{+}]} \quad \text{.....(45)}$$

$$\text{Rate} = (k_1 + k_2 K_{eq} [H^{+}]^{-1}) [RH_2^{+}][S_2O_5^{2-}] \quad \text{.....(46)}$$

Equation (46) conforms to the observed rate law, equation (33) where k_1 = b, and k_2 K_{eq} = a, and RH_2^{+} = ROS.

The negative salt effect observed in the reaction of the rosaniline monochloride with metabisulphite ion ($S_2O_5^{2-}$), indicates the interaction of opposite charges in the activated complex (Wilkins, *1974)*. This observation agrees with equation (41) in the proposed mechanism.

Analysis of Michealis-Menten plot gave zero intercept, (Figure 4.5.6) suggesting the absence of intermediate complex formation (Iyun, *et al.*, 1992).

The spectra of the reaction mixture showed a hypsochromic shift from 545 nm (λ_{max}) to 540nm, and there was no enhancement in absorbance (Figure 4.5.2).

The slight shift of 5nm may not be significant enough to be taken as spectroscopic evidence for presence of intermediate complex.

The anions (CH_3COO^-, NO_3^-) were observed to catalyze the reaction. The observed catalysis of the reaction by the anions suggests that the reaction is occurring by the outersphere mechanism.

Ion catalysis of reaction rate has been reported as characteristic of the outersphere reactions (Pennington and Haim 1967; Przystas and Sutin, 1973; Adegite *et al*, 1977).

The result from Michealis - Menten analysis, the lack of enhancement of absorbance of the reaction mixture, the acceleration of the reaction by the anions; all favour the outer sphere mechanism. Therefore the reaction of rosaniline with metabisulphite ($S_2O_5^{2-}$) ion is probably occurring by the outer-sphere mechanism. The outer-sphere mechanism has earlier been reported for some other sulphite reactions (Kalyan *et al.*, 1987, Ali, Saha and Banerjee, 1990).

5.2.0 ROSANILINE - $S_2O_4^{2-}$ SYSTEM

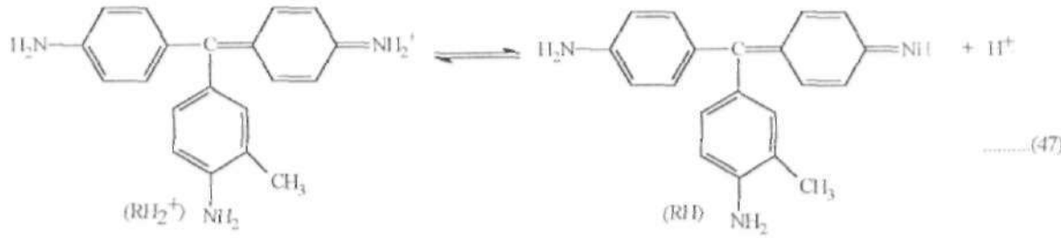
The stoichiometry of 1:1 is assumed for the rosaniline-$S_2O_4^{2-}$ system reaction. This assumed stoichiometry is consistent with the result obtained by Morello *et al.*, (1964) at excess dioxygen and that of Sutin and Creutz (1974) at excess dithionite for the reaction of $S_2O_4^{2-}$ and O_2.

The reaction showed first order dependence on the concentration of rosaniline and of $S_2O_4^{2-}$ ion. The order of one has been reported for $S_2O_4^{2-}$ ion concentration in the reduction

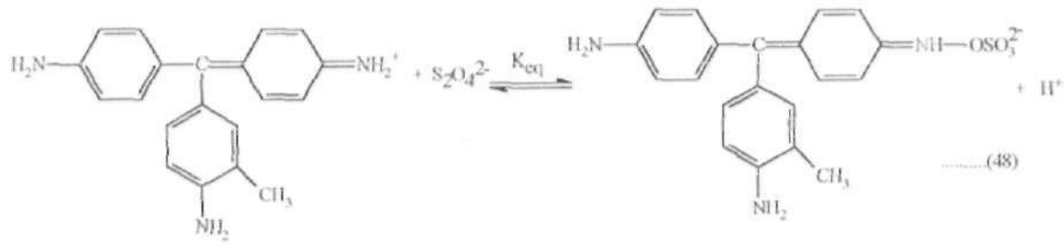
of anthraquinone, and ferricyanide with $S_2O_4^{2-}$ ion (Peter and Lepenge, 1962, Lambeth and Palmer, 1973) while in the reduction of *p*-phenylazobenzene sulphonic acid, dioxygen, hydrogen peroxide, Spinach plastocyanin and ferricytochrome-C by $S_2O_4^{2-}$ ion half order was reported for $[S_2O_4^{2-}]$ (Wasmuth *et al.*, 1965; Creutz and Sutin, 1974; Lambeth and Palmer, 1973).

The acid dependence observed for the reaction suggests the release of proton in a pre-equilibrium step and the deprotonated form of the reactant specie is reacting.

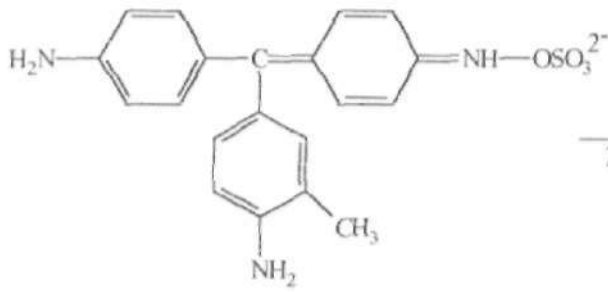
Plausible Mechanism consistent with the result is:



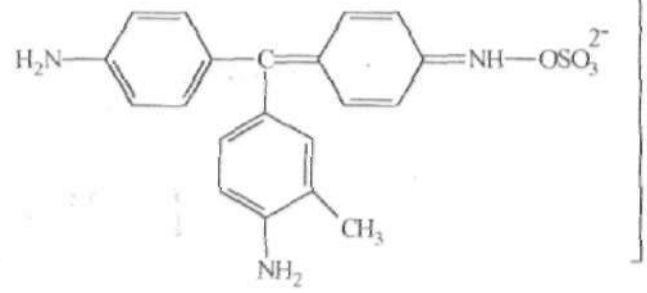
.....(47)

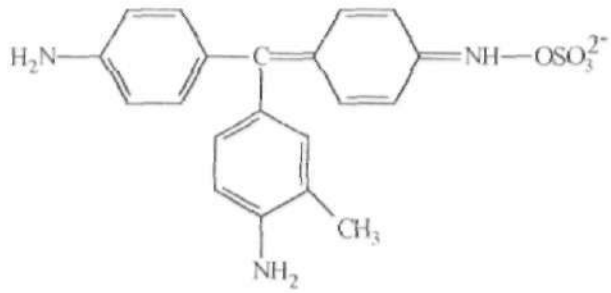


.....(48)



$$\xrightarrow[H_2O]{k_1} \text{Products} \qquad \text{.....(49)}$$

$$\text{Rate} = k_1 \left[\text{  } \right] \qquad \text{.....(50)}$$



$$= \frac{K_{cq}[RH_2^+][S_2O_4^{2-}]}{[H^+]} \qquad \text{.....(51)}$$

$$\text{Rate} = k_1 \frac{K_{eq}[RH_2^+][S_2O_4^{2-}]}{[H^+]} \qquad \text{.....(52)}$$

where $k_1K_{eq} = k$ and $RH_2^+ = ROS$.

Equation (52) conforms to the observed rate law, equation 32.

In many of the redox reactions involving $S_2O_4^{2-}$, like the reactions of dioxygen, hydrogen peroxide, spinach plastocyanin and ferricytochrome C (Lambeth and Palmer, 1973; Creutz and Sutin, 1974), the SO_2^- radical have been implicated as the more reactive specie than $S_2O_4^{2-}$ and in all those reactions an order of half was obtained with respect to $S_2O_4^{2-}$

concentration. The equilibrium $S_2O_4^{2-} \longrightarrow 2SO_2^{\cdot}$ has been established between the dimer and monomer species of dithionite (Ringer *et al.*, 1959; Burlamacchi *et al.*, 1967; Cotton and Wilkison, 1980).

The reduction of oxidant by dithionite involves either $S_2O_4^{2-}$ or $SO_2^{\cdot}$ as the reducing specie. For the reaction in which $SO_2^{\cdot}$ is the reducing specie an order of half was reported for $S_2O_4^{2-}$ concentration and in the case of reactions which $S_2O_4^{2-}$ is the reducing specie an order of one was reported for the $S_2O_4^{2-}$ concentration as obtained in the reduction of ferricyanide with dithionite (Lambeth and Palmer, 1973).

An order of one was obtained with respect to $S_2O_4^{2-}$ concentration in the reaction of rosaniline with $S_2O_4^{2-}$ and as such the mechanism of reaction should involve $S_2O_4^{2-}$ as the reducing specie. This mechanism is further supported by the lack of acrylamide polymerization of the reaction.

The reaction displayed negative salt effect, as the second order rate constant decreased with increasing ionic strength. This observation is suggestive of interaction of unlike charges in the activated complex (Wilkins, *1974*). This agrees with equation (48) in the reaction scheme.

Least square analysis of Michealis - Menten plot gave an intercept (Figure 4.5.5) and also the spectra of the reaction mixture showed a hypsochromic shift from 545 nm (λ_{max}) to 530 nm (Figure 4.5.1). Both evidences suggest the formation of intermediate complex.

Intermediate complex formation has been adduced as evidence in favour of the inner sphere mechanism.

The catalytic effect of the anions ($HCOO^-$ and CH_3COO^-) on the reaction rate is unexpected as per the evidences from kinetic and spectroscopic analysis that favours the inner–sphere mechanism; as ion catalysis of reaction rate has been reported to be characteristic of the outer-sphere mechanism (Pennignton and Haim 1967, Przystal and Sutin, 1973, Adegite *et al.*, 1977). The catalysis of the reaction rate by the anions may be due to medium effect.

However, the shift of 15 nm in the λ_{max} of the spectra of the reaction mixture and the significant intercept in the Michealis - Menten plot for the reaction are strong evidences in favour of the inner–sphere mechanism and this mechanism is probably operating in the rosaniline - $S_2O_4^{2-}$ reaction.

5.3.0 Rosaniline - NO_2^- System

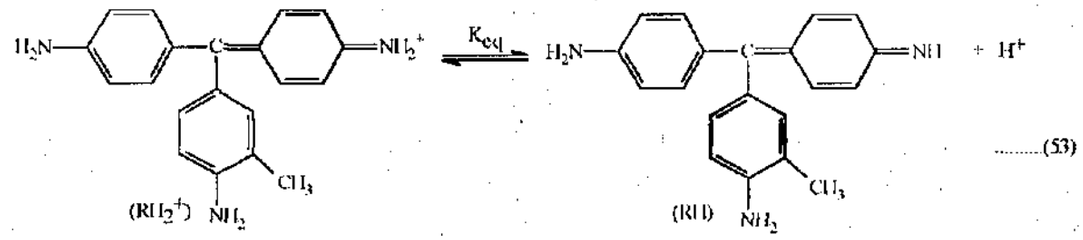
The order of the reaction with respect to the oxidant and reductant is one respectively. Order of one has been reported with respect to the oxidant and reductant for the oxidation of NO_2^- by $H_2PO_5^-$ (Luenok - Burmakina, Aleeva, Franchuk, 1968) dihalobis [Co-phenylene-bis (dimethylarsine)] Platinum (IV) with NO_2^- (Doketti, Peloso, 1967) and europium (II) ion reduction of nitrite (Fraser, Lee and Hayden, 1967).

The nature of acid dependence observed implies that there is a rapid equilibrium between protonated and unprotonated form of the reductant (NO_2^-) prior to the rate determining step and the protonated form is reactive. This form of acid dependence is not surprising for nitrite reactions as the equilibria in equation (54) has been established (Roberts

and Caserio, 1981).

The acid dependent component in the reduction of dioxo-bridged Manganese complex by NO_2^- is similar to one observed in this reaction (Chaudhuri, *et al.*, 1995)

The plausible mechanism for this reaction is:



.....(53)

$$NO_2^- + H^+ \xrightleftharpoons{K_1} HONO + H^+ \xrightleftharpoons{K_2} H_2ONO^+ \xrightleftharpoons{K_3} H_2O + {:}\overset{\oplus}{N}{=}O \quad \text{.....(54)}$$

$$RNH_2^+ + {:}\overset{\oplus}{N}{=}O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RH_2,NO]^{2+} \quad \text{.....(55)}$$

$$[RH_2,NO]^{2+} \xrightarrow{k_2} \text{Product} \quad \text{.....(56)}$$

$$\text{Rate} = k_2\,[RH_2,NO]^{2+} \quad \text{.....(57)}$$

$$-\frac{d[RH_2,NO]^{2+}}{dt} = k_1[RH_2^+][{:}\overset{\oplus}{N}{=}O] - k_{-1}[RH_2,NO]^{2+} - k_2[RH_2,NO]^{2+} \quad \text{.....(58)}$$

$$[RH_2NO]^{2+} = \frac{k_1[RH_2^+][N=O]}{k_{-1}+k_2} \quad \text{.....(59)}$$

But $[{:}\overset{\oplus}{N}{=}O] = K_3\,[H_2ONO^+]$ .....(60)

and $[H_2ONO^+] = K_2[HONO][H^+]$ .....(61)

and $[HONO] = K_1\,[NO_2^-]$ .....(62)

putting (62) in (61), and substituting for H_2ONO^+ in (60) gives

$[\ :\overset{\oplus}{N}{=}O] = K_3K_2K_1\ [H^+]\ [NO_2^-]$ .....(63)

Substituting for $:\overset{\oplus}{N}{=}O$ in 59 gives

$$[RH_2, NO]^{2+} = \frac{K_3K_2k_1K_1[H^+][RH_2^+][NO_2^-]}{k_{-1} + k_2} \quad \text{.....(64)}$$

putting 64 in 57,

Rate = $k\ [H^+][RH_2^+][NO_2^-]$ .....(65)

Equation (65) conforms to the observed rate law equation (34), where;

$$k = \frac{K_3K_2k_1k_2K_1}{k_1 + k_2} = a \text{ , and } RH_2^+ = ROS$$

The positive salt effect observed for the reaction showed the interaction of like charges or a charged reactant with a neutral molecule in the activated complex (Wilkins, 1974). This agrees with equation (55) in the reaction scheme.

Least square analysis of Michealis - Menten plot gave no intercept and there was no shift in the λ_{max} of the spectrum of the reaction mixture.

Both evidences suggest the absence of intermediate complex formation.

Added anions ($HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$) and cations (Ca^{2+}, Ba^{2+}) decreased the rate constant for the reaction. This suggests that substitution of the reactants into their inner co-ordination shell did not preceed electron transfer.

The inhibition of the reaction by the cations could be due to columbic effect as presence of many positively charged species in the activated complex will lead to the repulsion of the reactants and hence a diminution in rate. The inhibition of the reaction rate by the added anions, is unexpected. On purely columbic ground it is expected that anions

will accelerate the reaction.

For the outer-sphere reactions added ions should catalyze the reaction (Peningnton and Haim, 1967, Przystal and Sutin, 1973, Adegite, *et al.*, 1977). The result obtained for the reaction of rosaniline monochloride and nitrite ion did not conform to this. However, evidence from Michealis - Menten analysis and the spectrum of the reaction mixture greatly favours the outer-sphere mechanism. Therefore, the outer-sphere mechanism may be operating for this reaction.

5.4.0 Rosaniline - ClO_2^- System

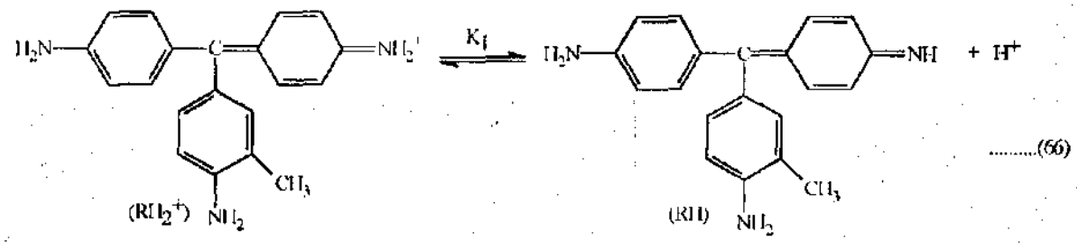
On the basis of the assumed stoichiometry, one mole of rosaniline is consumed by one mole of ClO_2^-. The stoichiometry obtained for the ClO_2^-/triphenylmethane dye and ClO_2^- /NO_2^- reactions however showed that one mole of ClO_2^- is consumed by two moles of triphenylmethane dye and NO_2^- respectively (Ramanauskas and Saprogoniene, 1970; Nagashi, *et al.*, 1977).

Kinetic studies of the reaction showed that the reaction is first-order with respect to rosaniline concentration and half-order with respect to the reductant concentration. The order of half obtained for the reductant concentration differs from the order of one in chlorite concentration earlier reported for the oxidation of formaldehyde by chlorite (Kudesia, 1972); oxidation of nitrite ion by chlorite (Nagaishi *et al.*, 1977) and oxidation of ethanol by Chlorite (Kudesia, 1979).

The acid dependence studies showed an acid independent/acid dependent pathways

and both the protonated and unprotonated species are reactive.

Possible mechanism consistent with the observed result is:



.....(66)

$$ClO_2^- \xrightarrow{K_2} ClO^- + O \quad \text{.....(67)}$$

$$RH_2^+ + ClO^- \xrightarrow{k_1} \text{Product.} \quad \text{.....(68)}$$

$$RH + ClO^- \xrightarrow{k_2} \text{Product} \quad \text{.....(69)}$$

$$\text{Rate} = k_1[RH_2^+][ClO^-] + k_2[RH][ClO^-] \quad \text{.....} \quad (70)$$

From equation 70

$$K_2 = \frac{[ClO^-][O]}{[ClO_2^-]} \quad \text{.....(71)}$$

if $[ClO^-] = [O]$

Then $[ClO^-][O] = [ClO^-]^2 = K_2[ClO_2^-]$ .....(72)

$$[ClO^-] = K_2^{1/2}[ClO_2^-]^{1/2} \quad \text{.....(73)}$$

$$[RH] = \frac{K_1[RH_2^+]}{[H^+]} \quad \text{.....(74)}$$

Putting (73) and (74) in (70) gives

$$\text{Rate} = K_2^{\frac{1}{2}} k_1 [RH_2^+][ClO_2^-]^{\frac{1}{2}} + K_2^{\frac{1}{2}} K_1 k_2 \frac{[RH_2^+][ClO_2^-]^{\frac{1}{2}}}{[H^+]} \quad (75)$$

$$\text{Rate} = \left(K_2^{\frac{1}{2}} k_1 + \frac{K_2^{\frac{1}{2}} K_1 k_2}{[H^+]} \right) [RH_2^+][ClO_2^-]^{\frac{1}{2}} \quad (76)$$

Equation (76) conforms to equation (30) the observed rate law where $K_2^{1/2} k_1 = b$ and $K^{1/2} K_1 k_2 = a$, $RH_2^+ = ROS$.

Equation (68) of the reaction mechanism confirms the negative salt effect observed in the reaction. Wilkins (1974) had established that negative salt effect display in reaction shows interaction of opposite charges in the activated Complex.

Analysis of Michealis - Mentens plot gave no intercept (Figure 4.5.7). This suggests the absence of intermediate complex formation.

The spectra of the reaction mixture gave a slight shift from 545 nm (λ_{max}) to 540 nm (Figure 4.5.3), this may be suggestive of ion-pair formation.

The observed catalytic effect of the anion ($HCOO^-$)on the three-half rate constant of the reaction, shows that the reaction is operating through the outersphere mechanism (Pennington and Haim 1967, Przystas and Sutin, 1973; Adegite *et al.*, 1977).

The anion ($C_2O_4^{2-}$) and cations (Li^+, Mg^{2+}) inhibited the reaction. Although this observation appears unusual, but it further shows that the reactant molecules are not bonded in the activated complex.

On the basis of the above evidences the reaction is probably operating by the outer-sphere mechanism. The same mechanism has earlier been reported for the reaction of

chlorite with *tris* (1.10 - phenanthroline) Iron (II) (Shakhashiri, 1969).

5.5.0 Summary and Conclusion

The redox reactions of rosaniline monochloride were studied with some oxyanions, $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^-, ClO_2^- in aqueous media.

The stoichiometry of 1:1 was observed for rosaniline - $S_2O_5^{2-}$ reaction and the same stoichiometry was assumed for the rest systems.

The order of the reaction with respect to the oxidant concentration was one for all the systems, while with respect to reductant concentration the order of one was obtained for the $S_2O_5^{2-}$, $S_2O_4^{2-}$, NO_2^- ions and half order for ClO_2^- ions.

The rates of the reactions showed three forms of acid dependencies viz:

(i) Inverse acid dependence with an intercept for the rosaniline - ClO_2^-, $S_2O_5^{2-}$ reactions.

(ii) Inverse acid dependence without an intercept for rosaniline - $S_2O_4^{2-}$, reaction.

(iii) positive acid dependence without an intercept for rosaniline - NO_2^- reaction.

The reactions therefore conform to the following rate equations:

$$-\frac{d[ROS]}{dt} = (b + a[H^+]^{-1})\,[ROS][R]$$

R = $[S_2O_5^{2-}]$ and $[ClO_2^-]^{1/2}$ for the reactions involving $S_2O_5^{2-}$ and ClO_2^-,

$$-\frac{d[ROS]}{dt} = a[H^+]^{-1}[ROS][S_2O_4^{2-}]$$ for the $S_2O_4^{2-}$ reaction and

$$-\frac{d[ROS]}{dt} = a[H^+][ROS][NO_2^-]$$ for the reaction involving NO_2^- ion.

The following rate constants for the reactions of the rosaniline and the oxy-anions were observed.

$k_2 (S_2O_5^{2-}) = (6.24 \pm 0.53) \times 10^{-1} M^{-1} s^{-1}$.

$k_2 (S_2O_4^{2-}) = (10.42 \pm 1.10) \times 10^{-1} M^{-1} s^{-1}$.

$k_2 (NO_2^-) = 7.81 \pm 1.58) \times 10^{-1} M^{-1} s^{-1}$.

$k_{3/2} (ClO_2^-) = (4.16 \pm 0.26) \times 10^{-3} M^{-1/2} s^{-1}$.

The rate of the reaction showed negative salt effect for the rosaniline - $S_2O_5^{2-}$, $S_2O_4^{2-}$, ClO_2^- reactions and positive salt effect for rosaniline - NO_2^- reaction.

Added anions and cations were observed to catalyse the reactions for all the systems. Free radical formation was not observed for any of the reactions.

The result of spectroscopic investigations and Michealis- Menten analysis showed evidence of intermediate complex formation for rosaniline - $S_2O_4^{2-}$ and none for the other systems.

From the experimental results obtained, the reactions of rosaniline with $S_2O_5^{2-}$, NO_2^-, ClO_2^- occurred through the outer-sphere mechanism while the reaction of rosaniline with $S_2O_4^{2-}$ occurred through the inner-sphere mechanism. Consequently, such mechanisms were proposed for the reactions respectively. For the reactions that occurred by the outer-sphere mechanism the rate of the reactions decreased in this order.

$k_2 (NO_2^-) > k_2 (S_2O_5^{2-}) > k_{3/2} (ClO_2^-)$

$((7.81 \pm 1.58) M^{-1}s^{-1} > (6.24 \pm 0.53) \times 10^{-1} M^{-1}s^{-1} > (4.16 \pm 0.26) \times 10^{-3} M^{-1/2} s^{-1})$

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