THE ELECTRON TRANSFER REACTIONS OF 3,7-BIS(DIMETHYLAMINE)PHENOTHIONIUM CHLORIDE (METHYLENE BLUE) WITH OXYANIONS IN AQUEOUS ACIDIC MEDIUM

BY

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DECLARATION

I declare that the work reported in the thesis entitled "the electron transfer reactions of 3,7-bis(dimethylamine)phenothionium chloride(methylene blue) with some oxyanions in aqueous acidic medium" has been performed by me in the Department of Chemistry, under the supervision of Prof. J.F. Iyun, Prof. G.F.S. Harrison and Prof. J.A. Lori. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any other University.

_____ _____ _____

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CERTIFICATION

This thesis entitled THE ELECTRON TRANSFER REACTIONS OF 3,7-BIS(DIMETHYLAMINE)PHENOTHIONIUM CHLORIDE (METHYLENE BLUE) WITH OXYNANIONS IN AQUEOUS ACIDIC MEDIUM by BUSARI ABDULAKEEM meets the regulations governing the award of the degree of Master of Science (M.Sc) of Ahmadu Bello University and its approved for its contribution to knowledge and literary presentation.

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DEDICATION

This project work is dedicated to the entire Busari family and to the memory of my late friend, Senator Momoh Jimoh Bello, may his soul rest in perfect peace, Amin.

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ABSTRACT

The kinetics and mechanisms of the redox reactions of 3,7-bis (dimethylamine)phenothionium chloride (MB^+) with the oxyanions, BrO_3^-, $S_2O_8^{2-}$ and SO_3^{2-}, have been studied. The rate of the reaction is first order in each oxidant and reductant concentrations for the three reactions. MB^+ was oxidized by BrO_3^- and $S_2O_8^{2-}$ and the order of reactivity is k_2 (BrO_3^-) > k_2 ($S_2O_8^{2-}$). The MB^+- $S_2O_8^{2-}$ reaction was Ag^+ catalysed. SO_3^{2-} reduced MB^+. The rates of the redox reactions of SO_3^{2-} an $S_2O_8^{2-}$ with MB^+ show no acid dependence, while that with BrO_3^- ion, showed acid independent and a second order acid dependence. All the reactions are affected by change in ionic strength. The stoichiometry is 2:3 for MB^+: BrO_3^- and 1:6 for MB^+: $S_2O_8^{2-}$. The stoichiometry for the MB^+- SO_3^{2-} could not be determined. The overall rate equation for the three reactions can be represented as shown below:

For the MB^+: BrO_3^- reaction:

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = k_2[MB^+][BrO_3^-]$$

where $k_2 = 10.16 \pm 0.29$ dm^3 mol^{-1} s^{-1}, at $[H^+] = 0.20$ mol dm^{-3} $\mu = 0.50$ mol dm^{-3} (NaCI) and T = 29.0 ± 1.0^0C.

For the Ag^+ catalysed MB^+: $S_2O_8^{2-}$ reaction

$$-\frac{d[MB^+]}{dt} = k_2[MB^+][S_2O_8^{2-}][Ag^+]$$

where $k_2 = 0.37 \pm 0.03$ dm^3 mol s^{-1} at $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3} $\mu = 0.10$ mol dm^{-3} ($NaNO_3$), $[Ag^+] = 5.0 \times 10^{-3}$ mol dm^{-3} and T= 26.0 ± 1.0^0C

For the MB^+: SO_3^{2-} reaction

$$-\frac{d[MB^+]}{dt} = k_2[MB^+][SO_3^{2-}]$$

where $k_2 = (3.02 \pm 0.22) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at $[H^+] = 1.0 \times 10^{-3}$ mol dm^3 $\mu = 0.10$ mol dm^{-3} (NaCI) and $T = 25.0 \pm 1.0^0C$

Free radicals were detected in the MB^+ reactions with $S_2O_8^{2-}$ and SO_3^{2-}. Spectroscopic investigation and kinetic evidence suggested the absence of short-lived intermediate complex in all the systems studied.

The experimental results obtained for all the systems are in favour of the outer-sphere mechanism.

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ABBREVIATION

Abbreviation		Names
Aq		Aqueous
B.D.H		British Drug House
bipy		2,2^{I}-bipyridine
Calc		Calculated
Cyt-c		Cytochrome C
ε	-	Dielectric constant of reaction medium
$\varepsilon_{ACETONE}$	-	Dielectric constant of acetone
$\varepsilon_{H\ O}$	-	Dielectric constant of water
E^0		Redox potential
EDTA		ethylenediaminetetraacetate
en		ethylenediamine
e.s.r		Electron Spin Resonance
G.P.R		General Purpose Reagent
I.S		Inner-sphere
k		rate constant
K	-	Equilibrium constant
L.R		Laboratory

Reagent		
N.M.R.	-	Nuclear Magnetic Resonance
obsd	-	Observed
O.S	-	Outer-sphere
phen	-	1,10-phenanthroline
py	-	pyridine
pyr	-	Pyrazine
μ	-	Ionic Strength
$V_{ACETONE}$	-	Volume of acetone
$V_{H\ O}$	-	Volume of water

CHAPTER ONE

1.0 Introduction

A reaction mechanism is the detailed stepwise process involving molecules, atoms, radicals or ions that occurs simultaneously or consecutively and culminates in the observed overall reaction (Cooke, 1979). The experimentally determined rate equation, the exact nature of both reactants and products, the presence of any equilibrium, and the stoichiometry of the reaction are all important information required for proper elucidation of mechanisms (Basolo and Johnson, 1964). Electron transfer is only one of many pathways by which redox reactions can occur (Basolo and Pearson, 1967; Burgess, 1978). Various reactions in inorganic and biological systems involve the transfer of electron at one stage or the other and proper understanding of these electron transfer processes helps in the understanding, development, and eventual effective control of a wide area of science and technology (Iyun, 1982). Also development in redox chemistry has shown that the basic principles which are operative for simpler systems involving metal ions in solution extends with some modifications to biologically important processes like the reactions of metalloproteins, photo-induced electron transfer processes, intervalence transfer and the reactions of the hydrated electron (Lippards, 1973).

1.1 Rate monitoring techniques

The method used to monitor the rate of a reaction depends on the species involved and the rapidity with which their concentration change with time (Atkins, 1997).

1.1.1 Conventional methods

These methods involve the measurement of the concentration or any physical property of one or more of the reactants or products that depends on their concentration as a function of time. The most important property of a complex ion which has been used for kinetic measurement is its absorption characteristics (Wilkins, 1962). The absorbance of any of the reactants or products is measured and related directly to its concentration (Wilkins, 1974).

1.1.2 Monitoring rates of fast reactions

Some reactions are so fast that special techniques have to be employed. Such techniques are of two main types. The first type employs the same principles as are used for slow reactions, the methods being modified to make them suitable for more rapid reactions. The second type is of a different character and involves special principles like temperature jump (Laidler and Meiser, 1982).

Flow technique: In the flow method the reactants are mixed as they flow together in a chamber. Different flow techniques can be employed, depending on the treatment given to the reaction after mixing (Caldin, 1964). In the quenching method, the reaction is stopped after it has been allowed to proceed for a certain time, and the composition is analyzed, by any conventional method.

In the continuous flow method the reaction is allowed to continue as the thoroughly mixed solution flow through the outlet tube, and the composition at different positions along the tube is observed. Spectrophotometric methods are commonly employed for the observation (Candlin and Halpern, 1965; Campion *et. al.*, 1964; McAuley and Hill, 1969).

Relaxation methods: These methods are used for systems at equilibrium (Eigen and Maeyer, 1963). In these cases, the equilibrium is displaced by some external parameters and the readjustment to a new equilibrium position is directly observed. Two main types of physical perturbation have been used: The stepwise or transient methods and the stationary methods.

Resonance technique: Both nuclear magnetic resonance and electron spin resonance techniques have been used to study complex formation (Pearson and Buch, 1962) and the aquation of metal ions (Connick and Poulson, 1959). The width of the resonance absorption line is related in n.m.r to the lifetime of the nucleus in a given spin state and in e.s.r to the lifetime of the paramagnetic species in a given energy state, and any reduction of the lifetime of these states by chemical interaction results in line broadening.

1.2 Theoretical consideration in election transfer processes

1.2.1 Franck-Condon principle

The principle states that nuclear motion is slow as compared to electronic motion and that election transfer occurs without an appreciable movement of the nuclei (Sutin, 1966). This implies that electron transitions are rapid compared with nuclear motions and electron transfer occurs without significant movement of the atoms. Exchange of electron can occur when the two particles have nearly identical structural and electronic configurations and the total change in energy involved in the process can be represented by equation (1.2) (Marcus, 1956)

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

$\Delta G_t^{\neq}$ = Association free energy

$\Delta G_i^{\neq}$ = lnner–sphere reorganisation energy

$\Delta G_o^{\neq}$ = Outer–sphere reorganisation energy

The principle also assumes that no angular momentum can be transferred to or from the transition state during electron transfer. It is also important that the two ions have identical spin states.

1.2.2 Electron tunneling theory

This theory states that solvent and ligands produce an electronic energy barrier that the transferring electron must penetrate (Weiss, 1954; Marcus, 1956). The implication is that the electron will be able to travel distances much greater than would correspond to the actual collision of reactants (Basolo and Pearson, 1967). Reorganization of the solvent molecules had to occur prior to electron transfer (Marcus, 1957). In terms of the transition state theory, their results may be written in the form

$$k = \frac{KTk^1}{h} \exp\left(-\frac{\Delta G_r^{\neq}}{RT} - \frac{\Delta G_e^{\neq}}{RT}\right) \quad \text{---------- (1.3)}$$

k^1 = electron transmission coefficient

k = rate constant

K = Boltzman constant

T = absolute temperature

$\Delta G_r^{\neq}$ = activation free energy for rearrangement of the hydration and coordination shells

$\Delta G_e^{\neq}$ = activation free energy for overcoming electric repulsion between the ions.

The transmission coefficient, which always remains less then one, increases, as the exchanging partners come closer together.

1.2.3 Solvated electron theory

This theory attributes the mechanism of electron transfer in solution to the ejection of an electron by the reductant into the solvent (equation 1.4). The solvent then solvates the electron and holds it until the oxidant picks it up (equation 1.5). The possibility that this mechanism operates in aqueous solution is remote, due to the fact that solvated electron with estimated potential of –2.70V (Latimer, 1952; Burgess, 1978) cannot exist in water without it reducing water (equation 1.6)

$$A + S = A^{+} + S^{-} \quad \text{---------- (1.4)}$$

$$S^{-} + B = [S^{-} + B]^{\neq} \longrightarrow S + B \quad \text{---------- (1.5)}$$

where A = Reductant

B = Oxidant

S = Solvent

$$e^{-}_{(aq)} + H_2O \rightarrow \tfrac{1}{2} H_{2(g)} + OH^{-} \quad \text{---------- (1.6)}$$

1.3 Oxidation –reduction reactions

Redox reactions are those in which the oxidation states of some atoms change. Generally, they can be classified into two broad groups: homonuclear (isotopic) exchange reacion and chemical or cross reactions (Edwards, 1964).

1.3.1 Homonuclear (Isotopic) exchange reactions.

This class of reactions involves transfer of electrons between two identical metal ion centers existing in different oxidation states. The reactants and products are the same and identical hence have the same concentrations. The free energy change for such

a reaction is mainly due to mixing and therefore is approximately zero (Sharpe, 1982). Examples of these reactions are given in equations (1.7) and (1.8).

$$[FeEDTA]^{2-} + {}^{*}[FeEDTA]^{-} = [FeEDTA]^{-} + {}^{*}[FeEDTA]^{2-} \text{ ----------(1.7)}$$

$$Tl^{I} + {}^{*}Tl^{III} = T1^{111} + {}^{*}T1^{1} \text{ ----------(1.8)}$$

(where * is an isotopically labeled specie)

In these types of electron transfers, there is no net chemical change and the equilibrium constant is one, since the rate constants for the forward and backward reactions are equal (Edwards, 1964). This class of reactions is studied by isotopic labeling (Burgess, 1978).

1.3.2 Heteronuclear (Cross) reactions

This class of reactions involves transfer of electrons between different metal ion centers and the products are chemically distinct from the reactants (Cooke, 1979). The net change in free energy in most cases is less than zero ($\Delta G < 0$). Examples of these reactions are given in equations (1.9) and (1.10)

$$2Fe^{2+} + Tl^{3+} = 2Fe^{3+} + Tl^{+} \text{ ---------- (1.9)}$$

$$2[Fe(phen)_3]^{3+} + 2I^{-} = 2[Fe(phen)_3]^{2+} + I_2 \text{ ---------- (1.10)}$$

Reactions of the type in which the oxidant and reductant change oxidation state by the same number of electrons are termed complimentary, as represented in equations (1.11) and (l.12) (Halpern, 1961).

$$[Co(en)_3]^{3+} + [Ru(NH_3)_6]^{2+} = [Co(en)_3]^{2+} + [Ru(NH_3)_6]^{3+} \text{ ----------(1.11)}$$

$$Fe^{II}cyt\text{–}c + [Ru(NH_3)_6]^{3+} = Fe^{III}cyt\text{-}c + [Ru(NH_3)_6]^{2+} \text{ ---------- (1.12)}$$

When the oxidant and reductant differ in their change in oxidation state (equations 1.13 and 1.14) the reactions are termed non-complementary reactions. These generally

proceed by complicated mechanisms (Burgess, 1978).

$$2V^{2+} + Br_2 = 2V^{3+} + 2Br^- \text{ ----------(1.13)}$$

$$2Eu^{2+} + C1_2 = 2Eu^{3+} + 2Cl^- \text{ ----------(1.14)}$$

1.4 Mechanism of redox reactions

The outer-sphere and the inner–sphere mechanism have been identified as the basic mechanisms that are operative when electrons are transferred between two metal ions in solution (Taube *et.al.,* 1953; Taube and Meyers, 1954; Taube, 1959).

1.4.1 The outer–sphere mechanism

This type of mechanism occurs when both reactants are inert with respect to substitution or when one of the reactants is relatively inert and does not present site for the labile reactant (Larsen and Wahl, 1965). The outer-sphere mechanism is characterized by low or zero ΔG or ΔE (Sharpe, 1982). The mode of activation of the outer-sphere mechanism can be illustrated as shown below for the reaction between $Fe(CN)_6^{4-}$ and $IrCl_6^{2-}$:

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}CI_6]^{2-} \longrightarrow [Fe^{III}(CN)_6]^{3-} + [Ir^{III}CI_6]^{3-} \text{ ----------(1.15)}$$

The above reaction takes place via the outer-sphere mechanism, and just like every other outer-sphere reaction, is thought to occur in four steps as shown below;

Step 1: Formation of precursor complex

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightarrow [(NC)_5Fe^{II}(CN)(ClIr^{IV}CI_5)]^{6-} \text{ ----------(1.16)}$$

Step 2: Activation of precursor complex

$$[(NC)_5Fe^{II}(CN)(ClIr^{IV}CI_5)]^{6-} \rightarrow [(NC)_5Fe^{II}(CN)(ClIr^{IV}\text{-}Cl_5)]^{6-\neq} \text{---(1.17)}$$

Step 3: Electron transfer and formation of successor complex

$$[(NC)_5Fe^{II}(CN)(ClIr^{IV}\text{-}Cl_5)]^{6-} \rightarrow [(NC)_5Fe^{III}(CN)(ClIr^{III}\text{-}Cl_5)]^{6-} \text{-----(1.18)}$$

Step 4: Decomposition of successor complex to give final products

$$[(NC)_5Fe^{III}(CN)(ClIr^{III}\text{-}Cl_5)]^{6-} \longrightarrow [Fe^{III}(CN)_6]^{3-} + [Ir^{III}CI_6]^{3-} \text{-------(1.19)}$$

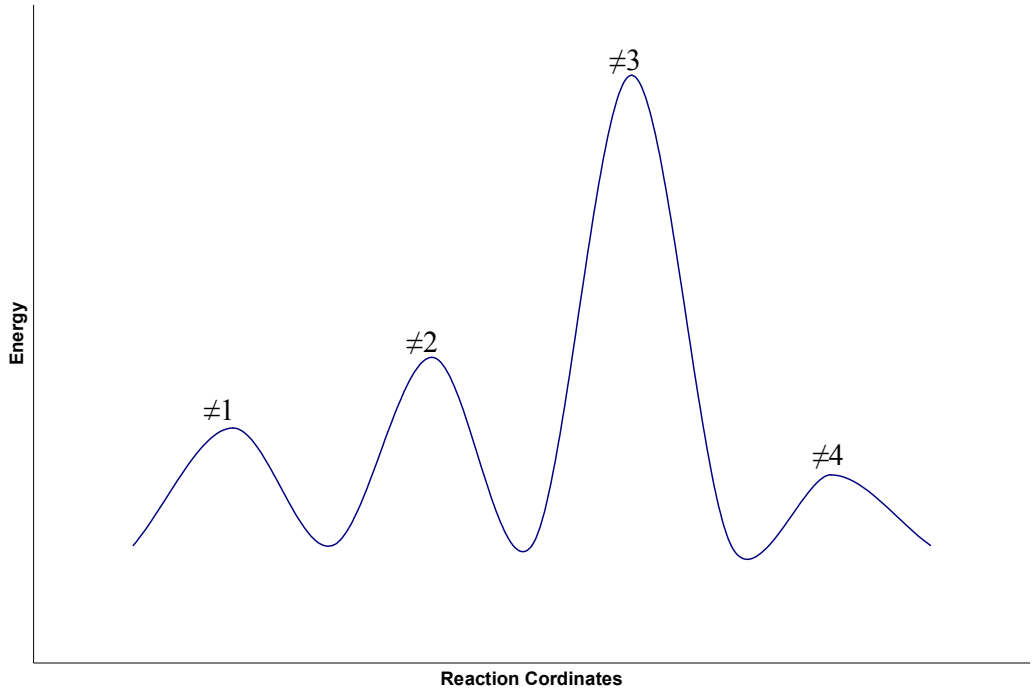


Fig. 1.1:- Energy profile diagram for a redox reaction which occur by the outer–sphere mechanism.

Although any of the steps can be the rate determining step, step 3- the electron transfer, is usually the rate determining step.

1.4.2. Inner-sphere mechanism

In this mechanism, electron transfer is preceeded by substitution into the coordination shell of one of the reactants, with the formation of a bridged intermediate in which two metal ions are linked by a common ligand (Halpern, 1961). Typical reactions that occur via this mechanism include reactions 1.20 and 1.21 below

$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \longrightarrow [Co^{II}(H_2O)_6]^{2+} + 5NH_4^+ + [Cr^{III}(H_2O)_5Cl]^{2+}$ ---- (1.20)

$[(Cr(OH_2)_5Cl]^{2+} + [Cr^*(OH_2)_6]^{2+} \longrightarrow [(Cr(OH_2)_6]^{2+} + [Cr^*(OH_2)_5Cl]^{2+}$------- (1.21)

In general, the inner–sphere mechanism can be represented by the following reaction scheme.

Step 1: Formation of encounter or collision complex

$$[L_5M^{III}X]^{m+} + [N^{II}(H_2O)_6]^{n+} \longrightarrow [L_5M^{III}X//N^{II}(H_2O)_6]^{(m+n)+} \text{----------(1.22)}$$

Step 2: Formation of a bridged precursor complex

$$[L_5M^{III}X//N^{II}(H_2O)_6]^{(m+n)+} \longrightarrow H_2O + [L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5]^{(m+n)+} \text{---------(1.23)}$$

Step 3: Activation of the precursor complex.

$$[L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5]^{(m+n)+} \longrightarrow [L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5]^{(m+n)+\neq} \text{---------- (1.24)}$$

Step 4: Electron transfer and formation of successor complex

$$[L_5M^{III}\text{-}X\text{-}N^{II}(H_2O)_5]^{(m+n)+\neq} \longrightarrow [L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5]^{(m+n)+\neq} \text{---------- (1.25)}$$

Step 5: Deactivation of successor complex

$$[L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5]^{(m+n)+\neq} \longrightarrow [L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5]^{(m+n)+} \text{----------(1.26)}$$

Step 6: Decomposition of activated complex

$$[L_5M^{II}\text{-}X\text{-}N^{III}(H_2O)_5]^{(m+n)+} \longrightarrow [L_5M^{II}(H_2O)]^{m+} + [XN^{III}(H_2O)_5]^{n+} \text{---(1.27)}$$

Investigations have revealed that the electron transfer step is usually the rate determining step (Iyun, 1982). Typical energy profile for a redox reaction which occurs by the inner–sphere mechanism can be illustrated by Figure (1.2)

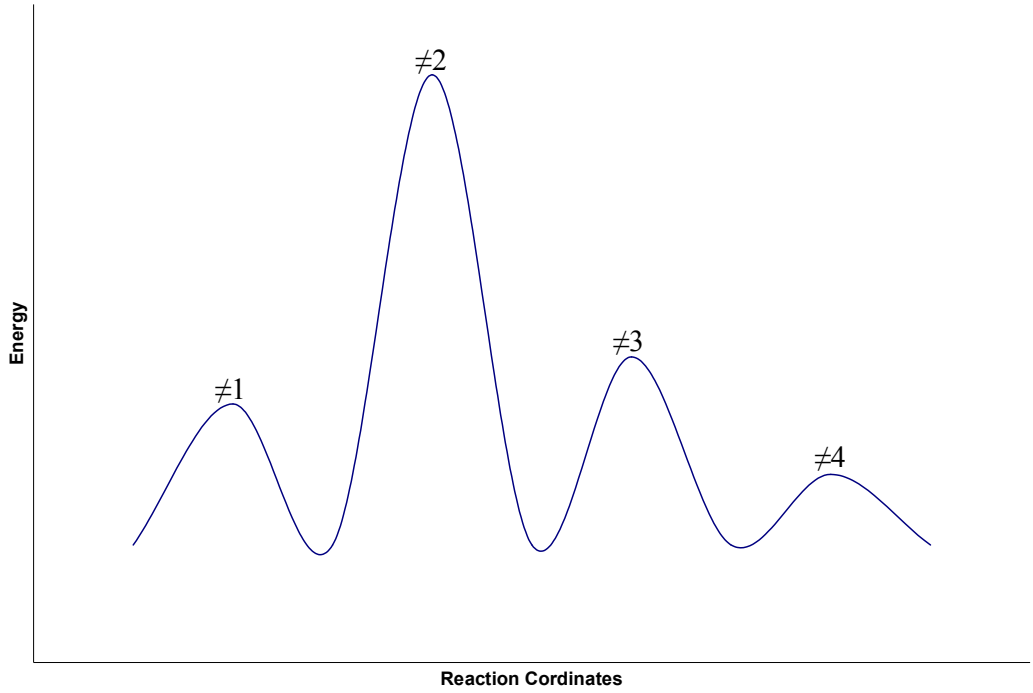


Fig. 1.2:-Typical energy profile for a redox reaction which occurs by the inner–sphere can be illustrated by figure

≠1 = Collision complex

≠2 = Bridged precursor complex formation

≠3 = Successor complex formation and the act of electron-transfer

≠4 = Decomposition of successor complex giving the products.

1.5 Diagnosis of redox reaction mechanism

Electron-transfer reactions may be occurring by either the outer- or the inner-sphere mechanisms. Some of the criteria that are used in assigning a mechanism for reactions are discussed below:

1.5.1 k_{redox} versus $k_{substitution}$

If the rate of electron-transfer is greater than the rate of substitution into the inner-coordination sphere of either of the complexes, the outer-sphere mechanism is indicated (equation 1.28) (Rosenheim *et.al.,* 1974).

$V^{2+} + Fe^{3+} \longrightarrow V^{3+} + Fe^{2+}$ ----------(1.28)

$k_{redox} = 1.8 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$

$k_{substitution} = 100\ s^{-1}$

The outer-sphere mechanism is established when rapid electron transfer occurs between two substantially inert complexes (Burgess, 1978).

However for reactions in which the rate of substitution into the inner-coordination sphere of either of the complexes is faster than the rate of electron transfer and where a bridging ligand is present, the inner–sphere mechanism is a possibility. For the reaction (equation 1.20), the reductant Cr^{II} is labile ($k_{substitution} = 1.0 \times 10^8\ s^{-1}$) and the reaction was assumed to involve rapid and reversible formation of the bridged intermediate followed by a slow electron transfer ($k_{redox} = 6.0 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$) (Cooke, 1979).

1.5.1 Identification of binuclear intermediate

The detection of an intermediate with a suitable bridging ligand is an indication that the redox reaction has occurred by means of a bridged activated complex and this provides a convincing evidence for the operation of the inner-sphere mechanism (Burgess, 1980).

The presence of an intermediate is also indicated if the rate law contains inverse orders, non-integral orders or orders larger than three (Edwards, 1964).

1.5.3 Product analysis.

Hints about the possible pathway for the redox reactions could be obtained from the isolation and characterization of the products of the reaction. It is also possible to establish the details of how electron transfer reactions occur based on isotopic labelling. The use of a particular isotope enables the observation of bond-breaking processes and the identification of atom or group of atoms transferred from one metal center to another. An example is equation (1.20) based on the reduction of substitutionally inert amine complexes of Co^{III} by substitutionally labile $Cr(H_2O)_6^{2+}$ and the introduction of labelled Cl^- into the reaction mixture. The appearance of unlabelled Cl^- in the inert Cr^{III} product indicated that both metal centers must have been bonded simultaneously to Cl^- as a bridging ligand when electron transfer occurred. (Taube, *et. al.,* 1953).

However, there are inner–sphere reactions which are not accompanied by atom transfer, equation (1.29) (Cooke, 1979). In this reaction it was demonstrated that bridge formation occurred but the bridging ligand was not transferred.

$$[Co(EDTA)]^{2-} + [Fe(CN)_6]^{3-} \longrightarrow [(EDTA)CoNCFe(CN)_5]^{5-}$$

$$\longrightarrow [Co(EDTA)]^- + [Fe(CN)_6]^{4-} \text{ ----------(1.29)}$$

1.5.4 Activation parameters.

The use of activation parameters, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ to determine the type of mechanism operating in a particular redox process is of little use, because there seems to be no direct correlation between activation parameters and the type of mechanism (Cotton and Wilkinson, 1980). However change in molar volume of activation ($\Delta V^{\neq}$) has been used in mechanistic diagnosis (Hubbard *et. al.,* 1991).

1.5.5 Reactivity pattern

(i) Relative rates of reaction of azido and thiocyanato complexes

Comparison of the effect of azido and thiocyanato ligands on the rates of electron transfer reactions involving metal ions and their complexes have been widely used as a basis for determining whether a particular reaction proceeds by the inner– or the outer–sphere mechanism (Ball and King, 1958; Espenson, 1965; Douglas and Sutin, 1970). If the metal centers of the oxidizing and reducing agents are hard and if transfer of the bridging group occurs during the reaction, then an inner-sphere mechanism should proceed faster when the bridging group is azido than when it is isothiocyanato.

(ii) The effect of added anion

The effect of added anions and cations give an indication of the type of mechanism operating in a redox process (Pennington and Haim, 1967; Przystas and Sutin, 1973; Adegite *et. al.,* 1977). The rate of oxidation of acetaldehyde by BrO_3^- was found to be inhibited by the added formate and nitrate ions. The reaction was therefore suggested to have occurred via the outer-sphere mechanism (Lohdip and Iyun, 1993). Although there are exceptions (Halpern, 1961) generally anion catalyzed reactions are presumed to be operating via the outer-sphere mechanism (Dulz *et. al.,* 1964; Przystas and Sutin, 1973).

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

The hydroxyl group (OH^-) is a better bridging ligand than H_2O, so the hydroxo complexes are expected to react faster via the inner–sphere mechanism, which involves the formation of bridged intermediate, thus where $k_{OH} >> k_{H\ O}$ the inner sphere mechanism is said to be operating (Cotton and Wilkinson, 1980).

(iv) Reactivity pattern with a wide range of reactants

The relative rates of oxidation of a series of reducing agents by two different oxidants should be independent of the identity of the reducing agent if both set of reactions are by the outer–sphere mechanism (Marcus, 1963). For the inner-sphere mechanism the rate is very sensitive to the nature of the reductant, the oxidant and the bridged atom (Edwards, 1964).

1.5.6 Marcus theory of electron transfer rates

This theory predicts a simple relationship (equation 1.30) between the rate constant k_{12} for an electron–transfer reaction, K_{12}, the equilibrium constant for the reaction, and k_{11} and k_{22}, the self exchange rate constant for the reductant and oxidant complexes (Marcus, 1963)

$$*Ox_1 + Red_2 \overset{K_{12}}{\rightleftharpoons} *Red_1 + Ox_2 \quad \text{---------- (1.32)}$$

$$*Ox_1 + Red_1 \overset{k_{11}}{\rightleftharpoons} *Red_1 + Ox_1 \quad \text{---------- (1.33)}$$

$$*Ox_2 + Red_2 \overset{k_{22}}{\rightleftharpoons} *Red_2 + Ox_2 \quad \text{---------- (1.34)}$$

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad \text{---------- (1.30)}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/z^2)} \quad \text{---------- (1.31)}$$

Z = collision frequency generally taken as 10^{11} dm^3 mol^{-1} s^{-1}

The theory is an adiabatic theory of electron transfer and assumes that within the activated complex for electron transfer, the probability of electron transfer is one. It also assumes that work terms for the self exchange and cross reactions are the same and that

the electron transfer reagents may be treated as spherical, structureless reactants.

Other theoretical treatments and modifications of Marcus theory include those of Hush (1961) and Sutin (1966). Good agreement between the observed rate and that calculated by Marcus-Cross relation suggests outer-sphere mechanism (Cotton and Wilkinson, 1980).

1.6 Research objective

Our main interest in this work is to study electron transfer reactions of methylene blue. We intend to gain more insight into the kinetics and mechanisms of its reactions by investigating the dynamics of its reactions with the oxyanions such as BrO_3^-, $S_2O_8^{2-}$ and SO_3^{2-}. This will also enable us to compare the reactions of these oxyanions with other reported electron transfer reactions of oxyanions.

CHAPTER TWO

2.0 Literature review

2.1 Biological stains

A biological stain is a dye used for making microscopic object more clearly visible than they would be when unstained (Arnold, 1973). Whether a particular object in a microscopical section is strongly or weakly coloured by a particular dye depends on three factors; chemical affinity between the object and the dye, the density of the object, and the permeability of the object by the dye (Baker, 1966). Those parts of the cell or tissue, which stains differently because of chemical and/or physical differences, can thus be more easily distinguished (Arnold, 1973).

Although natural dyes such as carmine and indigo were well known in the early days of the microscope, their use in staining microscopic preparations only began in about 1850 (Conn, 1961).

Most dyes contain chomophore and auxochromic groups attached to benzene rings, the colour being attributable to the chomophore and the dyeing property to the salt–forming auxochrome (Arnold, 1973). Also dyes often posses atoms, such as halogen, or group of atoms, such as methyl group, that are called modifiers, this modifies the colour of the dye, making it more slightly intense (Baker, 1966).

Generally, dyes are classified on the basis of the nature of their chromophores (Conn, 1961; Baker, 1966), and some of the important groups include:

(i) Nitroso dyes, such as naphthol green B

(ii) Nitro dyes, such as naphthol yellow S

(iii) Azo dyes, such as orange G, bismarck brown, and chlorazol black E.

(iv) Aryl methane dyes, such as fast green FCF and victoria blue.

(v) Xanthane dyes, such as pyronin Y, rhodanine B and the eosins.

(vi) Acridine dyes such as acridine orange

(vii) Quinone – imine dyes, including the arzocarmines, safrain O, thionin and the azures.

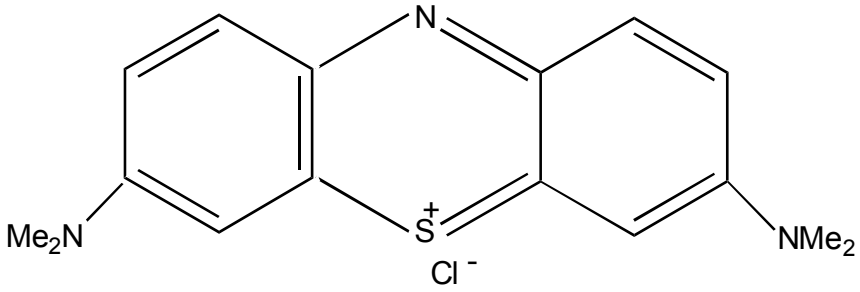
(viii) Natural dyes such as carmine and haematoxylin

(ix) The anthraquinone dyes, such as alizarin

(x) The thiazole dyes, such as titan yellow

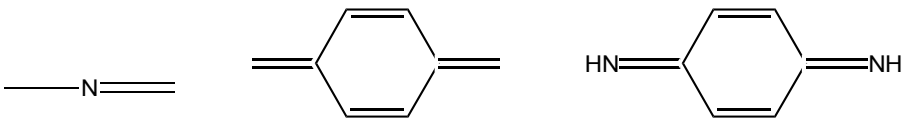
(xi) The quinline dyes, such as pinacyanol.

(xii) The phthalocyanine dyes, such as alcian blue



(2.1)

Methylene blue (2.1) belongs to the thiazin subgroup of the quinine-imine group of dyes. This group of dyes contains two chromophore groups, the indamine (2.2), and the quinoid benzene ring (2.3). They have paraquinonediimine (2.4) as their precursor.



(2.2) (2.3) (2.4)

This compound does not actually exist, but gives the name for the dye class. Other subgroup of the quinine-imine dyes important in histotechnology are the azins and the oxazins (Conn, 1961).

Methylene blue is the most valuable stain to the pathologist and the bacteriologist (Jones, 1950).

2.2 Redox reactions of methylene blue

Methylene blue stains cell nuclei and bacteria and is therefore used as a diagnostic aid, in the differential diagnosis of diphtheria and rabies (Jones, 1950). The stain is also a chemical oscillator (Burger and Field, 1984), which explains why it is used as an oxidation-reduction indicator (Vogel, 1978).

Literature indicates that very little has been done on the kinetics and mechanism of redox reactions of methylene blue (Burger and Field, 1984; Iyun and Asala, (1994); Ukoha and Iyun, 2000). Ukoha and Iyun (2000) investigated the kinetics and mechanism of the reduction of methylene blue by ascorbic acid. The structure of methylene blue was found to support a proton-coupled electron-transfer leading to loss in conjugation. This is likely to arise from the ease of protonation of the amino groups on methylene blue in acid medium. Many other types of organic redox reactions proceed by way of hydride transfer (Bartlett, 1956). This involves the simultaneous transfer of two electrons plus a proton and no intermediate free radical is produced.

There is electron reorganization on the oxidation of organic molecules and majority of organic oxidation involves the rupture of carbon-hydrogen or carbon-carbon bonds. Generally, all oxidizing agents produce the same alteration in organic compound with reducing property (Stewart, 1964). The corresponding situation holds for reducing agents. Michaelis and Schubert (1938) suggested that all oxidation of organic molecules

proceed in two successive univalent steps via intermediate free radicals. But most organic compounds tend to avoid reactions requiring one-equivalent steps. This is because stable organic compound normally do not have unpaired electrons (they are not radicals).

2.3 Electron transfer reactions of oxyanions

Oxyanions have found wide applications in many aspects of life. For example, bromate is a strong oxidant and is used for aromatic bromination (Schatz, 1996), peroxydisulphate is useful in photochemical reactions (Bolleta *et. al.,* 1980), while sulphite is used in the food industry as a preservative (Hill and Gray, 1996) as well as in photography, to protect developer solution from oxidation (Verma and Dhar, 1931).

It has been reported that the rates of reactions of oxyanions are markedly dependent on the acidity of the reaction medium. Orders of two or more in hydrogen ion concentration are obtained (Birk and Kozub, 1973; Ayoko *et. al.,* 1993). The proton weakens the strong bond between the negative oxygen atom and the positive central atom (Edwards, 1964).

The rate laws- rate = $k[XO_m^{n-}]\,[H^+]$ and rate = $k[XO_m^{n-}][H^+]\,[R]$, where X = Cl, Br, I, S, N and m = 2, 3, or 4 and n = 1 or 2, have been found to be followed by the oxygen exchange reaction between a reductant, R and oxyanions, NO_3^- (Aubar and Taube, 1954), SO_3^{2-} and SO_4^{2-} (Hoering and Kennedy, 1957), $C1O^-_3$, $C1O_4^-$, BrO_3^-, IO_4^-, and IO_3^- (Birk and Kozub, 1973). For oxyanions with highly charged and or small central atom such as NO_3^-, BrO_3^- and NO_2^- the rate law of the form:

$$\text{Rate} = k[XO_m^{m-}]\,[H^+]^2 \quad \text{----------(2.1)}$$

has been observed (Edwards, 1954). But when the central atom is large and or less highly charged, the second order dependence of rate on hydrogen ion is no longer

observed (Aubar and Taube, 1958; Murman, 1961; Aubar and Gutman, 1961; Baloga and Earley, 1963). For a series of closely related species, the lower the charge on the central atom of an oxyanion the higher the reactivity (Jolly, 1976). Therefore for chlorine oxyanions reaction rate increases in the order $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$. Also the larger the size of the central atom the higher the reactivity of the oxyanion.

Both the outer sphere (Birk and Kozub, 1978; Iyun *et.al.,* 1992) and the inner-sphere (Birk and Kozub, 1973) have been found operative for reactions of oxyanions, depending on the nature of the metal ion complex or organic substrate.

The oxyanions of interest in this work are BrO_3^-, $S_2O_8^{2-}$ and SO_3^{2-} and reviews on these are given below.

2.3.1 Electron transfer reactions of bromate ion

The redox reactions of bromate with metal ion complexes (Thompson, 1971; Birk, 1973, 1978; Birk and Kozub, 1973, 1978; Iyun *et. al.,* 1992) and of bromate with organic compound (Lohdip and Iyun, 1993; Lohdip *et. al.* 1995; Jonnalagadda and Samianyana, 1995) have all been studied. The rate of most of the reactions, is expressed by the rate law given by the general equation (2.2)

$$-\frac{d[BrO_3^-]}{dt} = (a + b[H^+]^n)[BrO_3^-][\text{Reductant}] \quad \text{----------(2.2)}$$

where n = 1 or 2.

The rate of redox reactions of bromate have been shown to depend strongly on acid concentration (Birk and Kozub, 1978; Ayoko *et. al.,* 1993). The hydrogen ion concentration dependence suggest that the oxidation reactions occur via two parallel pathways, involving protonated and unprotonated species, both reacting to give the product (Birk, 1973; Birk and Kozub, 1973; Lohdip *et. al.*, 1995). Both pathways can occur through the outer-sphere mechanism (Birk and Kozub, 1973; Lohdip *et. al.*,

1995). Cases have also been reported (Birk 1973) in which parallel outer- and inner-sphere mechanism was obtained, with the acid dependent path occurring via the outer-sphere. Some oxidation reactions of BrO_3^- exhibit complex kinetics. The oxidation of thymol blue (Jonnalagadda, *et. al.,* 1995) has a stoichiometry of 3:2 at low [BrO_3^-] and 4:5 when [Br O_3^-] is in excess.

2.3.2 Electron transfer reactions of peroxydisulphate ion

Peroxydisulphate ion is one of the powerful oxidizing agents known (Fordham and Leverne, 1951; Irvin, 1958). However, despite its redox potential of +2.01V for $S_2O_8^{2-}{}_{(aq)} \longrightarrow 2SO_4^{2-}{}_{(aq)}$ (Latimer, 1952) little or no reaction occurs in the absence of catalyst for some of its redox reactions. Ag(1) (Gupta and Misra, 1959; Ayoko *et. al.,* 1992) and Cu(II) (Penington and Haim, 1967) have all been used as a catalyst. The effectiveness of Ag(I)and Cu(II) as catalyst is due to their oxidation to Ag(II) or Ag(III) and Cu(III) states respectively (Brasted, 1961). The existence of either Ag^{2+} (Khandual, 1991) or Ag^{3+} (Gupta and Misra, 1959, Gupta and Ghosh, 1959) have all been reported in the redox reactions of $S_2O_8^{2-}$ catalysed by Ag(1).

A large number of investigations have been done in the field of the oxidation of metal ions (Yost and Clausen, 1931; Gupta and Misra, 1959), metal complexes (Irvin, 1958; Chlebek and Lister, 1967; Raman and Brubakar, 1969) and various organic compounds (Gupta and Gupta, 1981) by $S_2O_8^{2-}$.

Reactions of $S_2O_8^{2-}$ are characterized by the existence of free radical sulphate ion as intermediate (Uri, 1952; Irvin, 1958; Ayoko *et. al.,* 1992).

Most electron transfer reactions of $S_2O_8^{2-}$ occur by the outer–sphere mechanism (Penington and Haim, 1968; Ohasi *et. al.,* 1976; Ayoko *et. al.,* 1992). However, reactions with some positively charged metal complexes such as $Fe(bpy)_3^{2+}$,

$Fe(phen)_3^{2+}$, $Os(bpy)_3^{2+}$ occur by both the outer– and the inner– sphere mechanisms (Irvin, 1958; Raman and Brubakar, 1969).

Except, when the reducing agent can be protonated, the redox reaction of $S_2O_8^{2-}$ was found to be independent of hydrogen ion concentration (Gupta and Ghosh, 1959; Gupta and Gupta, 1981; Banerjeee and Pujari, 1981; Lawal, 1997).

2.3.3 Electron transfer reactions of sulphite ion

The sulphite ion is a powerful reducing agent. The stoichiometry and products of reactions involving sulphite allows a distinction to be made among one- and two-equivalent oxidizing agents (Higginson and Marshal, 1957; Davies *et. al.,* 1969). The possible reaction paths, equations (2.3) and (2.4) give dithionate and sulphate respectively.

$$SO_3^{2-} \xrightarrow{1e^-} SO_4^{2-} \longrightarrow 1/2S_2O_6^{2-} \text{ ----------(2.3)}$$

$$SO_3^{2-} \xrightarrow{2e^-} SO_4^{2-} \text{ ----------(2.4)}$$

Some reactions with one-equivalent oxidants such as $Fe(CN)_6^{3-}$ produced sulphate and not dithionate (Murray, 1968). Oxidation of sulphur(IV) by oxidizing agents such as Cr(IV) and Mn(VII) yielded dithionate as well as sulphate as the reaction products (Basset, 1903; Dennis *et. al.,* 1983).

Both the outer–sphere mechanism (Stapp and Calyle, 1974; Dennis *et. al.,* 1983) and the inner–sphere mechanism (Lohdip, 1989; Kraft and Eldick, 1989; Iyun *et. al.,* 1992) have been observed for the redox reactions of SO_3^{2-} ions.

In aqueous solution, SO_3^{2-} ions exist in equilibrium with HSO_3^- (equation 2.5) (Stapp and Carlyle, 1974; Dennis, *et. al.,* 1983; Sen Gupta, 1987)

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^- \text{ ----------(2.5)}$$

CHAPTER THREE

3.0 Experimental

3.1 Materials and reagents

All solutions were prepared with distilled water except otherwise stated.

3.1.1 Preparation of 9.36×10^{-6} mol dm^{-3} methylene blue solution

Analar grade of methylene blue obtained from B.D.H, hereafter refer to as MB^+, was used without further purification. 50 mg of methylene blue was dissolved in 250 cm^3 of distilled water. To obtain a solution suitable for spectrum determination, 3 cm^3 of this solution was diluted to 200 cm^3 with distilled water. Absorption maximum was broad at 660 – 665 nm, Literature value =664 – 666 nm (Conn, 1961).

3.1.2 Preparation and standardization of 0.01 mol dm^{-3} sodium thiosulphate solution

The thiosulphate solution was prepared by dissolving an appropriate amount of $Na_2S_2O_3.5H_2O$ (B.D.H Laboratory Reagent) in distilled water and standardized by iodometric method (Vogel, 1978). 0.15 g of the pure, dried KIO_3 was weighed and dissolved in 25 cm^3 of distilled water, with 2 g of KI and 5 cm^3concentrated sulphuric acid added. The liberated iodine was then titrated against the thiosulphate solution, using starch iodide indicator. When the colour of the solution became pale yellow, the solution was diluted to 200 cm^3 with distilled water, 2 cm^3 of starch iodide indicator was added and the titration continued until there was a colour change from blue to colourless. The iodometric method of determination is based on the following equations:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \quad \text{---------- (3.1)}$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-} \quad \text{---------- (3.2)}$$

3.1.3 Preparation of 0.10 mol dm^{-3} potassuim bromate solution

The bromate solution was prepared by dissolving an appropriate amount of the dried $KBrO_3$ (B.D.H, Analar grade) in distilled water and standardized with the standard, $Na_2S_2O_3$ solution. 10 cm^3 of the bromate solution was diluted to 50 cm^3 and treated with 3 g of potassium iodide and 7 cm^3 of concentrated sulphuric acid. The liberated iodine was titrated against the standard $Na_2S_2O_3$ solution, using 2 cm^3 of starch–iodide indicator. This method of determination is based on the following equations:

$$BrO_3^- + 5I^- + 6H^+ = 5/2I_2 + 3H_2O + Br^- \text{ ----------(3.3)}$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-} \text{ ---------- (3.4)}$$

3.1.4 Preparation of 0.10 mol dm^{-3} sodium peroxydisulphate solution

The peroxydisulphate solution was prepared by dissolving an accurate weight of $Na_2S_2O_8$ (B.D.H) Laboratory Reagent) in distilled water. Due to the gradual decomposition of the peroxydisulphate solution, fresh solutions were prepared daily. In addition the containers were wrapped with aluminium foil to prevent photo-induced decomposition (Gupta and Ghosh, 1959; Ayoko *et. al.,* 1992).

3.1.5 Preparation of 0.10 mol dm^{-3} sodium sulphite solution

The sulphite solution was prepared by dissolving an appropriate amount of Na_2SO_3 (B.D.H, Laboratory Reagent) in distilled water and standardized by iodometric method (Vogel, 1978). 25 cm^3 of standard 0.10 mol dm^{-3} iodine solution was pipetted into 250 cm^3 conical flask, then 5 cm^3 of 2.0 mol dm^{-3} HCl and 150 cm^3 distilled water were added. 20 cm^3 of 0.10 mol dm^{-3} Na_2SO_3 solution was added slowly into the mixture with constant stirring. The excess iodine was titrated with standard, 0.10 mol dm^{-3} $Na_2S_2O_3$ solution using starch indicator. The iodometric method of

determination is based on the following equations:

$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2H^+ + 2I^-$ ----------(3.5)

$HSO_3^- + I_2 + H_2O = SO_4^{2-} + 3H^+ + 2I^-$ ----------(3.6)

3.1.6 Preparation of 0.10 mol dm^{-3} iodine solution

About 5 g of iodine free KI (B.D.H, Analar) was dissolved in 10 cm^3 of distilled water in a glass stoppered 250 cm^3 graduated flask and 3.175 g of iodine (B.D.H, Analar) was transferred into the concentrated KI solution. The glass stopper was inserted into the flask and shaken in the cold until all the iodine dissolved. The solution was then allowed to acquire room temperature and made up to the mark with distilled water. It was standardized against $Na_2S_2O_3$ solution and kept in a cool dark place.

3.1.7 Preparation of 1.0 mol dm^{-3} sodium chloride solution

5.85 g of NaCl (B.D.H, Laboratory Reagent) was accurately weighed and poured into a 100 cm^3 volumetric flask containing about 50 cm^3 distilled water. The solution was made up to mark with more distilled water.

3.1.8 Preparation of 1.0 mol dm^{-3} sodium nitrate solution

This was prepared by weighing 8.50 g of $NaNO_3$ (B.D.H, Laboratory Reagent) in distilled water and making up the solution to 100 cm^3 in a volumetric flask.

3.1.9 Preparation of 0.50 mol dm^{-3} sodium carbonate solution

2.6548 g of the dried Na_2CO_3 (dried at 220 ^0C for an hour) was weighed and dissolved in distilled water contained in a 50 cm^3 volumetric flask. The solution was made up to mark with distilled water to give a 0.50 mol dm^{-3} solution of Na_2CO_3.

3.1.10 Preparation of 1.0 mol dm^{-3} hydrochloric acid solution

A stock solution of hydrochloric acid, 1.0 mol dm^{-3} was made by the dilution of concentrated solution of HCl (B.D.H, Analar). The HCl was standardized by

volumetric analysis using sodium carbonate as primary standard. Methyl orange was used as indicator. From the result obtained, the concentration of the acid was determined according to the equation of the reaction below (Vogel, 1978):

$$2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2 \quad \text{---------- (3.7)}$$

3.1.11 Preparation of 1.0 mol dm^{-3} nitric acid solution

The 1.0 mol dm^{-3} solution of nitric acid prepared from the concentrated solution nitric acid (B.D.H, Analar), was standardized with sodium carbonate using methyl orange as indicator. The concentration of the acid was determined using the equation below.

$$2HNO_3 + Na_2CO_3 = 2NaNO_3 + H_2O + CO_2 \quad \text{---------- (3.8)}$$

3.1.12 Preparation of 0.10 mol dm^{-3} sodium formate solution

0.17 g of HCOONa (B.D.H, Laboratory Reagent) was accurately weighed and poured into a 25 cm^3 volumetric flask containing about 10 cm^3 distilled water. The solution was made up to mark with more distilled water.

3.1.13 Preparation of 0.10 mol dm^{-3} sodium sulphate solution

This was prepared by weighing 0.355 g of $NaSO_4$ (B.D.H, Laboratory Reagent) in distilled water and making up the solution to 25 cm^3 in a volumetric flask.

3.1.14 Preparation of 0.50 mol dm^{-3} silver nitrate solution

0.05 g of $AgNO_3$ (Griffin Certified Reagent) was accurately weighed and poured into a 100 cm^3 volumetric flask containing about 50 cm^3 distilled water. The solution was made up to mark with more distilled water.

3.2 Stoichiometric studies

The stoichiometries of the reactions were determined by spectrophotometric titration using the mole ratio method (Ayoko *et. al.,* 1991; Lohdip and Iyun, 1993). In

all cases the concentration of the metheylene blue was kept constant while that of the oxyanions were varied as follows:

For MB^+: BrO_3^- reaction:

$[MB^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 1.0 \times 10^{-5} - 1.1 \times 10^{-4}$ mol dm^{-3}, T = 29.0±1.0^{0}C

$[H^+]$=0.20 mol dm^{-3}, μ = 0.50 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.

For the Ag^+ catalysed MB^+: $S_2O_8^{2-}$ reaction:

$[MB^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 2.0 \times 10^{-5} - 2.0 \times 10^{-4}$ mol dm^{-3}, T = 26.0±1.0^{0}C

$[H^+] = 1.0 \times 10^4$ mol dm^{-3}, $[Ag^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, μ = 0.10 mol dm^{-3} ($NaNO_3$) and λ_{max} =665 nm.

For MB^+: SO_3^{2-} reaction:

$[MB^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[SO_3^{2-}] = 2.5 \times 10^{-6} - 7.0 \times 10^{-5}$ mol dm^{-3}, T = 25.0±1.0^{0}C

$[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, μ = 0.1 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.

The reactions were allowed to go to completion for all the systems. This was ascertained by taking the absorbances of the mixtures at intervals. The reaction was taken to be complete when the absorbance remained constant after series of repeated readings.

The absorbances of the solutions were measured at 665 nm, the wavelength of maximum absorption of methylene blue, having certified that none of the reactants nor the products absorbed at this wavelength. Infact BrO_3^-, $S_2O_8^{2-}$, SO_3^{2-} and all other products obtained were all colourless and therefore do not absorb in the visible region (400 – 700 nm). The stoichiometries, indicated by the point of inflexion, were evaluated from the plot of absorbances versus concentrations of oxyanions.

3.3 Kinetic measurements

The rates of the reactions were monitored on a Corning Colorimeter 253. The rate of reaction of each oxyanions (BrO_3^-, $S_2O_8^{2-}$, and SO_3^{2-}) with methylene blue was

studied by monitoring decrease in absorbance of the methylene blue at 665nm.

All kinetic measurements were carried out under pseudo-first order conditions with respective oxyanion concentrations in at least 210, 18 and 200-fold excess over the methylene blue concentrations for the MB^+ - BrO_3^-, MB^+ - $S_2O_8^{2-}$, and MB^+ - SO_3^{2-} systems respectively.

The conditions under which the orders of the reactions with respect to the reactants were determined are as follows:

For the MB^+: BrO_3^- reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 6.0 \times 10^{-3} – 1.1 \times 10^{-2}$ mol dm^{-3},

T = 29.0±1.0^{0}C, $[H^+] = 0.20$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3} (NaCl) and $\lambda_{max} = 665$ nm.

For the Ag^+ catalysed MB^+: $S_2O_8^{2-}$ reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 2.0 \times 10^{-3} – 1.6 \times 10^{-2}$ mol dm^{-3},

T = 26.0±1.0^{0}C, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[Ag^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.10$ mol dm^{-3} ($NaNO_3$) and λ_{max} =665 nm.

The order with respect to $[Ag^+]$ was determined by varying $[Ag^+]$ in the $2.0 \times 10^{-3} – 1.5 \times 10^{-2}$ mol dm^{-3} range and maintaining $[S_2O_8^{2-}]$ at 8.0×10^{-3} mol dm^{-3} while all other conditions remains the same as above.

For the MB^+: SO_3^{2-} reaction:

$[MB^+] = 1.25 \times 10^{-5}$ mol dm^{-3}, $[SO_3^{2-}] = 1.0 \times 10^{-2} – 3.0 \times 10^{-2}$ mol dm^{-3}, T = 25.0±1.0^{0}C

$[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3} (NaCl) and $\lambda_{max} = 665$ nm.

The effects of $[H^+]$ on the rate of the reactions were determined under the following conditions:

For the MB^+: BrO_3^- reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 6.0 \times 10^{-3}$ mol dm^{-3}, T = 29.0 ± 1.0^{0}C,

$[H^+]$ = 0.175 – 0.30 mol dm^{-3}, μ = 0.50 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.

For the Ag^+ catalysed MB^+: $S_2O_8^{2-}$ reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 8.0 \times 10^{-3}$ mol dm^{-3}, T = 26.0 ± 1.0^0C,

$[H^+] = 1.0 \times 10^{-5} – 1.0 \times 10^{-2}$ mol dm^{-3}, $[Ag^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, μ = 0.10 mol dm^{-3} ($NaNO_3$) and λ_{max} =665 nm.

For the MB^+: SO_3^{2-} reaction:

$[MB^+] = 1.25 \times 10^{-5}$ mol dm^{-3}, $[SO_3^{2-}] = 1.0 \times 10^{-2} – 3.0 \times 10^{-2}$ mol dm^{-3}, T = 25.0±1.0^0C

$[H^+] = 1.0 \times 10^{-5} - 5.0 \times 10^{-3}$ mol dm^{-3}, μ = 0.1 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.

The effect of ionic strength on the rate constants of the reactions were found by keeping the concentration of reactants constant and varying the concentration of the inert electrolyte, NaCl for the MB^+ - BrO_3^- and MB^+ - SO_3^{2-} while $NaNO_3$ was used for the MB^+ - $S_2O_8^{2-}$ system. The ionic strength of the solutions were adjusted based on the relationship below (equation 3.9)

$$\mu = \tfrac{1}{2} \sum c_i z_i^2 \quad \text{----------(3.9)}$$

where z_i is the charge number of an ion i (positive for cations and negative for anions).

c_i is the concentration of the ion in solution

The conditions under which the effects of ionic strength on the reaction rate were monitored are as follows:

For the MB^+: BrO_3^- reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-] = 8.0 \times 10^{-3}$, T = 29.0±1.0^0C,

$[H^+]$ = 0.20 mol dm^{-3}, μ = 0.40 – 0.70 mol dm^{-3} (NaCl) and λ_{max} = 665 nm.

For the Ag^+ catalysed MB^+: $S_2O_8^{2-}$ reaction:

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 8.0 \times 10^{-3}$, T = 26.0±$1.0^0$C,

$[H^+] = 1.0 \times 10^{4}$ mol dm^{-3}, $[Ag^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, μ = 0.05 – 0.50 mol dm^{-3} ($NaNO_3$) and λ_{max} =665 nm.

For the MB^+: SO_3^{2-} reaction:

$[MB^+] = 1.25 \times 10^{-5}$ mol dm^{-3}, $[SO_3^{2-}] = 2.6 \times 10^{-2}$ mol dm^{-3}, T = 25.0±1.0^{0}C

$[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, μ = 0.10 – 0.60 mol dm^{-3} (NaCI) and λ_{max} = 665 nm.

The effect of medium dielectric constant on the reaction rate was observed by carrying out the reactions in medium of varying dielectric constants. The medium dielectric constants were varied by combining water and acetone in different ratio and the dielectric constant of the solutions were calculated using equation (3.10)

$$\varepsilon = \frac{\varepsilon_{H_2O} V_{H_2O} + \varepsilon_{ACETONE} V_{ACETONE}}{V_{TOTAL}} \quad \text{----------(3.)}$$

3.4 Test for the presence of intermediate complex

3.4.1 Spectrophotometric investigation

This was carried out on all the systems studied in order to find out whether spectroscopically determinable intermediate complex were formed between methylene blue and the respective oxyanions during the course of each reaction. The spectra of the reaction mixture were taken over the 400 – 700 nm range, immediately after the reactions were initiated. For the MB^+ - SO_3^{2-} system, the reaction was slow enough (about 1 hour) for the spectrum to be ran after every 15 minutes. Similar spectrum was determined for methylene blue (Figure 3.1). The formation of an intermediate complex is indicated by an increase in peak height or shift in λ_{max} of the methylene blue.

3.5 Free radical test

5 cm^3 of acrylamide was added to partially oxidized reaction mixture of bromate and methylene blue. This was followed by a large excess of methanol. The acrylamide was also added to a solution of the bromate and methylene blue separately. This served as control. In place of acrylamide, allylacetate, a known sulphate radical scavenger was used for the MB^+- $S_2O_8^{2-}$ and MB^+ -SO_3^{2-} systems.

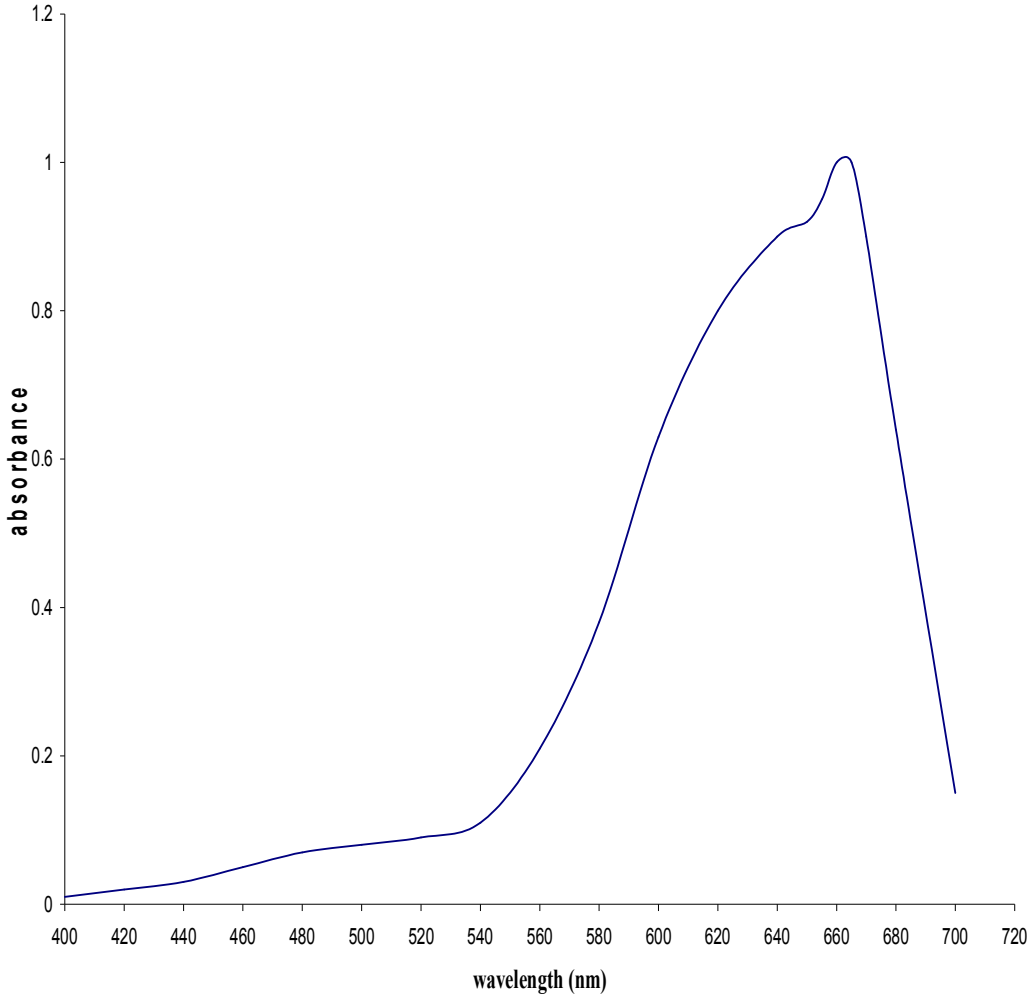


Figure 3.1:- Spectrum of methylene blue.

CHAPTER FOUR

4.0 Results

4.1 Stoichiometry

4.1.1 Methylene blue-bromate system

The result of the stoichiometry showed that two moles of methylene blue were consumed by three moles of BrO_3^-. The titration curve from which the stoichiometry was determined is presented in Figure (4.1). On the basis of this result, the overall equation for this can be represented by equation (4.1)

$$2MB^+ + 3BrO_3^- + 18H^+ = \text{products} + 3/2Br_2 \text{ ---------- (4.1)}$$

4.1.2 Silver(I) catalysed methylene blue – peroxydisulphate system

The stoichiometry was found to be 1:6 (MB^+:$S_2O_8^{2-}$) in excess $S_2O_8^{2-}$ (Figure 4.2). Thus the reaction may be represented by equaton (4.2).

$$MB^+ + 6S_2O_8^{2-} = \text{products} + 12SO_4^{2-} \text{ ---------- (4.2)}$$

4.1.3 Methylene blue – sulphite system

The stoichiometry could not be determined over the range of concentration studied. This is because the reaction was too slow and since stoichiometry is determined by combining the two reactants in simple whole ratio, little changes was observed in the absorbances of the reaction mixture containing varying concentration of SO_3^{2-} and constant methylene blue concentration.

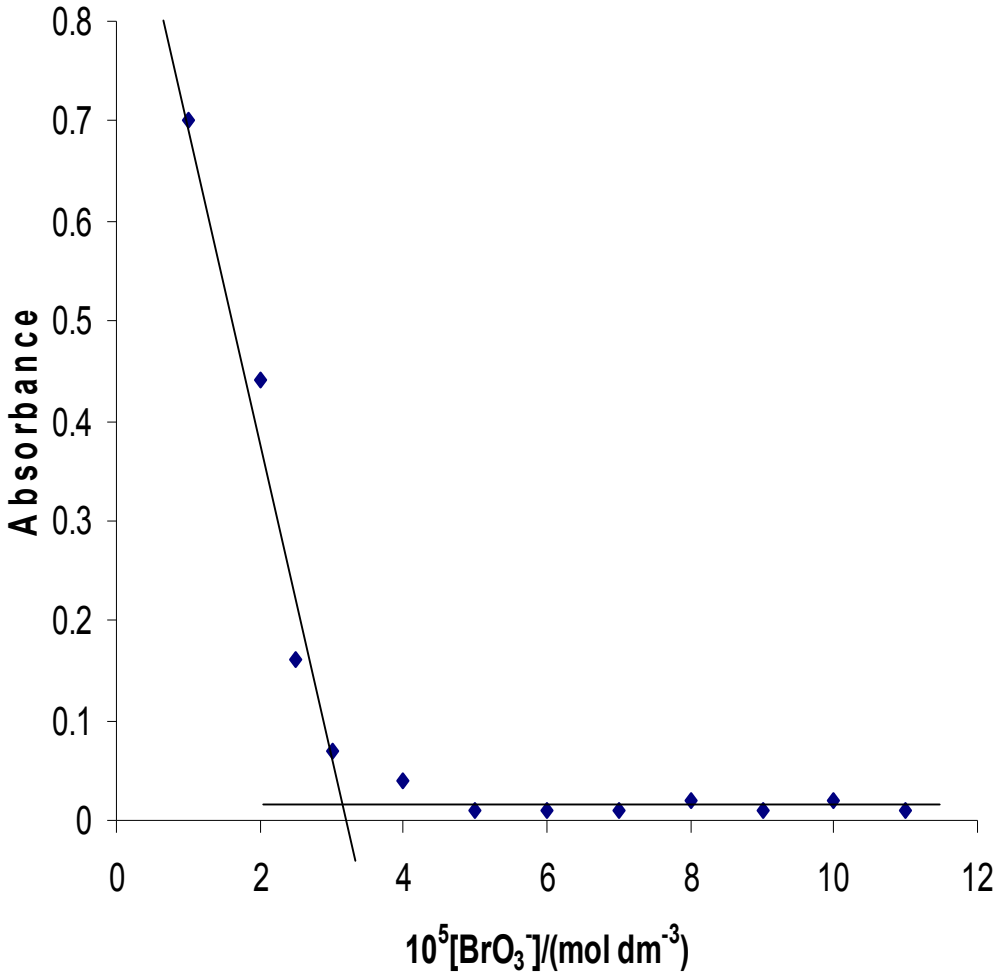


Figure 4.1:-Plot of absorbance versus $[BrO_3^-]$ for the redox reaction between MB^+ and BrO_3^-

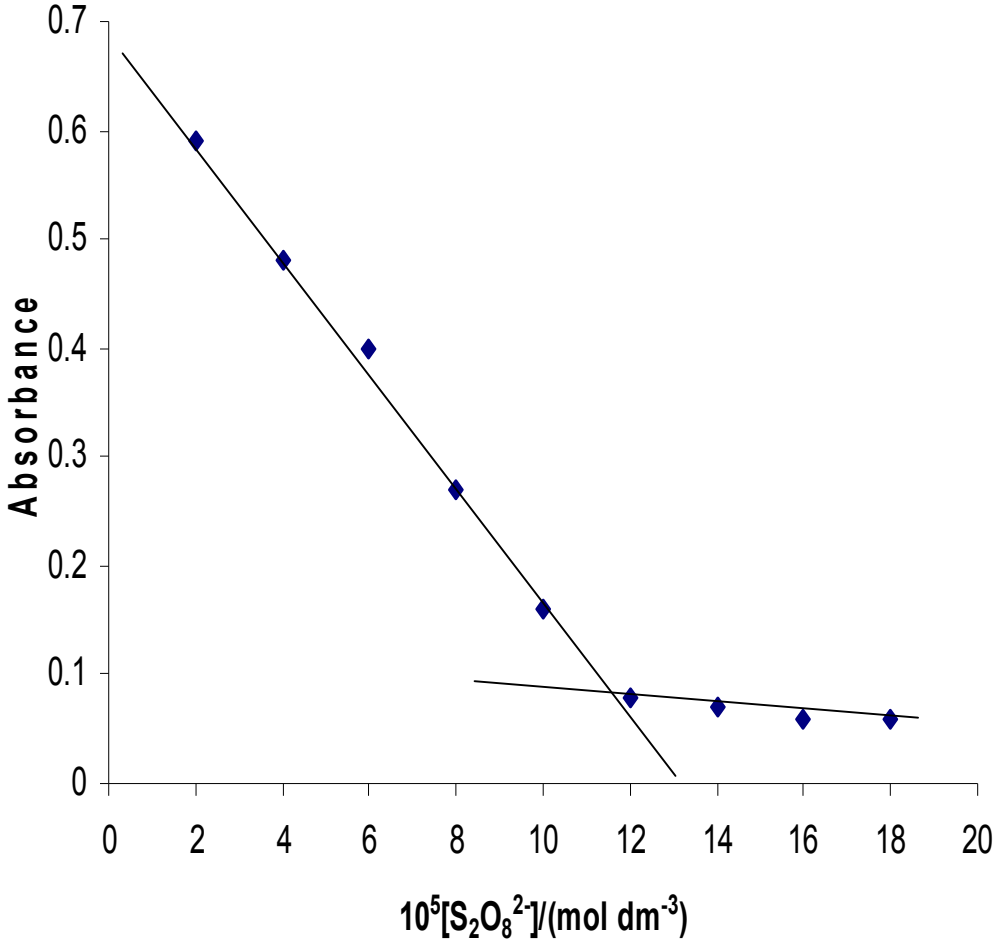


Figure 4.2:- Plot of absorbance versus $[S_2O_8^{2-}]$ for the redox reaction between MB^+ and $S_2O_8^{2-}$

4.2 Determination of order with respect to reactants

4.2.1 Methylene blue – bromate system

The pseudo – first order plots of log (A_t - A_∞) versus time were linear to more than 60% extent of reaction. This suggests a first order dependence of rate on [MB^+]. The typical plot is shown in Figure 4.3. The pseudo-first order rate constants, k_{obsd} were determined at various initial concentration of bromate ion, and at constant [MB^+] and [H^+] and are reported in Table 4.1.

Plot of logk_{obsd} versus log[BrO_3^-] for the reaction of MB^+ and BrO_3^-, gave a slope of 1.08 (Figure 4.4). Similarly least square plot of k_{obsd} versus [BrO_3^-] gave a straight line with r = 1.00 (Figure 4.5). This observation further showed that the order of the redox reaction with respect to [BrO_3^-] is one. The reaction is second order overall and the second order rate constant were determined as k_{obsd} /[BrO_3^-] and were found to be fairly constant (Table 4.1). This reaction can be fitted into equation (4.3).

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = k_2 [MB^+] [BrO_3^-] \quad \text{---------- (4.3)}$$

where k_2 = 10.16 ± 0.29 mol dm^{-3} at [H^+]= 0.20 mol dm^{-3}, μ = 0.5 mol dm^{-3} (NaCl) and T = 29.0±1.0 ^{0}C

4.2.2 Silver(I) catalysed methylene blue – peroxydisulphate system

The pseudo–first order plots of log (A_t - A_∞) versus time were linear to more than 13 % extent of reaction. This suggests a first order dependence of rate on [MB^+]. The non-linearity of the pseudo first order plots after about 13 % extent of the reaction probably arises through participation in the reaction of the sulphate ion radical produced in the primary step (Irvin, 1958). $SO_4^{\cdot-}$ is a powerful oxidizing agent (Bolletta *et. al.,* 1980)

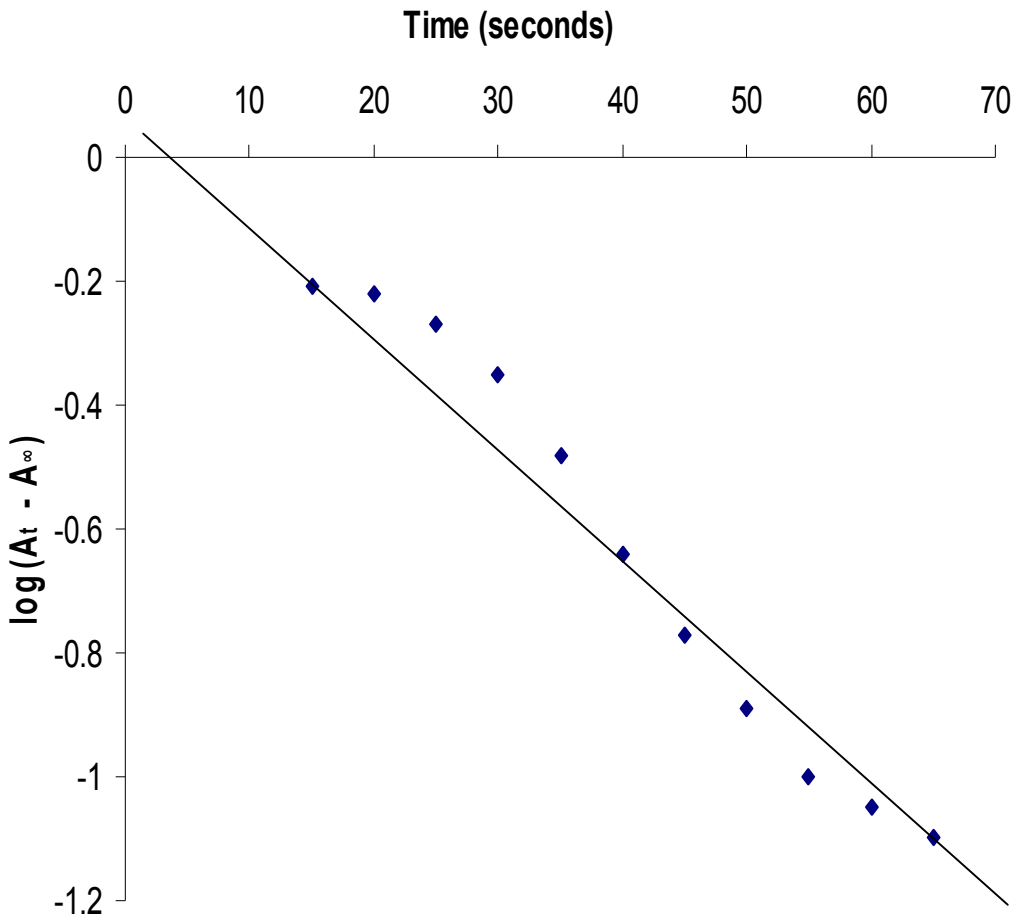


Figure 4.3:- A typical pseudo-first order plot for the oxidation of MB^+ by BrO_3^-

TABLE 4.1: Pseudo-first and second order rate constants for the redox reaction of methylene blue and bromate ion. $[MB^+]=1.87x10^{-5}$ mol dm^{-3}, T= 29.0±1.0^{0}C and λ_{max} = 665 nm.

$10^3[BrO_3^-]$/ (mol dm^{-3})	$[H^+]$/(mol dm^{-3})	μ(NaCl)/ (mol dm^{-3})	$10^2 k_{obsd}$/ s^{-1}	k_2/ (dm^3 mol^{-1} s^{-1})
6.0	0.20	0.50	6.15	10.25
7.0	0.20	0.50	6.91	9.87
8.0	0.20	0.50	8.24	10.30
9.0	0.20	0.50	9.21	10.23
10.0	0.20	0.50	10.20	10.20
11.0	0.20	0.50	11.10	10.09
8.0	0.175	0.50	6.29	7.86
8.0	0.20	0.50	8,24	10.30
8.0	0.225	0.50	9.90	12.38
8.0	0.25	0.50	11.50	14.38
8.0	0.275	0.50	13.80	17.25
8.0	0.30	0.50	16.60	20.75
8.0	0.20	0.50	6.59	8.24
8.0	0.20	0.40	7.60	9.50
8.0	0.20	0.45	8.24	10.30
8.0	0.20	0.55	8.54	10.68
8.0	0.20	0.60	9.44	11.80
8.0	0.20	0.65	10.80	13.50
8.0	0.20	0.70	11.70	14.63

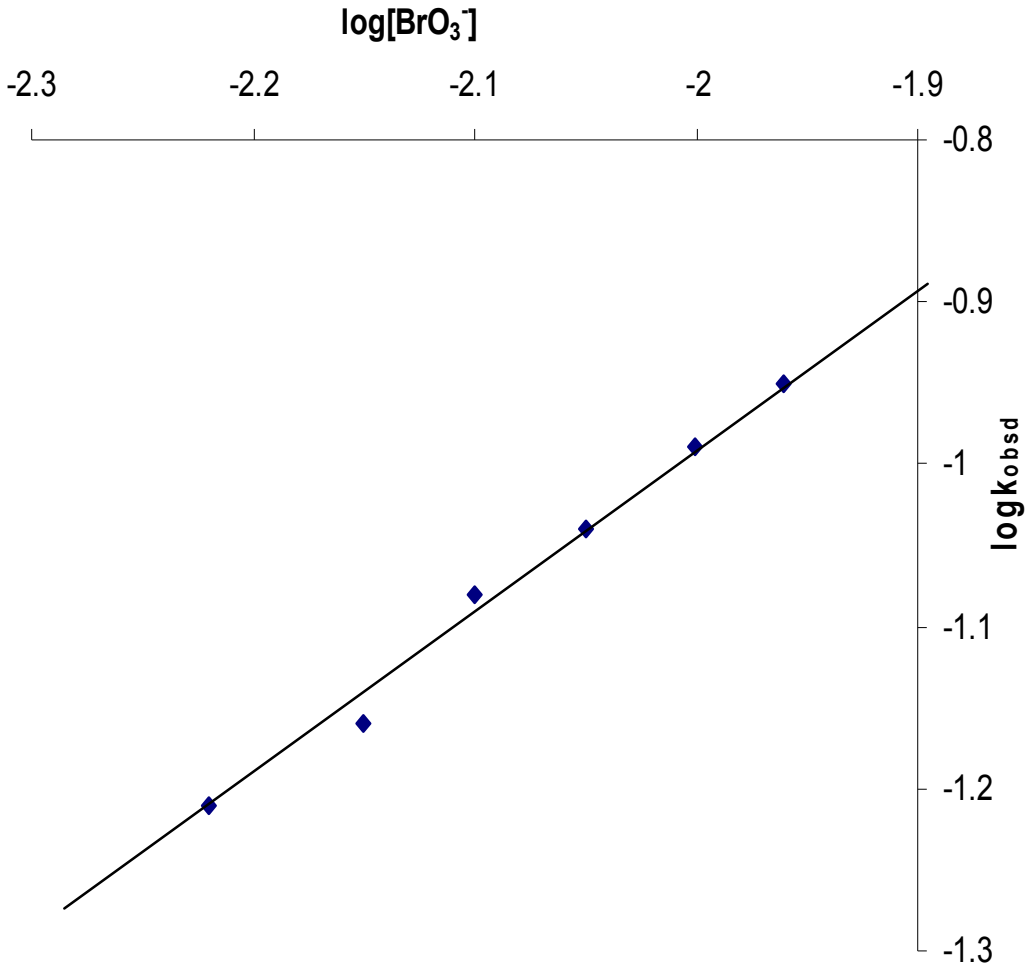


Figure 4.4:- Plot of $\log k_{obsd}$ versus $\log[BrO_3^-]$ for the reaction of MB^+ and BrO_3^-

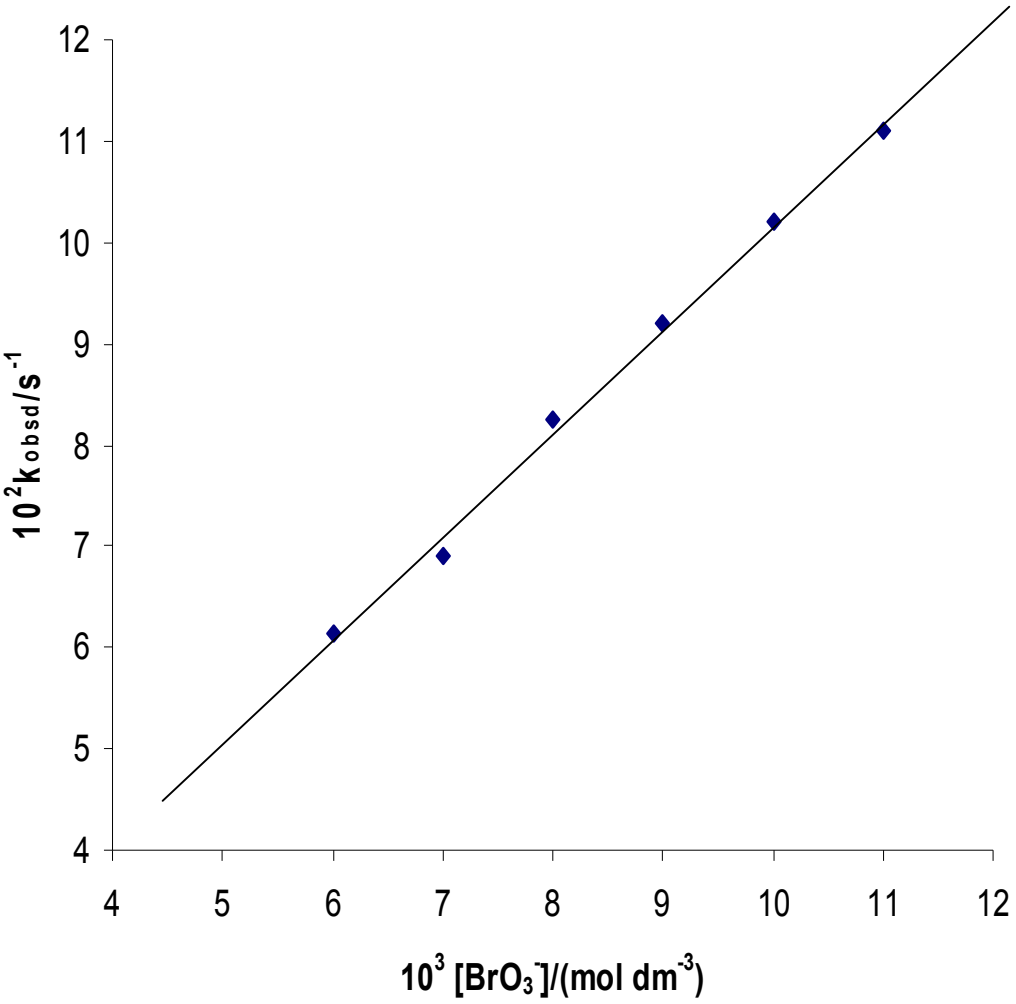


Figure 4.5:- Plot of k_{obsd} versus $[BrO_3^-]$ for the oxidation of MB^+ by BrO_3^-

and formed a parallel reaction. The typical pseudo first-order plot is shown in Figure (4.6). The pseudo first order rate constants, k_{obsd}, were determined at different initial concentrations of $S_2O_8^{2-}$ at constant $[MB^+]$, $[Ag^+]$ and $[H^+]$ of 1.87×10^{-5} mol dm^{-3}, 5.0×10^{-3} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3} respectively (Table 4.2). Plot of $\log k_{obsd}$ versus $\log[S_2O_8^{2-}]$ gave a slope of 1.06 (Figure 4.7), showing that the rate of reaction is first order with respect to $[S_2O_8^{2-}]$. Similarly plot of k_{obsd} versus $[S_2O_8^{2-}]$ was linear, (Figure 4.8) with r = 0.976, further suggesting that the order of the reaction with respect to $[S_2O_8^{2-}]$ is one. The second order rate constant was determined from as k_{obsd},/ $[S_2O_8^{2-}]$ and was found to be fairly constant (Table 4.2).

The order with respect to the $[Ag^+]$ was investigated at constant $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 8.0 \times 10^{-3}$ mol dm^{-3} and $[Ag^+]$ in the range ($2.0 \times 10^{-3} - 15.0 \times 10^{-3}$ mol dm^{-3}). Plot of $\log k_{obsd}$ versus $\log[Ag^+]$ gave a slope of 1.11 (Figure 4.9). Also plot of k_{obsd} versus $[Ag^+]$ (Figure 4.10), was linear with r = 0.986. Both results showed that the order with respect to $[Ag^+]$ is one.

A combination of the result of kinetic studies suggests that the empirical rate equation is represented by equation (4.4)

$$-\frac{d[MB^+]}{dt} = k_2 [MB^+] [S_2O_8^{2-}] [Ag^+] \quad \text{---------- (4.4)}$$

where, $k_2 = 0.37 \pm 0.03$ dm^3 mol^{-1} s^{-1} at $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3},

$\mu = 0.10$mol dm^{-3} ($NaNO_3$), $[Ag^+] = 5.0 \times 10^{-3}$ mol dm^{-3} and $T = 26.0 \pm 1.0$ ^{0}C.

$$-\frac{d[MB^+]}{dt} = (a + b [Ag^+]) [MB^+] [S_2O_8^{2-}] \quad \text{---------- (4.4)}$$

4.2.3 Methylene blue – sulphite system

The pseudo-first order plot of log $(A_t - A_\infty)$ versus time was linear to more 80% extent of reaction. This suggests a first order dependence of rate on $[MB^+]$.

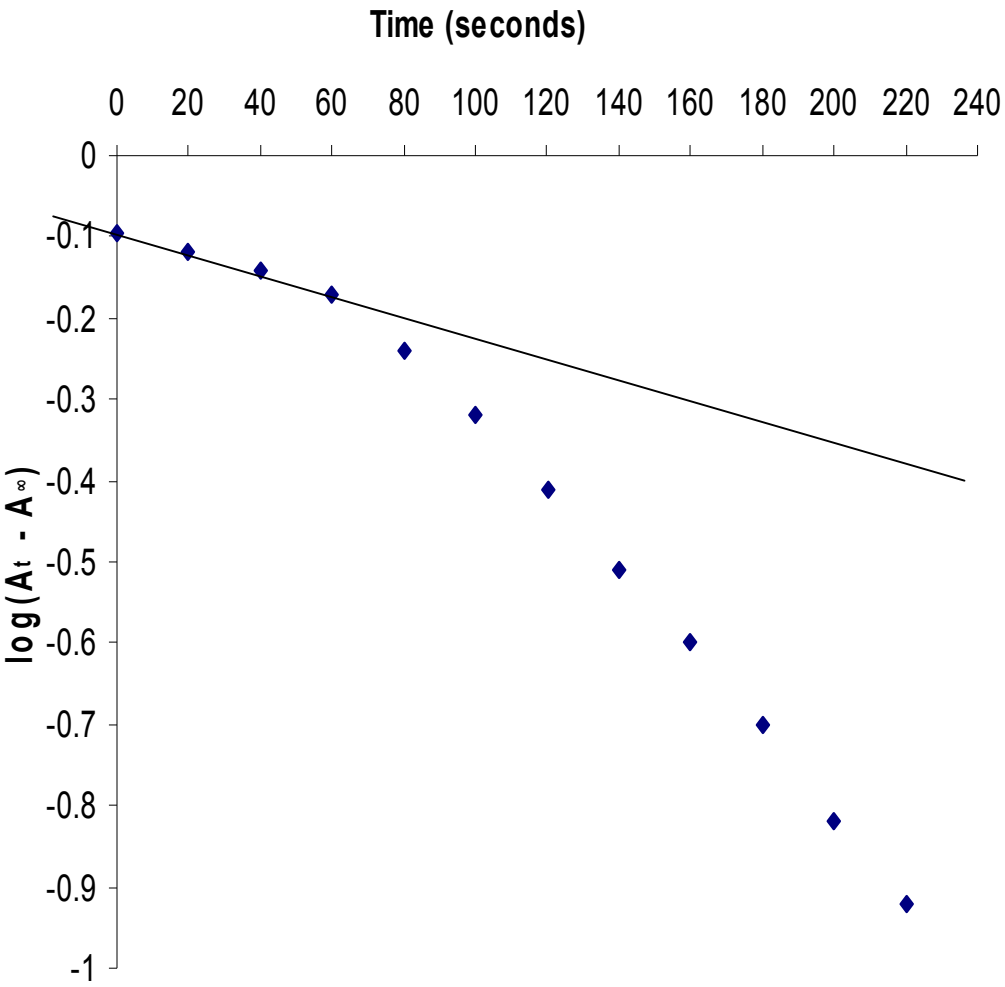


Figure 4.6:- A typical pseudo-first order plot for the Ag^{+} catalysed oxidation of MB^{+} by $S_2O_8^{2-}$

TABLE 4.2:-Pseudo-first and second order rate constants for the Ag^+ catalysed redox reaction of methlylene blue and peroxydisulphate ion. $[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, T=26.0 ± 1.0 ^{0}C and λ_{max} = 665 nm.

$10^3[S_2O_8^{2-}]$/ (mol dm^{-3})	$10^5[H^+]$/ (mol dm^{-3})	μ/ (mol dm^{-3})($NaNO_3$)	$10^3[Ag^+]$/ (mol dm^{-3})	$10^3 k_{obsd}$/ s^{-1}	k_2/ (dm^3 mol^{-1} s^{-1})
2.0	10	0.10	5.0	0.67	0.34
4.0	10	0.10	5.0	1.5	0.38
6.0	10	0.10	5.0	2.1	0.35
8.0	10	0.10	5.0	2.8	0.35
10.0	10	0.10	5.0	3.7	0.37
12.0	10	0.10	5.0	4.6	0.38
14.0	10	0.10	5.0	5.1	0.36
16.0	10	0.10	5.0	6.2	0.39
8.0	10	0.10	2.0	1.2	0.15
8.0	10	0.10	5.0	2.8	0.35
8.0	10	0.10	7.5	3.7	0.46
8.0	10	0.10	10	6.7	0.84
8.0	10	0.10	12.5	9.0	1.18
8.0	10	0.10	15	11.0	1.13
8.0	10	0.05	5.0	3.5	1.38
8.0	10	0.10	5.0	2.8	0.44
8.0	10	0.20	5.0	2.1	0.35
8.0	10	0.30	5.0	1.8	0.26
8.0	10	0.40	5.0	1.7	0.23
8.0	10	0.50	5.0	1.6	0.21
8.0	1.0	0.10	5.0	3.0	0.21
8.0	5.0	0.10	5.0	2.8	0.35
8.0	10	0.10	5.0	2.8	0.35
8.0	50	0.10	5.0	2.8	0.35
8.0	100	0.10	5.0	3.0	0.35
8.0	500	0.10	5.0	2.8	0.35
8.0	1000	0.10	5.0	2.8	0.35

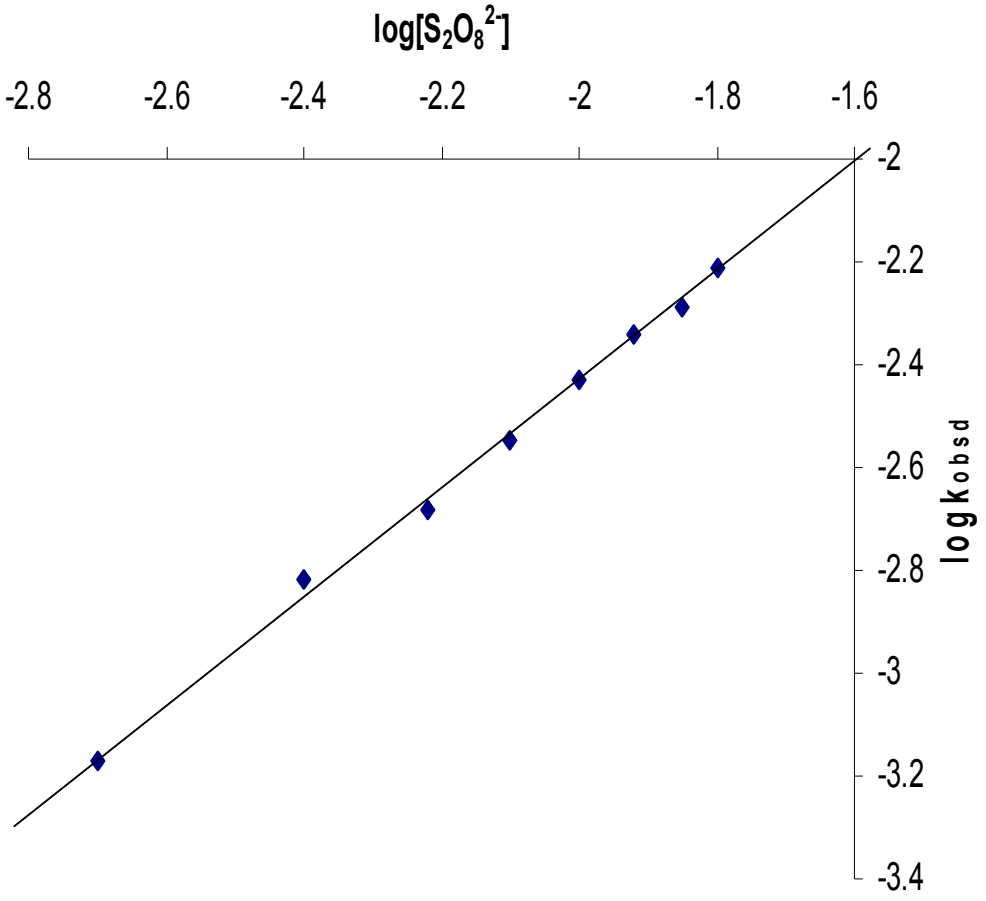


Figure 4.7:- Plot of $\log k_{obsd}$ versus $\log[S_2O_8^{2-}]$ for the Ag^+ catalysed reaction of MB^+ and $S_2O_8^{2-}$

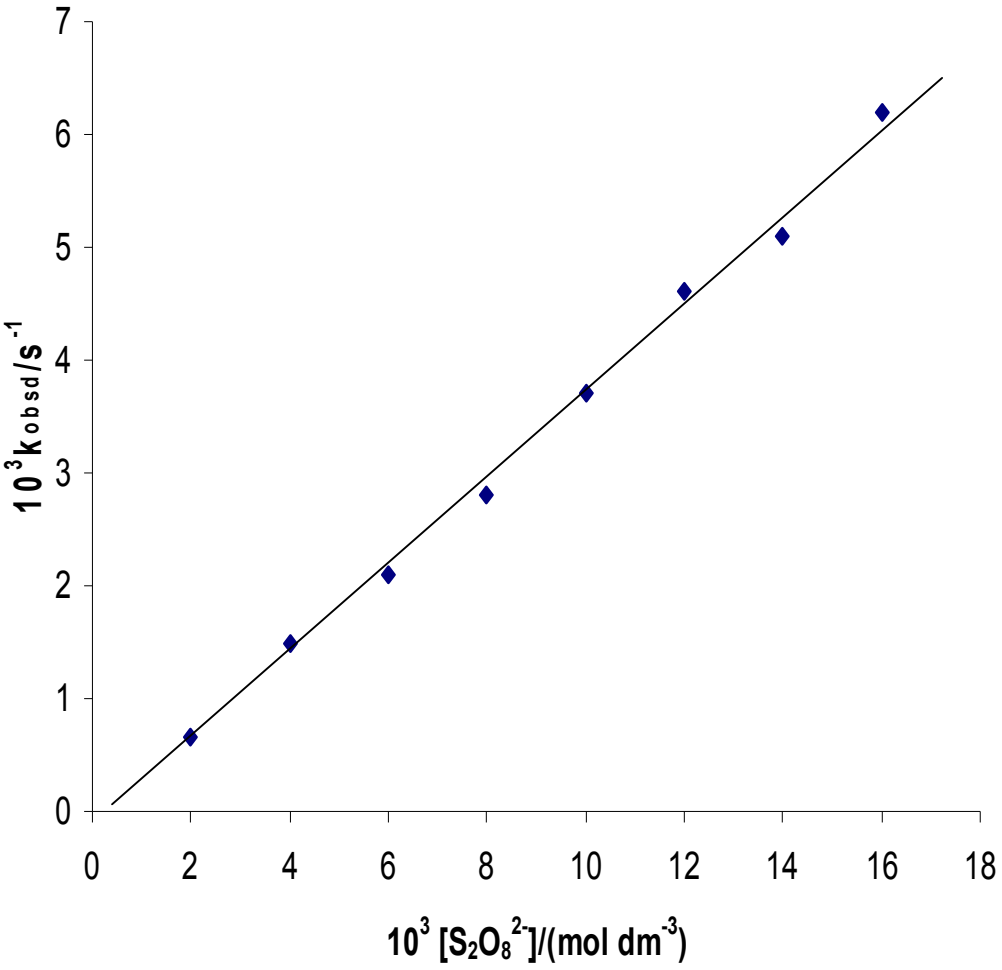


Figure 4.8:- Plot of k_{obsd} versus $[S_2O_8^{2-}]$ for the Ag^+ catalysed oxidation of MB^+ by $S_2O_8^{2-}$

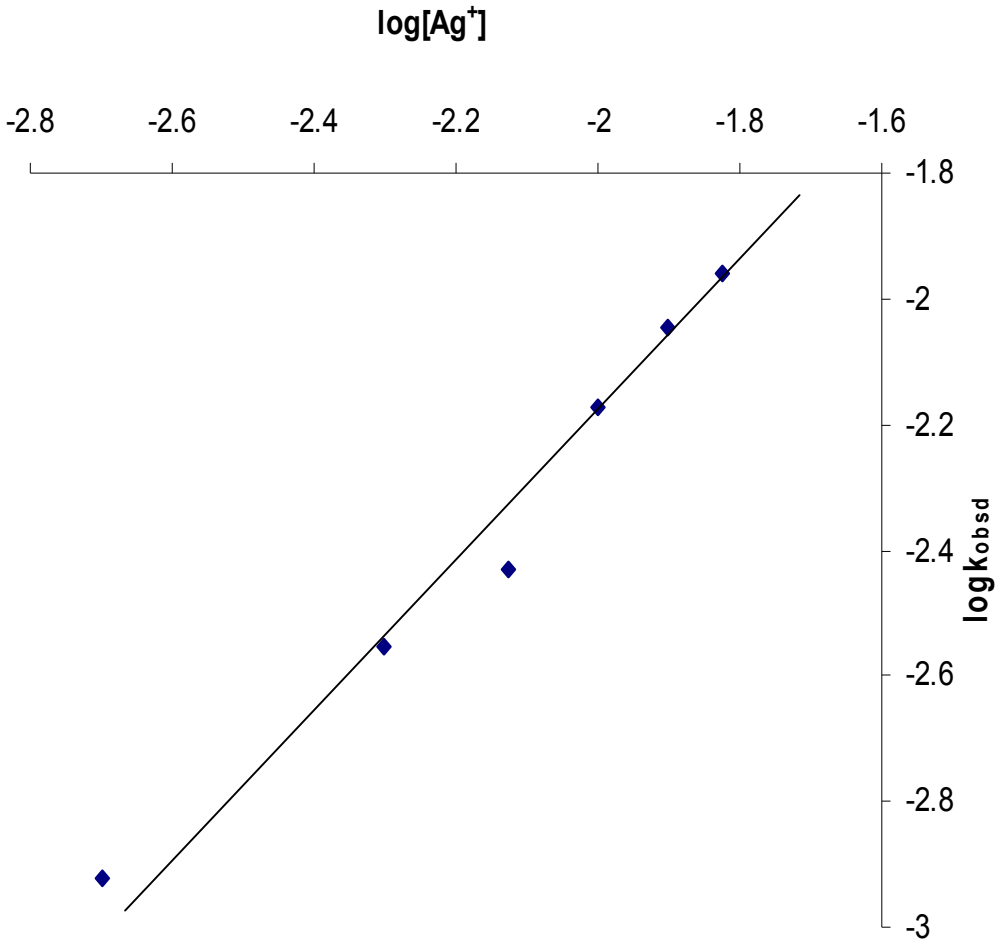


Figure 4.9:- Plot of $\log k_{obsd}$ versus $\log[Ag^+]$ for the Ag^+ catalysed reaction of MB^+ and $S_2O_8^{2-}$

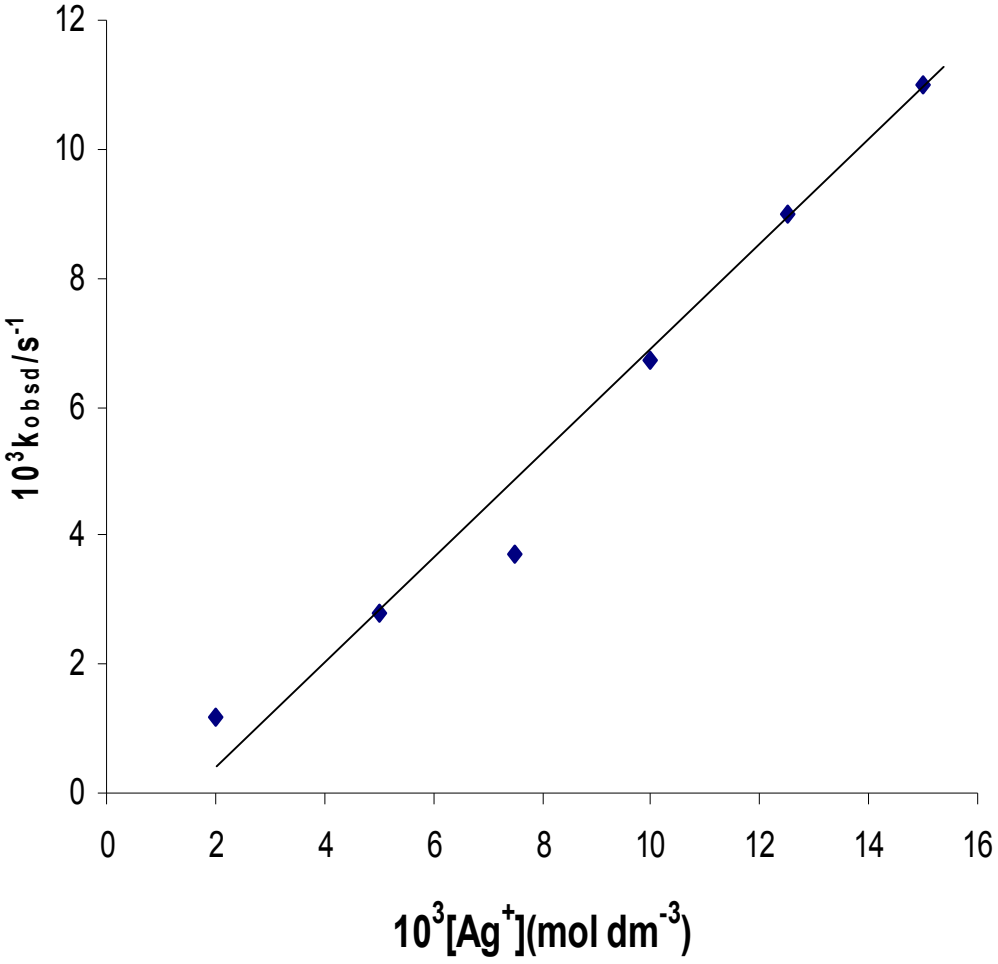


Figure 4.10:- Plot of k_{obsd} versus $[Ag^+]$ for the Ag^+ catalysed reaction of MB^+ and $S_2O_8^{2-}$

The typical plot is shown in Figure 4.11. The pseudo-first order rate constants, k_{obsd}, were determined at different initial concentration of sulphite, at constant $[MB^+]$ and $[H^+]$ of 1.25 x 10^{-5} mol dm^{-3} and 1.0 x 10^{-3} mol dm^{-3} respectively (Table 4.3).

The slope of 1.05 obtained for the plot of $\log k_{obsd}$ versus $\log[SO_3^{2-}]$ (Figure 4.12) as well the linearity of the plot of k_{obsd} versus $[SO_3^{2-}]$ (Figure 4.13) proved that the rate of reaction is first-order with respect to $[SO_3^{2-}]$.

The equation for the reaction of methylene blue and SO_3^{2-} can best be represented by equation (4.5).

$$-\frac{d[MB^+]}{dt} = k_2 [MB^+] [SO_3^{2-}] \quad \text{---------- (4.5)}$$

$k_2 = (3.02 \pm 0.22)$ x 10^{-3} dm^3 mol^{-1} s^{-1} at $[H^+] = 1.0$ x 10^{-3} mol dm^{-3},

T = 25.0 ± 1.0 ^{0}C and μ = 0.10 mol dm^{-3}(NaCl).

4.3 Effect of hydrogen ion concentration on the rate of the reactions

4.3.1 Methylene blue – bromate system

The effect of acid on the rate of the reaction was investigated at the acid range of 0.175 – 0.30 mol dm^{-3} (Table 4.1), while the concentration of methylene blue and that of the bromate ions were kept constant at 1.87 x 10^{-5} mol dm^{-3} and 8.0 x 10^{-3} mol dm^{-3} respectively. The reaction was carried out at 29.0 ±1.0^{0}C and μ= 0.50 mol dm^{-3} (NaCl). A plot of k_2 versus $[H^+]^2$ (Figure 4.14) was linear with r =0.999 and fitted into equation (4.6)

$$k_2 = a + b [H^+]^2 \quad \text{---------- (4.6)}$$

Least square analysis of the plot gave a = 210 dm^3 mol^{-1} s^{-1} and b = 1.6 dm^9 mol^{-3} s^{-1} at T = 29.0 ±1.0 ^{0}C.

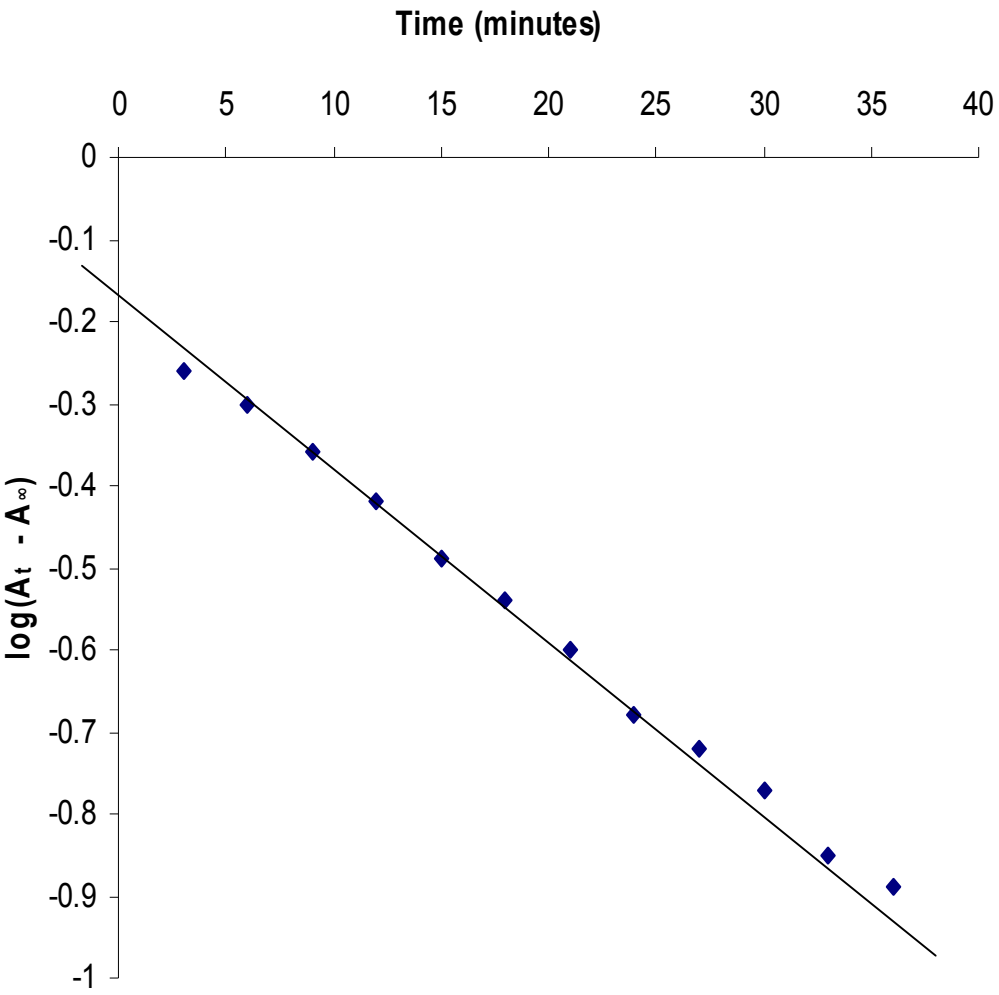


Figure 4.11:- A typical pseudo-first order plot for the reduction of MB^+ by SO_3^{2-}

TABLE 4.3:-Pseudo-first order and second order rate constants for the redox reaction of methylene blue and sulphite ion. $[MB^+] = 1.25 \times 10^{-5}$ mol dm^{-3}, T = 25.0 ± 1.0^{0}C and λ_{max} = 665 nm.

10^2 $[SO_3^{2-}]$/ (mol dm^{-3})	10^5 $[H^+]$/ (mol dm^{-3})	μ (NaCl)/ (mol dm^{-3})	10^4 k_{obsd}/ s^{-1}	10^2 k_2/ (mol dm^{-3})
1.0	100	0.10	3.2	3.2
1.4	100	0.10	3.9	2.8
1.8	100	0.10	5.3	2.9
2.2	100	0.10	6.9	3.1
2.6	100	0.10	7.6	2.6
3.0	100	0.10	9.7	3.2
2.6	1.0	0.10	7.6	2.9
2.6	5.0	0.10	7.6	2.9
2.6	10	0.10	7.6	2.9
2.6	50	0.10	7.6	2.9
2.6	10	0.10	7.6	2.9
2.6	50	0.10	7.6	2.9
2.6	100	0.10	7.6	2.9
2.6	500	0.10	7.6	2.9
2.6	100	0.10	7.6	2.9
2.6	100	0.20	6.5	2.5
2.6	100	0.30	5.3	2.0
2.6	100	0.40	4.1	1.6
2.6	100	0.50	3.5	1.3
2.6	100	0.60	3.0	1.2

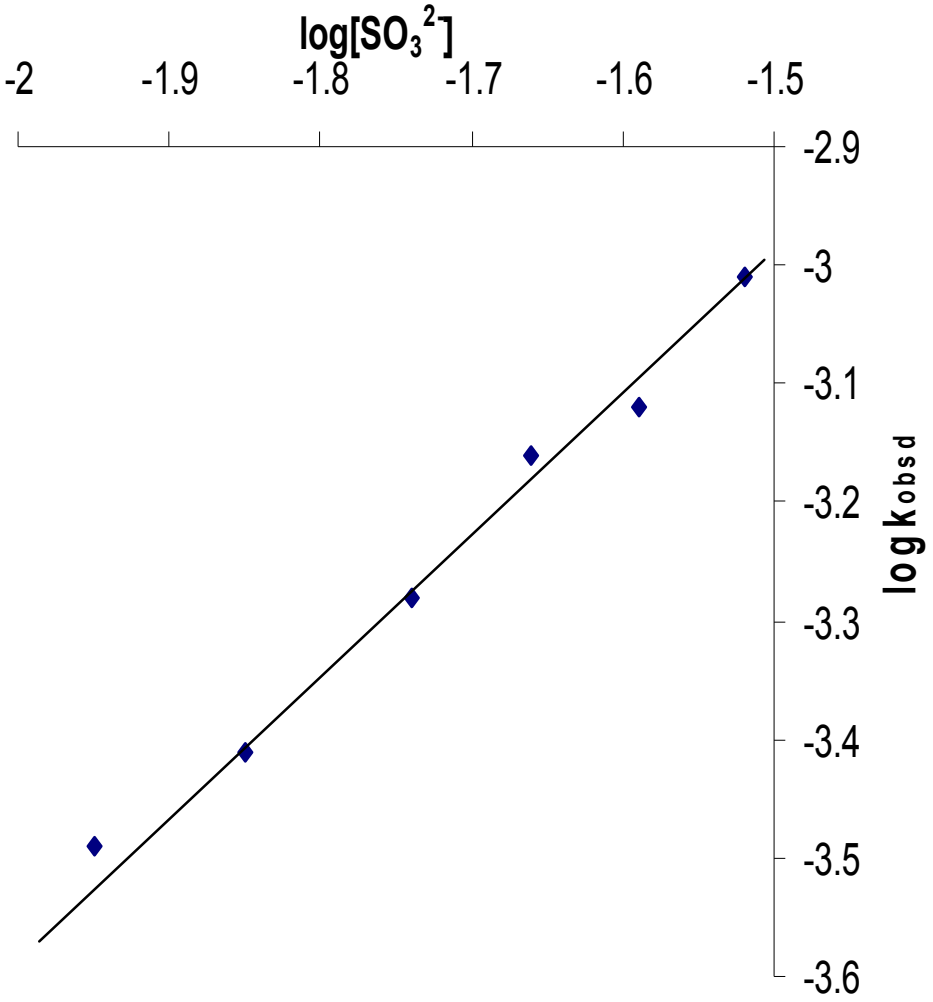


Figure 4.12:- Plot of $logk_{obsd}$ versus $log[SO_3^{2-}]$ for the reaction of MB^+ and SO_3^{2-}

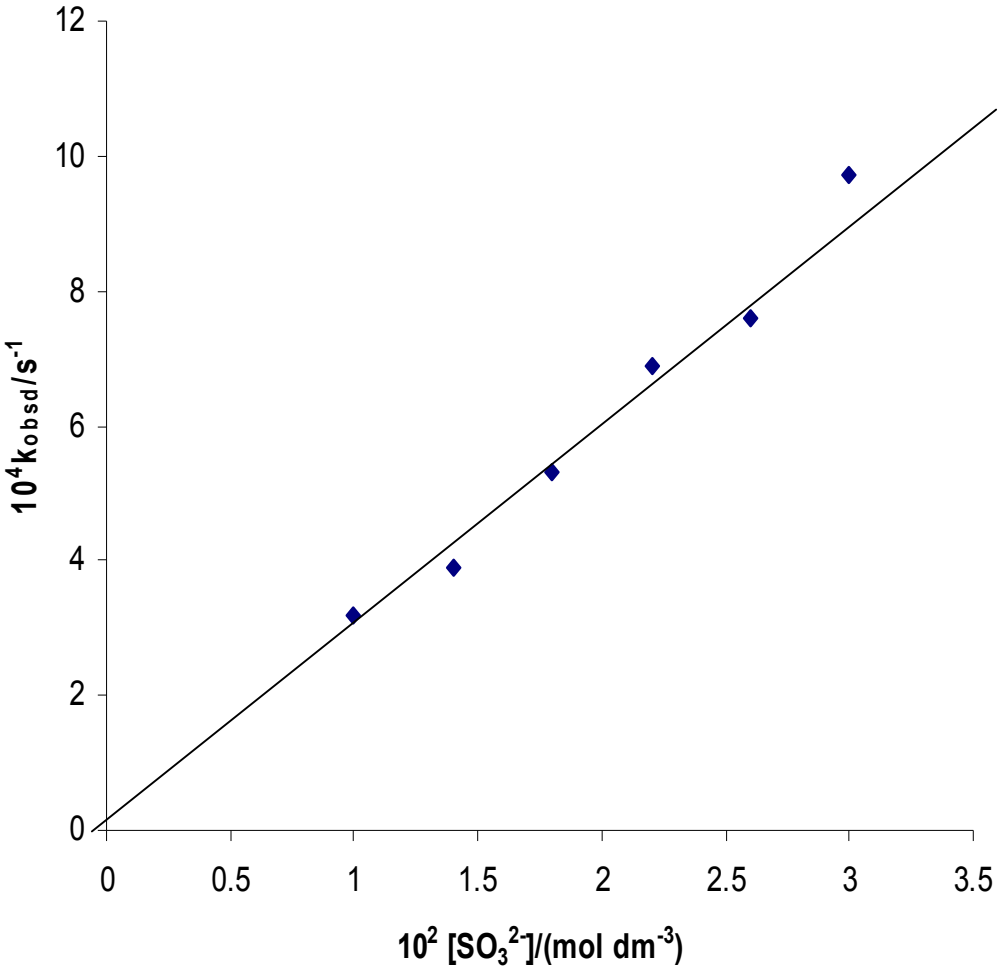


Figure 4.13:- Plot of k_{obsd} versus $[SO_3^{2-}]$ for the reduction of MB^+ by SO_3^{2-}

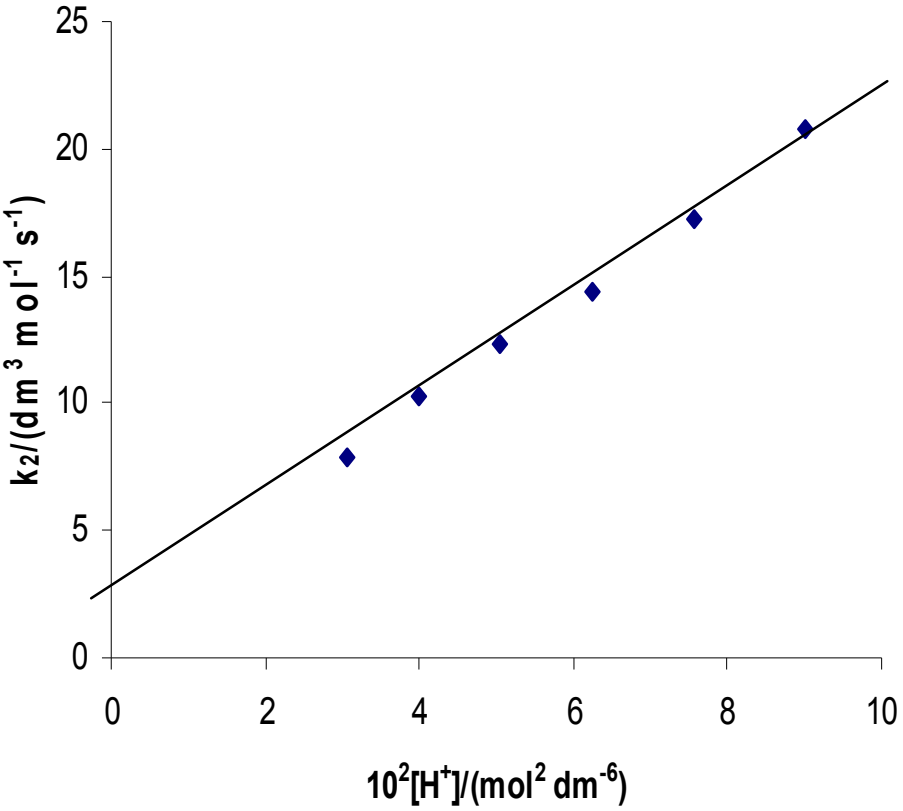


Figure 4.14:- Plot of k_2 versus $[H^+]^2$ for the reaction of MB^+ and BrO_3^-

The reaction thus occurs by an acid independent and second order acid dependent pathways. Therefore, the rate law can be represented by equation (4.7)

$$-\frac{d[MB^+]}{dt} = (a + b[H^+]^2)[MB^+][BrO_3^-] \quad \text{----------(4.7)}$$

4.3.2 Silver(I) catalysed methylene blue – peroxydisulphate system

Keeping the concentrations of all other reactants constants, the effect of acid on the rate of the reaction was investigated in the acid range 0.1 x 10^{-4} – 100 x 10^{-4} mol dm^{-3} at 26.0 ± 1.0^{0}C, and 0.10 mol dm^{-3} ($NaNO_3$) ionic strength. The reaction was found to occur by an acid independent pathway.

4.3.3 Methylene blue – sulphite system

The rate of the reaction was found to be unaffected by change in hydrogen ion concentration in the range 1.0 x 10^{-5} – 500 x 10^{-3} mol dm^{-3} at 25.0 ± 1.0 ^{0}C and μ = 0.10 mol dm^{-3}, with the concentration of MB^+ and SO_3^{2-} kept constant at 1.25 x10^{-5} mol dm^{-3} and 2.6 x 10^{-3} mol dm^{-3} respectively.

4.4 The effect of added anions

4.4.1 Methylene blue – bromate system

The effect of added $HCOO^-$ and SO_4^{2-} ions on the rate of the reaction was investigated and the results presented in Table 4.4 shows that both anions reduce the reaction rate. It was first ascertained that both anions do no react with MB^+ and BrO_3^-

4.4.2 Silver(I) catalysed methylene blue – peroxydisulphate system

Keeping the concentrations of all other reactants constant and at constant ionic strength of 0.10 mol dm^{-3} ($NaNO_3$), $HCOO^-$ and SO_4^{2-} added were observed to have no effect on the rate of the reaction.

TABLE 4.4:- Effect of anions on observed first order and second order on rate constants for the methylene blue-bromate ion reaction.

$[MB^+]$ = 1.87 x 10^{-5} mol dm^{-3}, $[BrO_3^-]$ = 7.0 x 10^{-3} mol dm^{-3}, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.60 mol dm^{-3} [NaCl], T = 29.0±1.0 ^{0}C and λ_{max} = 665nm

X	**10^2 [X]/ (mol dm^{-3})**	**10^2 k_{obsd}/ s^{-1}**	**k_2 /(dm^3 mol^{-1} s^{-1})**
$HCOO^-$	0.0	6.91	9.81
	1.0	6.68	9.54
	2.0	6.22	8.89
	3.0	5.64	8.06
	4.0	4.49	6.41
	5.0	3.45	4.93
SO_4^{2-}	0.0	6.91	9.87
	1.0	6.91	9.87
	2.0	5.30	7.57
	3.0	4.26	6.09
	4.0	3.68	5.26

4.4.3 Methylene blue – sulphite system

The rate constant of $(3.02 \pm 0.22) \times 10^{-3}$ obtained for this reaction at $25.0 \pm 1.0\ ^0C$ and $\mu = 0.10$ mol dm^{-3} was found to remain unchanged when $HCOO^-$ and SO_4^{2-} were added.

4.5 Test for intermediate complex

4.5.1 Spectrophotometric investigation

This was carried out on all the systems studied in order to find out whether any spectroscopically determinable intermediate complex was formed between MB^+ and each of the oxyanions during the reaction. There was no clear shift from 660 – 665 nm (Figure 3.1), the wavelength of maximum absorption of MB^+, for all the systems studied.

4.5.2 Michaelis–Menten plot

The Michaelis – Menten model of enzyme action is of the form:

$$\frac{-\,d[\text{product}]}{dt} = k_{obsd}\,[E^0] \quad \text{----------(4.8)}$$

with $k_{obsd} = k_1\,[S] / k_m + [S]$ ----------(4.9)

The expression for the k_{obsd} in equation (4.10) can be rearranged

into $1/k_{obsd} = 1/k_1 + (k_m/k_r)\,[S]^{-1}$ ---------- (4.10)

where k_{obsd} = rate constant for the overall reaction

$[E^0]$ = total enzyme concentration

k_m = Michaelis-Menten rate constant

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

S = Substrate (S = Oxyanions in the reaction studied).

Least square analysis of the plots of $1/k_{obsd}$ versus 1/[oxyanions], where [oxyanion] = $[BrO_3^-]$, $[S_2O_8^{2-}]$ or $[SO_3^{2-}]$, gave a straight line with zero or negligible intercept for all the systems studied. These plots are represented in Figures 4.15, 4.16 and 4.17. This suggests the absence of intermediate complex formation in the three systems.

4.6 Free radical test

Acrylamide was added to a partially oxidized reaction mixture of MB^+ - BrO_3^-. When followed by a large excess of methanol, there was no gel formation. This probably suggests that no free radical is formed in the reaction. Allyl acetate, an effective sulphate ion free radical scavenger was polymerized when it was added with excess methanol to partially oxidized reaction mixture of MB^+ - $S_2O_8^{2-}$ and MB^+ - SO_3^{2-}. Allyl acetate did not polymerize with each of the reactant alone. This indicates that free radicals are formed in the MB^+ - $S_2O_8^{2-}$ and MB^+ - SO_3^{2-} systems.

4.7 The effect of ionic strength

4.7.1 Methylene blue – bromate system

The effect of changing ionic strength on the rate of the reaction was investigated in the range μ = 040 – 0.70 mol dm^{-3} (NaCl), with concentration of other reactants kept constant at 29.0 ± 1.0 ^{0}C. The rate constant was found to increase with increase in ionic strength and linear plot (r =0.996) was obtained for $\log k_2$ versus $\mu^{½}$, (Figure 4.18).

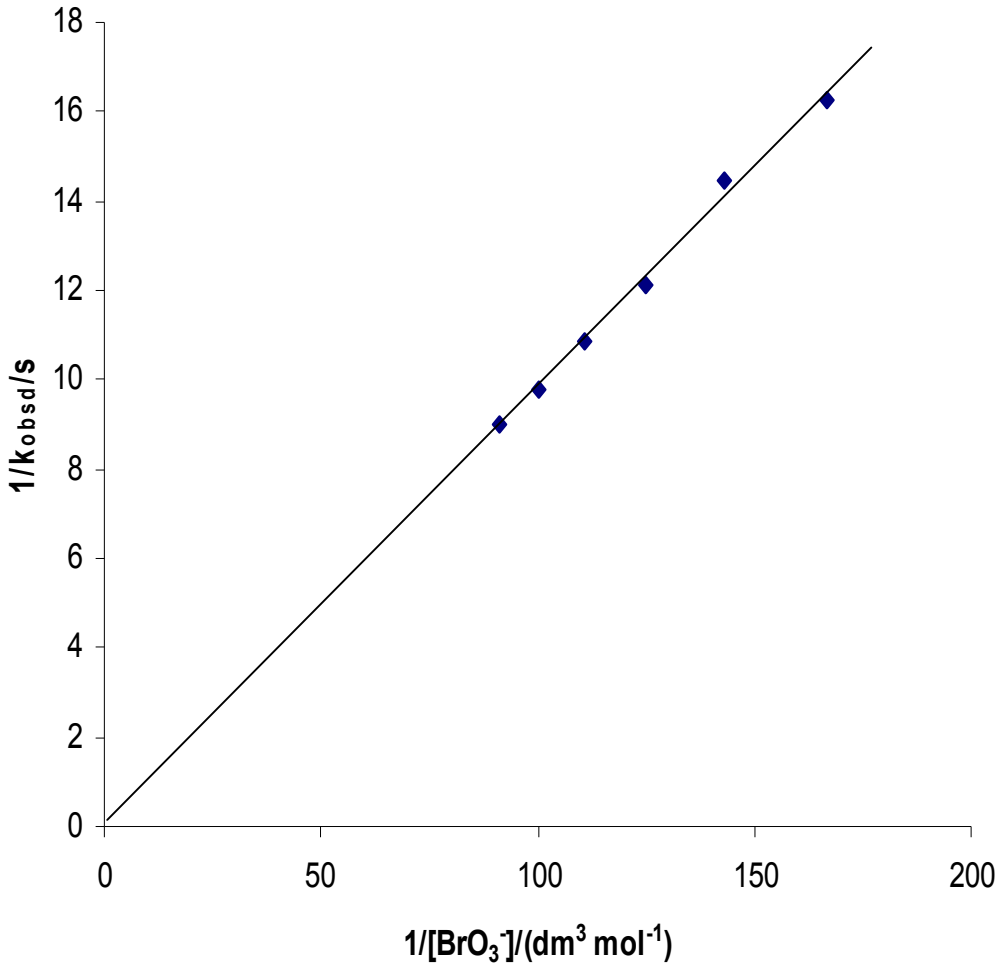


Figure 4.15:- Michaelis-Menten plot for the reaction of MB^+ and BrO_3^-

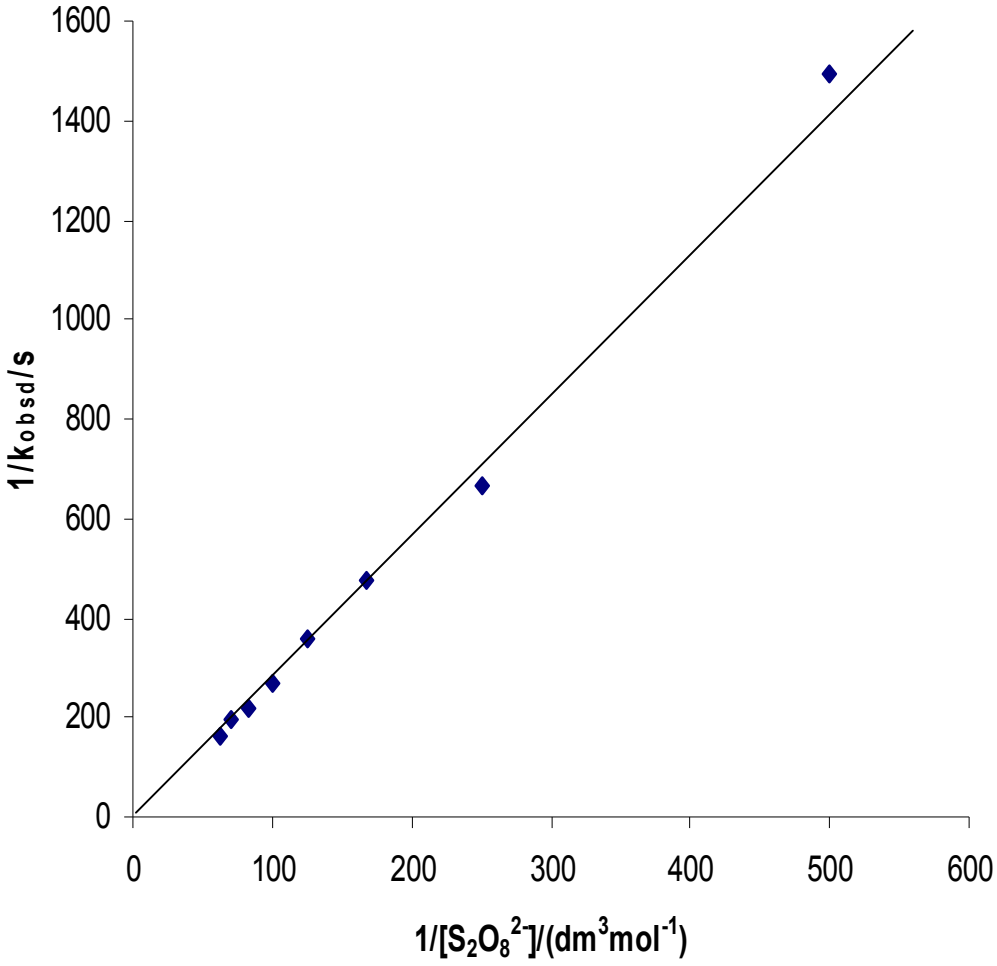


Figure 4.16:- Michaelis-Menten plot for the Ag^{+} catalysed reaction of MB^{+} and $S_2O_8^{2-}$

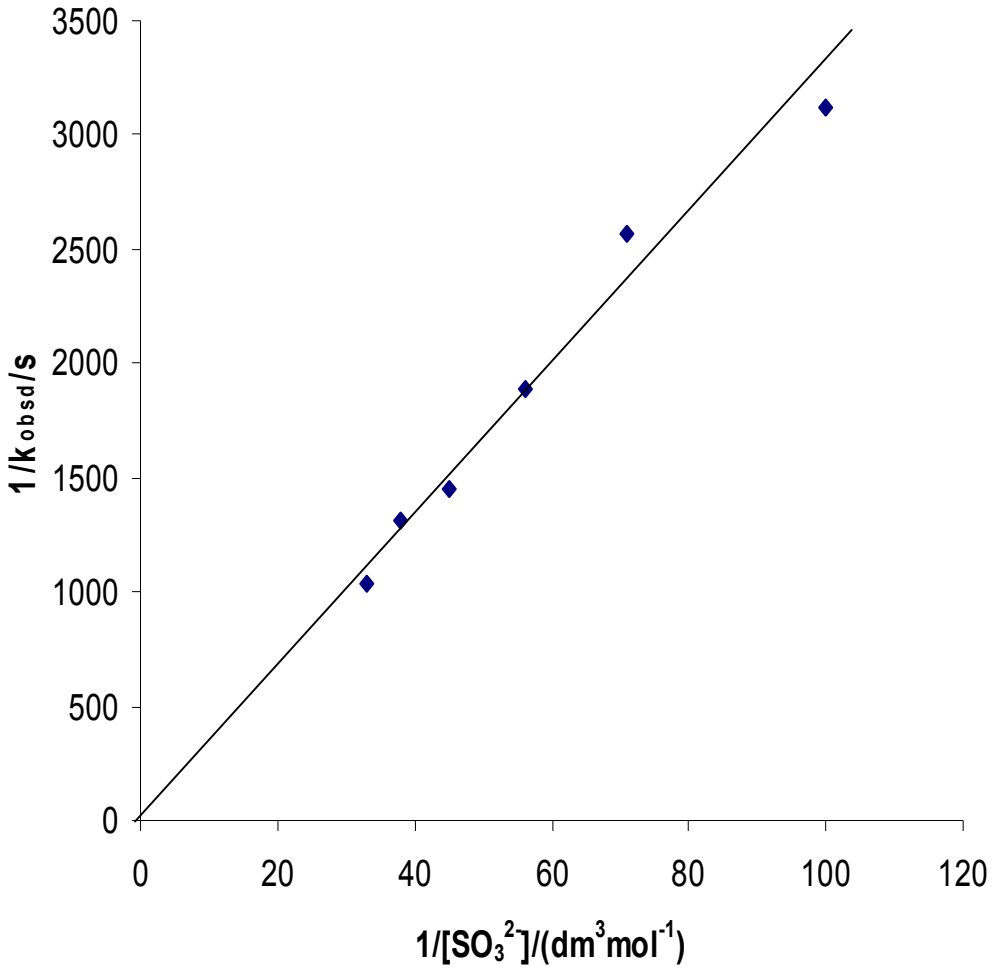


Figure 4.17:- Michaelis-Menten plot for the reaction of MB^{+} and SO_3^{2-}

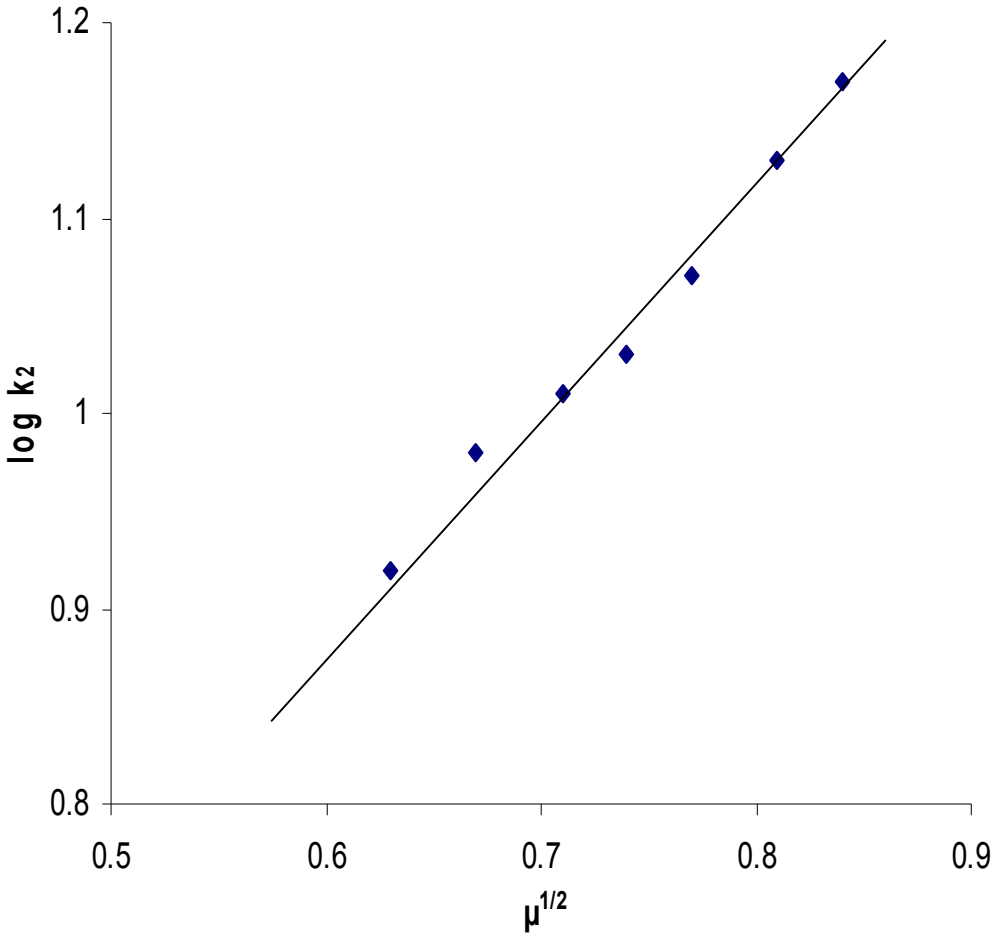


Figure 4.18:- Plot of $\log k_2$ versus $\mu^{1/2}$ for the reaction of MB^+ and BrO_3^-

4.7.2 Silver(I) catalysed methylene blue – peroxydisulphate system

The variation of ionic strength from 0.05 – 0.50 mol dm^{-3} ($NaNO_3$) led to a decrease in the rate constant (Figure 4.19). The concentrations of other reactants were kept constant at 26.0 ± 1.0 ^{0}C.

4.7.3 Methylene blue – sulphite system

Five reaction mixture of various ionic strengths in the 0.10 – 0.50 mol dm^{-3} range and containing fixed concentrations of MB^+, SO_3^{2-}, and H^+ were monitored to determined the effect of ionic strength on this reaction. The rate was found to decrease with increase in ionic strength, and a linear plot (r =0.973) was obtained for graph of $\log k_2$ versus $\mu^{1/2}$ (Figure 4.20).

4.8 Effect of change in dielectric constant of the reaction medium

The rate of reaction of MB^+ and $S_2O_8^{2-}$ was found to decrease with decrease in the dielectric constant of the reaction medium (Table 4.5), while for the MB^+- SO_3^{2-} system, the rate was found to increase with decrease in dielectric constant of the reaction medium (Table 4.6).

4.9 Product analysis

In all cases of the reaction of oxyanions with MB^+, a colourless solution was obtained as product at the end of the reaction, indicating the destruction of the quinoid chromophore group. The organic product of the reaction of MB^+ with BrO_3^- and $S_2O_8^{2-}$ gave a yellow precipitate with 2,4-dinitrophenylhydrazine, confirming the presence of carbonyl group. These DNP derivatives were recrystallised with ethanol and dried at 50°C for one hour. Using the melting point apparatus, the MB^+ - BrO_3^- derivative was found to have a melting point of 157 - 160ºC, while for the MB^+ - $S_2O_8^{2-}$ system, the derivative melts at 172 - 174ºC.

TABLE 4.5:- Effect of change in dielectric constant on rate constants for methylene blue-peroxydisulphate ion reaction.

$[MB^+] = 1.87 \times 10^{-5}$ mol dm^{-3}, $[S_2O_8^{2-}] = 8.0 \times 10^{-3}$ mol dm^{-3}, T = 26.0 ± 1.0 ^{0}C and λ_{max} = 665 nm.

Dielectric constant	**10^3 k_{obsd}/ s^{-1}**	**k_2/ (dm^3 mol^{-1} s^{-1})**
81	2.5	0.31
75	1.7	0.21
69	1.3	0.16
63	0.67	0.084
57	0.27	0.034

TABLE 4.6:- Effect of change in dielectric constant on rate constants for methylene blue-sulphite ion reaction.

$[MB^+] = 1.25 \times 10^{-5}$ mol dm $^{-3}$, $[SO_3^{2-}] = 2.6 \times 10^{-2}$ mol dm^{-3}, T = 25.0 ± 1.0^{0}C and λ_{max} = 665 nm.

Dielectric constant	**10^3 k_{obsd}/ s^{-1}**	**k_2/ ($dm^3$$mol^{-1}$ s^{-1})**
81	7.6	2.9
75	8.1	3.1
69	14	5.4
63	16	6.2
57	18	6.9
51	32	12.3

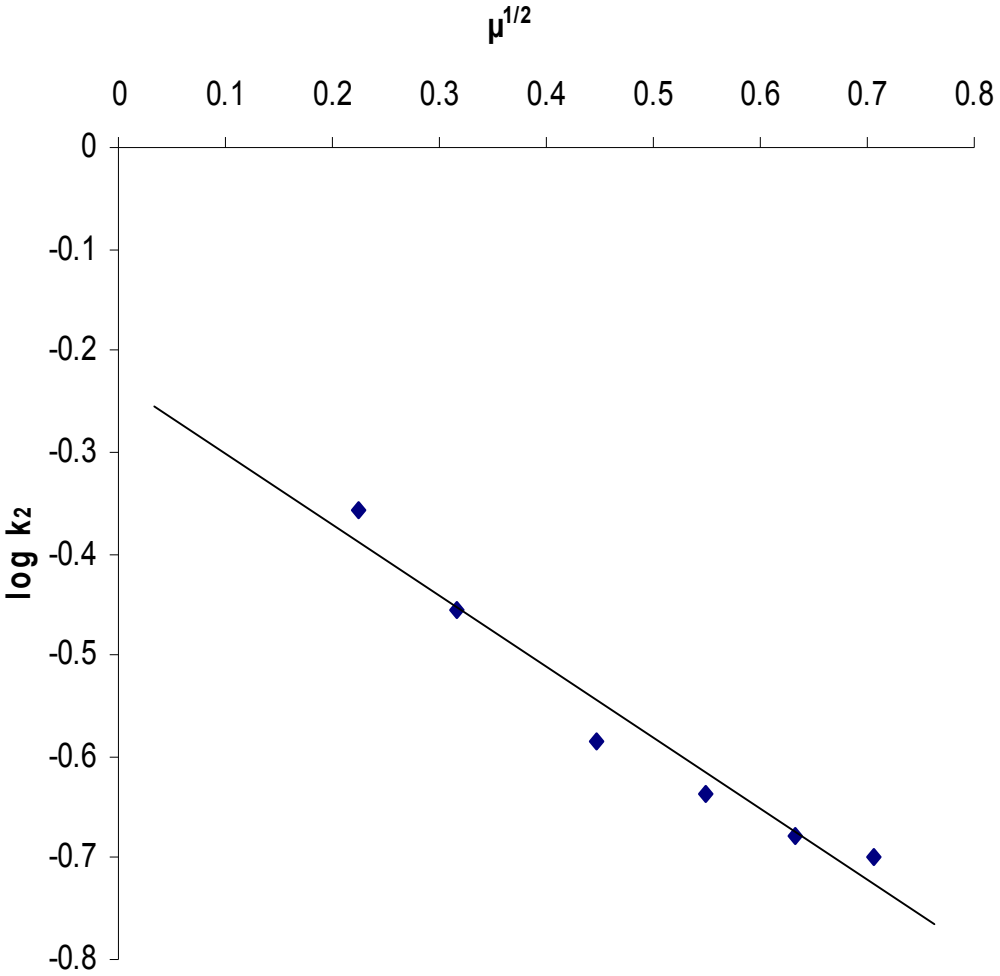


Figure 4.19:- Plot of $\log k_2$ versus $\mu^{1/2}$ for the Ag^+ catalysed reaction of MB^+ and $S_2O_8^{2-}$

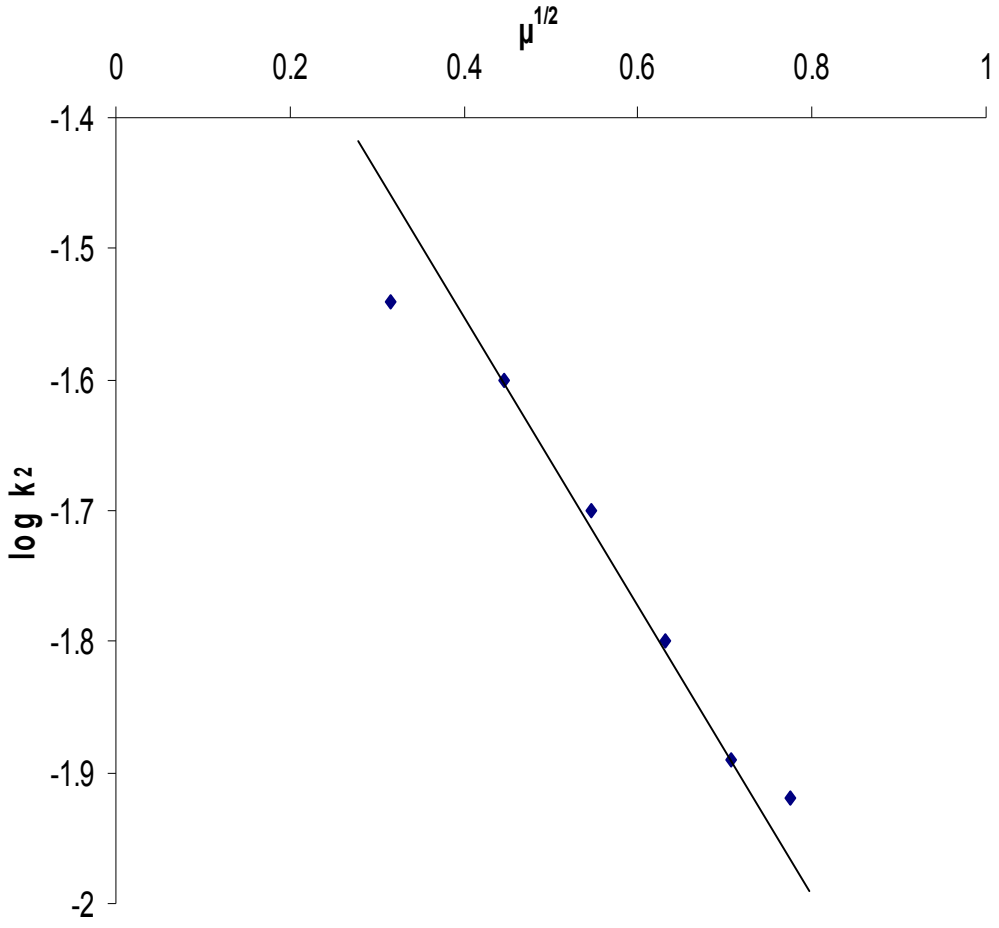


Figure 4.20:- Plot of $\log k_2$ versus $\mu^{1/2}$ for the reaction of MB^+ and SO_3^{2-}

The inorganic product of the reaction of MB^+ and $BrO_3^-$was found, qualitatively to be bromine. The red, dense bromine liquid was noticed to settle at the bottom of the test tube when the solution was kept for some time confirming the inorganic product to be bromine. Additon of $BaCl_2$ and dilute HCl solution confirms the inorganic product of the MB^+- $S_2O_8^{2-}$ reaction to be SO_4^{2-}. The inorganic product of the MB^+ - SO_3^{2-} system was also confirmed, qualitatively using $BaCl_2$ to be SO_4^{2-}. The organic product of the reaction of MB^+ with SO_3^{2-} was suspected to be leuco-methylene blue, MBH. This is because it was noticed that the MBH was oxidized back to the MB^+ after about ten hours, possibly by the dissolved oxygen in the solution.

CHAPTER FIVE

5.0 Discussion

5.1 Methylene blue – bromate reaction

The result of stoichiometry studies showed that for every two moles of MB^+ oxidized three moles of BrO_3^- were reduced according to equation (4.1).

A colourless solution obtained at the end of the reaction indicated destruction of the quinoid chromophore group. The organic product gave a yellow precipitate with 2,4–dinitrophenylhydrazine, confirming the presence of carbonyl functional group. The inorganic product was, qualitatively confirmed to be bromine, using $AgNO_3$ solution. The formation of bromine is a common feature of redox reaction of bromate ions (Ayoko *et. al.,* 1991; Lohdip and lyun, 1993; Lohdip *et. al.,* 1995).

The observed first order dependence of rate of reaction on both $[MB^+]$ and $[BrO_3^-]$ observed is very common in the reactions of bromate ions (Birk, 1973; Ayoko *et. at*., 1991; Lohdip *et. al.,* 1995). At $[H^+] = 0.2$ mol dm^{-3}, the reaction is second order overall and can be represented by equation (4.4).

The second order rate constant was determined as a function of $[H^+]$ in the range $0.175 \leq [H^+] \leq 0.30$ mol dm^{-3} and the results presented in Table 4.1. The nature of the acid dependence observed can be fitted into equation (4.6). It shows that parallel reactions of protonated and unprotonated species of BrO_3^- occur as in most other reactions of BrO_3^- (Birk, 1973; Birk and Kozub, 1973; Lohdip and Iyun, 1993). The second order $[H^+]$ dependence term was rationalized in term of the pre-equilibrium protonation of BrO_3^- to give $H_2BrO_3^+$ (Birk, 1973; Thompson and Knight, 1973;

Ayoko *et. al*., 1991; Iyun *et.al*., 1992). It is thought that the protons serve to weaken the bonds between the oxygen atoms and central bromine atom thereby facilitating the reducibility of the later (Edwards, 1964). Since MB^+ is positively charged, the slope of +1.32 observed for the plot of $\log k_2$ versus $\mu^{1/2}$ (Figure 4.18), confirms the existence of $H_2BrO_3^+$ as one of the reactive species in the medium.

Lack of spectrophotometric evidence for the formation of intermediate complex, suggests an outer–sphere mechanism. Michaelis – Menten plot, Figure (4.15) (Atkins, 1997) was linear (r =0.997) with negligible intercept, further suggesting the absence of pre-electron transfer complex formation in this reaction. This view is reinforced by the observed anion inhibition (Table 4.4) which is a characteristic of the outer- sphere mechanism (Przystas and Sutin, 1973; Adegite et. *al.,* 1977; Lohdip and Iyun, 1993). On the basis of the above the following reaction scheme is proposed for this reaction.

$$BrO_3^- + 2H^+ \underset{}{\overset{K_3}{\rightleftharpoons}} H_2BrO_3^+ \text{ ----------(5.1)}$$

$$BrO_3^- + MB^+ \xrightarrow{k_4} MB^{2+} + BrO_3^{2-} \text{ ----------(5.2)}$$

$$H_2BrO_3^+ + MB^+ \xrightarrow{k_5} MB^{2+} + BrO_2 + H_2O \text{ ----------(5.3)}$$

$$BrO_3^{2-} + 2H^+ \xrightarrow{k_6} BrO_2 + H_2O \text{ ----------(5.4)}$$

$$2MB^{2+} + 2BrO_2 + 8H^+ \xrightarrow{k_7} \text{products} + 2Br^- \text{ ----------(5.5)}$$

$$2Br^- + BrO_3^- + 6H^+ \xrightarrow{k_8} 3/2\ Br_2 + 3H_2O \text{ ----------(5.6)}$$

Reaction in equation (5.6) occurs only in the presence of excess bromate ion. With equation (5.2) and (5.3) as the rate determining step, the equation for the reaction can be written as

$$\frac{-1}{2}\frac{d[MB^+]}{dt} = k_4[MB^+][BrO_3^-] + k_s[MB^+][H_2BrO_3^+] \text{ ----------(5.7)}$$

When substitution is made for $H_2BrO_3^+$ from equation (5.1), then equation (5.7) becomes

$$-\frac{1}{2}\frac{d[MB^+]}{dt} = (k_4 + k_5 K_3 [H^+]^2)[MB^+][BrO_3^-] \text{ ----------(5.8)}$$

Comparing equations (4.7) and (5.8); $k_4 = a = 210\ dm^3\ mol^{-1}\ s^{-1}$ and

$k_5K_3 = b = 1.6\ dm^9\ mol^{-3}\ s^{-1}$ at $29.0 \pm 1.0\ ^0C$

5.2 Silver(I) catalysed reaction of methylene blue and peroxydisulphate ion

The result of stoichiometry studies reveals that one mole of MB^+ reacted quantitatively with six moles of $S_2O_8^{2-}$. Thus the overall reaction may be represented by equation (4.2).

Although $S_2O_8^{2-}$ requires two electrons to be converted into SO_4^{2-}, we propose that the reaction occurs via two successive univalent changes generating the highly reactive $SO_4^{-\cdot}$ radical, which is well established as an intermediate in $S_2O_8^{2-}$ reaction (Ohashi. *et.al.,* 1967; Banerjee and Pujari, 1983; Ayoko *et.al.,* 1992). The polymerization of allyl acetate provides support for the existence of free radical in this reaction.

Kinetic studies indicated first order dependence of rate of reaction on $[MB^+]$, $[S_2O_8^{2-}]$ and $[Ag^+]$ respectively. Thus at $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3} and $26.0 \pm 1.0\ ^0C$, the rate equation is as shown by equation (4.4). Under the experimental conditions employed k_2 was found to be $0.37 \pm 0.03\ dm^3\ mol^{-1}\ s^{-1}$.

A plot of $\log k_2$ versus $\mu^{1/2}$ (Figure 4.19) showed that rate constant decreases with increase in ionic strength. This means that both species at the activated complex are of opposite charges and the product of their charges is - 0.591. The non-integral

value for the product of the species at the activated complex indicates that some other interaction is taking place (Ayoko *et. al.,* 1992). The negative Debye-Bronsted salt effect gives further support to the observation that the rate constants decrease with decrease in the dielectric constant of reaction medium (Table 4.5).

The rate of the reaction showed lack of hydrogen ion concentration dependence in the range $0.10 \times 10^{-4} \leq [H^+] \leq 1.0 \times 10^{-2}$ mol dm^{-3}. Similar results have been reported for redox reaction of $S_2O_8^{2-}$(Gupta and Ghosh, 1959; Banerjee and Pujari, 1983; Rao *et. el.*, 1987). This is due to non-protonation of $S_2O_8^{2-}$(Gupta and Ghosh, 1981; Pujari and Banerjee, 1983; El-Idris, 1991).

Spectroscopic evidence and Michaelis-Menten's plot of $1/k_{obsd}$ versus $1/[S_2O_8^{2-}]$ (Figure 4.16) suggests that intermediates may be unimportant in the rate determining step.

On the basis of the above findings, the mechanism below is proposed for this reaction.

$$Ag^+ + S_2O_8^{2-} \underset{}{\overset{K_3}{\rightleftharpoons}} AgS_2O_8^- \text{ ----------(5.9)}$$

$$MB^+ + AgS_2O_8^- \xrightarrow{k_4} MB^{2+} + Ag^+ + SO_4^- + SO_4^{2-} \text{ ------(5.10)}$$

$$MB^{2+} + SO_4^- \xrightarrow{k_5} \text{Product} + SO_4^{2-} \text{ ----------(5.11)}$$

$$MB^+ + 5S_2O_8^{2-} \xrightarrow{k_6} \text{Product} + 10SO_4^{2-} \text{ ----------(5.12)}$$

With equation (5.10) as the rate determining steps, the equation for this reaction can be written as:

$$\frac{-d[MB^+]}{dt} = k_4[MB^+][AgS_2O_8^-] \text{ ----------(5.13)}$$

when substitution is made for $[AgS_2O_8^-]$ from equation (5.9), equation (5.13) becomes.

$$-\frac{d[MB^+]}{dt} = k_4K_3\,[MB^+]\,[S_2O_8^{2-}]\,[Ag^+] \text{ ----------(5.14)}$$

5.3 Methylene blue – sulphite reaction

The stoichiometry could not be determined because the reaction only proceeds at fast rate when the SO_3^{2-} was in 800-fold and above. Since determination of stoichiometry involves combining the reactants in simple whole number ratio, there were little changes in the absorbances of the reaction mixtures containing various MB^+ and SO_3^{2-} concentrations.

Addition of $BaCl_2$ to the solution gave a white precipitate which was insoluble in dilute HCI confirming the presence of SO_4^{2-}. The test for free radical was positive in this reaction. Similar observation was made in other reactions of SO_3^{2-} (Higginson and Marshal, 1957; Davies *et.al*., 1969; Eldik *et.al.,* 1994; Kraft and Eldik, 1989). This is also an indication of the formation of SO_4^{2-} as product (Higginson and Marshal, 1957; Davies *et al.*, 1969).

The reaction was found to be independent of hydrogen ion concentration over the range $1.0 \times 10^{-5} – 5.0 \times 10^{-3}$ mol dm^{-3}, indicating that the reaction occurs through an acid-independent pathway. The non–dependence of this reaction on change in hydrogen ion concentration is uncommon for redox reactions of SO_3^{2-}. Inverse dependence of rate reported (Staph and Calyle, 1974; Sen Gupta, 1987; Iyun *et. al.,* 1992). The overall on $[H^+]$ has been widely equation for the reaction is given by equation (4.5).

The redox reaction showed negative salt effect, with the rate decreasing with increase in ionic strength from 0.10 – 0.60 mol dm^{-3} (NaCl). The plot of $logk_2$ versus $I^{1/2}$ (Figure 4.20) gave a straight line with a slope of – 0.80. This observation of negative Debye-Bronsted salt indicates that the species at the activated complex are of opposite charges. The rate constants also increased as the dielectric constant of reaction medium decreased (Table 4.6.).

Lack of spectrophotometric evidence for the formation of intermediate complex as well as the linearity (r =0.987), with zero intercept of least square fit of Michaelis – Menten's plot (Atkins, 1997) of $1/k_{obsd}$ versus $1/[SO_3^{2-}]$ (Figure 4.17) supports the outer-sphere mechanism. Also absence of catalysis on addition of $HCOO^-$ and SO_4^{2-} ions is explained in terms of ion-pair complex formation with an outer-sphere character (Iyun *et. al.,* 1995).

Based on experimental results of investigation, the following mechanistic steps are proposed:

In aqueous solution, SO_3^{2-} ion exists in equilibrium with HSO_3^-;

$$SO_3^{2-} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HSO_3^- \text{ ----------(5.16)}$$

It is this HSO_3^- that reduced MB^+ to leuco form(MBH), viz

$$HSO_3^- + MB^+ \xrightarrow{k_2} [HSO_3^- : MB^+] \text{ ----------(5.17)}$$

$$[HSO_3^- : MB^+] + H_2O \xrightarrow{k_3} MBH + SO_4^{2-} + 2H^+ \text{ -----(5.18)}$$

The reduction of MB^+ by SO_3^{2-} was completed in about an hour. This was confirmed by observed repeated absorbance readings. After keeping the reaction mixture for some

hours, the absorbance was found to increase, indicating the oxidation of the leucomethylene blue back to methylene blue by the dissolved oxygen in the solution (Burger and Field, 1984).

$$MBH + 1/2O_2 \xrightarrow{k_4} MB^+ + OH^- \text{ ---------- } (5.19)$$

5.4 Comparison of the MB^+ - BrO_3^- and the MB^+ - $S_2O_8^{2-}$ systems

In this work, methylene blue was oxidized by two oxidant; $S_2O_8^{2-}$ with k_2= 0.37± 0.03 dm^3 mol^{-1} s^{-1} and BrO_3^- with k_2 = 10.16± 029 dm^3 mol^{-1} s^{-1}. Despite the remarkably high oxidation potentials for $S_2O_8^{2-}$ (+2.01V) compared to that of BrO_3^- (+1.52), reaction of methylene blue and $S_2O_8^{2-}$ is very slow. This explains why the reaction was Ag^+ catalysed. This may be due to the fact that the theoretical oxidation potential of 2.01V for $S_2O_8^{2-}$ is never reached in acid media (Brasted, 1961). This may also account for why BrO_3^- is a stronger oxidant than $S_2O_8^{2-}$ in their reaction with MB^+ in acidic medium.

The BrO_3^- reaction occurs by both an acid-independent and a second order acid-dependent pathway while that of $S_2O_8^{2-}$ occur by an acid-independent pathway. Both systems were affected by change in ionic strength.

5.5 Summary and conclusion

The redox reaction of MB^+ was studied with the oxyanions- BrO_3^-, $S_2O_8^{2-}$ and SO_3^{2-}. The reactions were second order at constant $[H^+]$ for the MB^+ - BrO_3^- and MB^+-SO_3^{2-} systems and second order at constant $[H^+]$ and $[Ag^+]$ for the MB^+-$S_2O_8^{2-}$ system. The redox reaction of MB^+ with $S_2O_8^{2-}$ and SO_3^{2-} were independent of $[H^+]$, while the rate of oxidation of MB^+ by BrO_3^- occurs by both an acid-independent and a second order acid-dependent pathways, suggesting protonation of the oxidant.

The stoichiometries of the reactions were 2:3 for MB^+:BrO_3^- ; 1:6 for MB^+:$S_2O_8^{2-}$, while that for MB^+:SO_3^{2-} system could not be determined. The rate of the reactions of MB^+ with $S_2O_8^{2-}$ and SO_3^{2-} were not affected by added anions, but for the MB^+ - BrO_3^- system the rate was inhibited by the added $HCOO^-$ and SO_4^{2-}. Free radical intermediate were observed for the reactions of MB^+ with $S_2O_8^{2-}$ and SO_3^{2-} . All the reactions were sensitive to change in ionic strength and they all occurred via the outer mechanistic pathways.

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